Simulation of stream water alkalinity concentrations using coupled models of soil air CO_2 and stream water chemistry

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Abstract. The ability to predict stream alkalinity values over timescales shorter than monthly or annually is needed to understand the response of stream chemistry to acidic inputs which occur across short time scales (days). We develop and apply a coupled series of physically-based models which are able to predict daily stream alkalinity values by first calculating soil air CO_2 concentrations. We apply the model to a 9 year record of discharge and stream chemistry from a small catchment in the Shenandoah National park of Virginia. We find that we are able to accurately predict the minimum daily stream alkalinity values for all years and we are able to accurately predict the entire annual cycle for 6 of the 9 years (Nash–Sutcliffe criterion equals 0.26). For the 3 years which we overpredict summer stream alkalinity, summer precipitation was greater than normal and much greater than the period for which the model was calibrated.

Introduction

Alkalinity concentrations in headwater streams vary over multiple time scales. Alkalinity varies over decadal periods in response to changes in catchment soil characteristics and atmospheric deposition of strong acid anions (Neal and Whitehead 1988). A seasonal time scale is also evident in response to seasonal fluctuations in soil temperature (Castelle and Galloway 1993; Norton et al. 2001). The shortest time scale, on the order of days or hours, results in alkalinity fluctuations in response to rapidly changing soil respiration values and changes in stream discharge from storms (Hyer et al. 1995; Wigington et al. 1996; Lawrence 2002; Welsch and Hornberger 2004).

This paper seeks to answer two fundamental questions. First, how can we model stream alkalinity variations in response to environmental conditions in a humid forest catchment? Second, what about the physical, chemical, and biological processes occurring in the watershed can we learn from this modeling if we are successful? In order to answer these questions, we will take a coupled-model approach where the following steps are followed: (1) identify

the areas of the catchment that are contributing water rapidly to the stream; (2) estimate soil temperature in these areas on a daily time step; (3) estimate soil moisture status in these areas on a daily time step; (4) use temperature and moisture estimates to make estimates of soil air CO_2; and (5) finally use soil air CO_2 concentrations to determine daily alkalinity concentrations for stream water.

The principal hypotheses around which the models have been constructed include:

H1. Soil temperature is responsible for limiting the production of CO_2 seasonally, but when soils are warm, soil moisture becomes limiting.

H2. Rapid (daily) variations in soil moisture results in daily variation in stream alkalinity occurring in the same time scale.

Stream water alkalinity concentrations are critical to understanding fish habitat in streams (Dennis and Bulger 1995) and assessing how controls on atmospheric deposition impact aquatic and terrestrial ecosystems (Norton et al. 2001). One approach to modeling alkalinity is to focus on monthly stream alkalinity concentrations (Cosby et al. 1985a, 2001). Alkalinity (HCO_3) concentrations in streams and soil water are tightly tied to soil air CO_2 concentrations through the following series of reactions:

$$CO_2(g) = CO_2(aq) \tag{1a}$$

$$CO_2(aq) + H_2O = H^+ + HCO_3^- \tag{1b}$$

$$CaCO_3 + H^+ = HCO_3^- + Ca^{2+} \tag{1c}$$
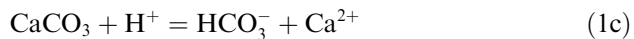
David and Vance (1989) subjected soil material to leaching under pCO_2 ranging from atmospheric ($10^{-3.5}$ atm) to pure CO_2 (1 atm) and found that alkalinity increased from -5 to 163 μeq/l, respectively. In acidification models like MAGIC (Model of Acidification of Groundwater In Catchments, (Cosby et al. 1985a, b)) variations in the specified concentration of soil air CO_2 can have large effects on the calculated alkalinity (Neal and Whitehead 1988). The calculations are based on chemical mechanisms and are supported by empirical observations.

The approach used in MAGIC ignores alkalinity variation that occurs over much shorter time scales (Hyer et al. 1995; Wigington et al. 1996; Lawrence 2002). The large observed variation in CO_2 concentrations that can occur over hours or days suggest that effects on stream alkalinity due to these deviations may be appreciable. Inclusion of diel variation in soil CO_2 into acidification models would be facilitated by the ability to model CO_2 variation in response to soil moisture and soil temperature. In MAGIC, soil CO_2 values are input as either annual or monthly time series. At these time scales, reasonable values can be obtained from a few field measurements or from literature. However, to run the model at greater than a monthly scale, simulated soil air CO_2 concentrations are required.

Physically based modeling of soil air CO_2 values is difficult because of the complexity of coupling production and transport equations. Soil respiration, CO_2 concentrations, and efflux from the soil surface have typically been simulated using empirical relationships between soil moisture and, more often, soil temperature (Winkler et al. 1996). While these functions can be used to reasonably model seasonal and annual fluxes, they are unable to track short term changes in CO_2 processes (Davidson et al. 1998). What is needed is a dynamic model for soil CO_2 production and transport.

In this paper, we present a series of physically based models that simulate soil temperature, soil moisture, soil CO_2 production and transport, and stream alkalinity concentration on a daily time step. The model is applied for a 8 year period from 1983 to 1990 for a small watershed in the Blue Ridge of Virginia. We find that the model performs very well during the climatic conditions for which the model is calibrated, but outside those climatic conditions model performance deteriorates.

Methods

Field site and field data collection

The study was conducted in the watershed of the South Fork of Brokenback Run, a small (237 ha) forested catchment in the Shenandoah National Park, Virginia. The catchment is mountainous, with overall relief of 523 m. Vegetation is second growth dominated by oak (*Quercus* spp.), hickory (*Carya* spp.), and poplar (*Liriodendron tulipifera*), with lesser amounts of eastern hemlock (*Tsuga canadensis*) and pine (*Pinus* spp.). The catchment is underlain with Precambrian Old Rag granite composed predominantly of microcline and quartz (Gaithright 1976). Catchment soils are principally of the Tusquitee and Unison series, and are approximately 1m thick (Elder and Pettry 1975). Both series contain clay or clay films in the B horizon. The pH of catchment soils averages 4.7, and the soils have an average base saturation of 20%. Total C in catchment soils is 2.9%, determined by combustion of composite samples obtained from 20 cm and 50 cm depth. Depth to groundwater was not measured during this study, but in a previous study, depth to groundwater in a well 300 m from the stream was found to average 8.8 m below the surface, with a minimum value of 2.26 m (Scanlon et al. 2000). The catchment has been described in more detail by Scanlon et al. (2000).

Stream discharge measurements and samples for stream water chemistry were collected from the catchment by the US Geological Survey between 1983 and 1990. Samples for chemical analysis were collected weekly through 1984 and then on a monthly basis for the remainder of the study. Data for calibration of the model presented here were collected from June 2001 to January 2002. Data collected in 2001 include stream discharge measured with a

pressure transducer in a stilling well located in a natural pool in the stream. The pressure transducer was connected to a digital datalogger (Campbell Scientific, CR21X), and stage heights were converted to discharge through the use of a constantly updated rating curve. Soil CO_2 concentrations were determined every 15 min using a PP Systems EGM-3 portable infra-red gas analyzer (IRGA) connected to a soil gas well open at 30 cm below the soil surface, as described by Andrews and Schlesinger (2001). Soil temperature at this same depth was determined using thermisters (Hobo loggers) connected to a digital datalogger. Soil tension was measured using a tensiometer (Soil-moisture Inc. 2710ARL18) equipped with a pressure transducer (Soilmoisture Inc, 5301 current transducer) connected to a digital datalogger. Volumetric soil water content (measured with a Campbell Scientific CS620), soil temperature (ReoTemp analog thermometer), and soil air CO_2 were measured weekly at 10 locations representing the topographic variability seen in the catchment (Figure 1). Stream samples obtained in 2001 for alkalinity determination through titration were collected from the catchment outlet manually on a weekly basis and automatically on an hourly basis during storms. A more detailed description of field data collection is given in Welsch and Hornberger (2004).
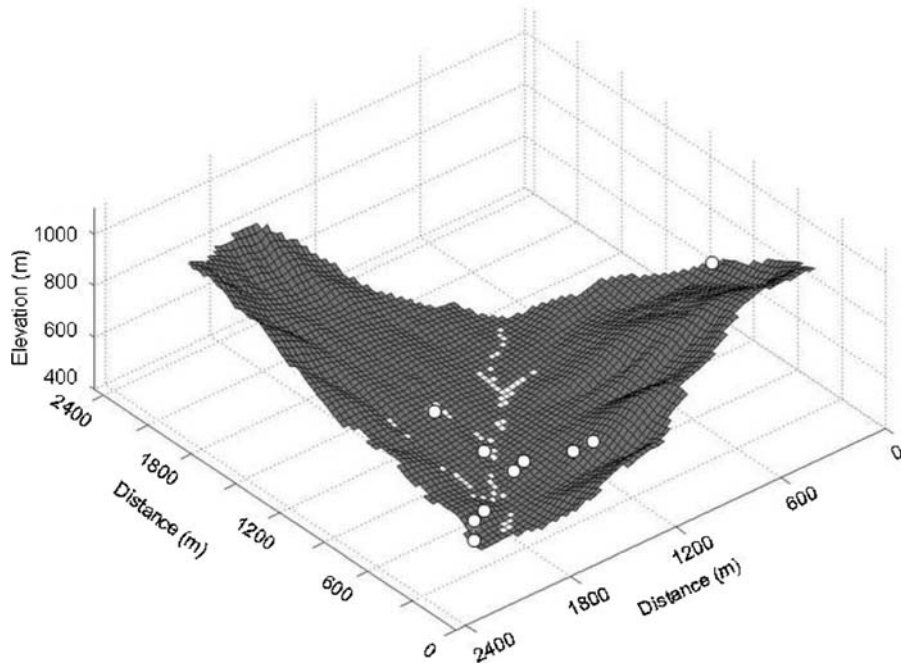

Figure 1. Map of the South Fork of Brokenback Run watershed, located in Shenandoah National Park, Virginia. Light colored cells indicate those determined by topographic analysis to be representative of those cells contributing water directly to the stream. These are the cells for which the models were run. Circles indicate location of weekly sampling locations where soil moisture, soil temperature, and soil air CO_2 were measured.

Outline of simulations

The objective of this study is to simulate measured stream water alkalinity concentrations between 1983 and 1990. We are working with the assumption of equilibrium chemistry with very rapid kinetics; therefore we assume that the chemistry of the water entering the stream is determined in the soil immediately adjacent to the stream channel. Because the catchment outlet (where our measurements are made) is an integration of waters discharged from the soil to the stream along the channel length, we have to consider soil processes not at one site, but along the stream channel.

The basic steps in this investigation are outlined below and described in more detail in the following sections. We first identify the cells adjacent to the stream which discharge water to the stream using topographic analysis of the digital elevation model (DEM) of the catchment. Next, we determine the soil temperature for each day in the simulation for each of the contributing cells. Then we determine the soil tension in each cell for each day using a semi-empirical relationship between the saturation deficit produced by TOPMODEL and observed tension. Once soil tension and soil temperature are known, we use these as inputs into the model of soil CO_2 production and transport to determine a soil air CO_2 concentration in each contributing cell for each day, taken as an average of CO_2 simulated at 30 and 70 cm. An average soil air CO_2 concentration is determined from all contributing cells for each day, and this value is used in the acid-base reaction equations in MAGIC to determine stream alkalinity. Output from MAGIC is then corrected for discharge to account for flushing and dilution effects not considered in MAGIC according to a concentration-discharge relationship determined for the catchment using the USGS concentration-discharge record.

All models with the exception of MAGIC were calibrated using the field data collected in 2001. MAGIC was calibrated using annual flow-weighted stream chemistry values from the 1983 to 1991 period. The calibrated models were then applied to the 1983–1991 period in order to simulate the daily stream chemical response. A summary of variable definitions, values, and sources is given in Table 1.

Air temperature and precipitation data for the simulated period came from a composite of two nearby National Weather Service weather stations. Big Meadows station is located < 3 km from the catchment, and is at an elevation similar to the top of the watershed. Madison station is located < 10 km from the watershed at an elevation similar to the outlet of the watershed. Daily values for air temperature and precipitation were obtained from an average of values from each station for each day.

Table 1. Summary of important variables used in the coupled series of models including definition, value used in the simulations, units, and how the value was obtained.

Variable	Definition	Value	Units	Source
Soil Temperature Model				
K_s	Thermal diffusivity	0.006	$cm^2\ s^{-1}$	Calibrated
LAI	Leaf area index	Minimum of 1, maximum of 4	$m^2\ m^{-2}$	Calibrated
Litter	litter LAI equivalent	Minimum of 2.3, maximum of 4	$m^2\ m^{-2}$	Estimated
k	Beer–Lambert extinction coefficient for radiation in a canopy	0.45	Unitless	Estimated
Soil Tension Model				
Max–max tension	Tension measured at the driest spot in the simulation on a very dry day	100	cm	Calibrated, informed by field data
Min–max tension	Tension measured a at the driest spot in the simulation on a very wet day	7	cm	Calibrated, informed by field data
CO_2 Model				
γ_m	Optimal microbial respiration rate	1×10^{-6}	$mg\ CO_2\ m^{-2}\ s^{-1}$	Calibrated
γ_r	Optimal root respiration rate	1×10^{-5}	$mg\ CO_2\ m^{-2}\ s^{-1}$	Calibrated
h_1	Tension where CO_2 production stops because it is to wet	0.01	cm	Estimated from field data of moisture content and CO_2
h_2	Tension where CO_2 production is optimum	3	cm	Estimated from field data of moisture content and CO_2
h_3	Tension where CO_2 production slows significantly because it is to dry	150	cm	Estimated from field data of moisture content and CO_2
MAGIC Model				
DDF	Dry deposition factor	2.0 for NH_4^+ and NO_3^- 1.7 for SO_4^{-2} 1 for all others	Unitless	Obtained from NADP and CASTNET data collected nearby
N Uptake	Catchment N uptake	80	% of input flux	Calibrated
SO_4^{2-} half sat	Half saturation constant for SO_4^{2-}	226	$\mu eq\ m^{-3}$	Calibrated
Weathering Rates	Weathering rates of catchment rocks	Mg: 4.2; Na: 14.3; Ca: 0.6	$\mu eq\ m^{-2}\ yr^{-1}$	Calibrated

Determination of contributing cells

Topographic analysis of the catchment DEM was used to determine cells contributing water rapidly to the stream. Because we are using a DEM with 30 m resolution and the width of the stream channel is < 5 m, we could not simply define the cells adjacent to either side of the stream as those contributing cells. Further, we could not define the cells that make up the stream because those cells should theoretically have very little soil respiration due to saturated conditions. Therefore, we used a series of topographic masks to exclude cells from analysis to define a group of cells that represent those contributing water directly to the stream channel.

The first two topographic masks were based on the soil wetness index developed by Beven and Kirkby (1979), defined for each pixel as $\ln(a/\tan\beta)$ where a is the upslope contributing area of the cell, and $\tan\beta$ is the local slope angle of the cell. This topographic index (TI) can be considered a temporally static quantification of the two properties contributing wetness to any point on a catchment; the area draining through that point, and the rate at which that water moves out of the cell, indicated by the slope. Wet locations (low slopes, high upslope contributing areas such as valley bottoms) typically have high TI values, and dry locations (steep slopes, low upslope contributing areas, such as ridge tops) typically have low TI values.

The first mask that we applied was to exclude all of the cells that define the stream itself. This was done by excluding all cells with a topographic index greater than 11.9. The next mask excluded hillslope cells not contributing directly to the channel. We did this by excluding cells where the topographic index value was less than 9.9. The final mask excluded cells that met the first two criteria but could not logically contribute directly to the steam. These cells include topographic hollows on the hillslopes and were excluded by applying an elevation mask of 580 m to the selection. This analysis resulted in 57 cells that we take as representative of those which are important to setting the chemical signature of the stream water (Figure 1).

Soil temperature

The model of soil temperature used here is based on a hybrid physical–empirical technique developed by Kang et al. (2000) that predicts spatial and temporal variation in soil temperature in topographically varied forested regions, incorporating the effects of topography, canopy cover, and ground litter. The model is based on the heat transfer equation for soil

$$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho c} \frac{\partial^2 T}{\partial z^2} \qquad (2)$$

where T is soil temperature, t is time, λ the thermal conductivity, ρ the soil bulk density, c the specific heat capacity of soil and z is the soil depth. This is then

coupled with an empirical linkage between soil temperature and air temperature. The equations used to determine soil temperature through space (including z) and time are, for when $A_j > T_{j-1}$

$$T_j(z) = T_{j-1}(z) + \left[A_j - T_{j-1}(z)\right]\exp\left[-z\left(\frac{\pi}{k_s p}\right)^{\frac{1}{2}}\right]\exp\left[-k\left(\text{LAI}_j + \text{Litter}_j\right)\right] \quad (3)$$

and when $A_j \leq T_{j-1}$

$$T_j(z) = T_{j-1}(z) + \left[A_j - T_{j-1}(z)\right]\exp\left[-z\left(\frac{\pi}{k_s p}\right)^{\frac{1}{2}}\right]\exp\left[-k^*\text{Litter}_j\right] \quad (4)$$

where A_j is the average daily air temperature, T_{j-1} is the soil temperature on the previous day, z is depth into the soil, k_s the thermal diffusivity, and p the period of diurnal or annual temperature variation (seconds). Litter_j is the leaf area index (LAI) equivalent for ground litter, and k is the Beer–Lambert extinction coefficient for radiation in a canopy. This is done for each contributing cell for each day in the simulation using calibration parameters determined using the data from 2001. A more through description of the model is given in Kang et al. (2000) and in Welsch and Hornberger (2004).

Soil tension

Soil tension varies through both time and space in response to precipitation, evapotranspiration, and soil properties. We related the value of the saturation deficit calculated by the rainfall-runoff model TOPMODEL to measured soil tension through a two step process. First, we use our measured soil moisture to inform an estimate of the tension seen in the driest spot in the catchment each day. Next, using this maximum tension as an upper bound, we linearly relate the saturation deficit derived by TOPMODEL (for each cell for each time step) to soil tension using an empirical relationship between modeled saturation deficit and tension observed every 15 min near the catchment outlet and weekly at 10 locations within the catchment (Figure 1). Figure 2 presents a flowchart of the process described below. We use the rainfall-runoff model TOPMODEL, developed by Beven and Kirkby (1979), to calculate a water balance for each pixel in the catchment. As part of that balance, the model computes a saturation deficit for each cell for each time step in the simulation. The saturation deficit is defined as the depth of water that would have to be added to that cell at that time step to saturate it. We use a version of TOPMODEL that simulates a shallow stormflow zone and a relatively deeper groundwater zone, and thus produces a stormflow zone saturation deficit, and a groundwater zone saturation deficit (Scanlon et al. 2000). We chose to use the groundwater saturation deficit because in the modified version of TOPMODEL, the
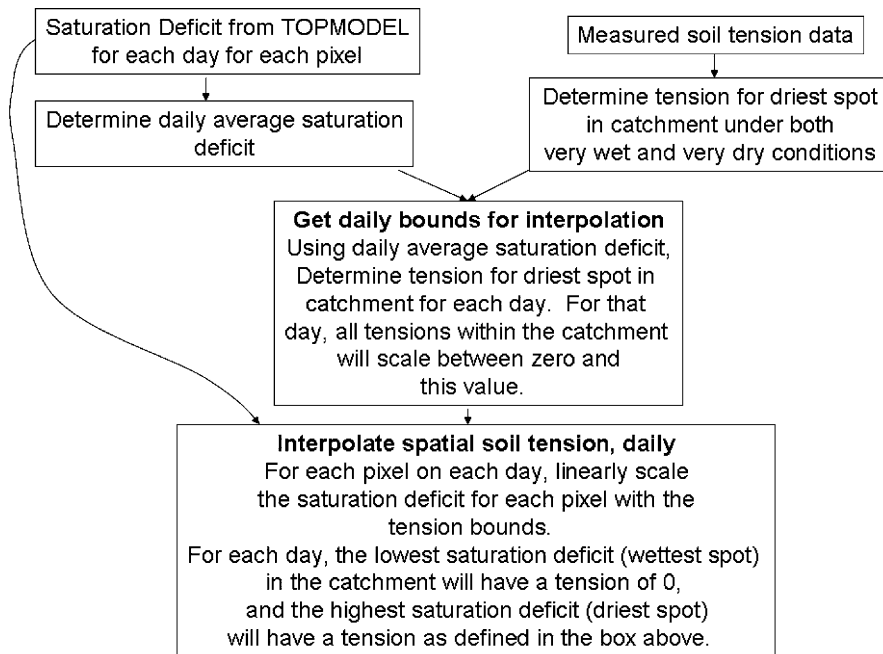
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┌─────────────────────────────────┐        ┌─────────────────────────────┐
│ Saturation Deficit from TOPMODEL│        │ Measured soil tension data  │
│      for each day for each pixel│        └─────────────────────────────┘
└─────────────────────────────────┘                      │
              │                            ┌─────────────────────────────┐
              ↓                            │ Determine tension for driest│
┌─────────────────────────────────┐       │   spot in catchment under   │
│ Determine daily average         │       │ both very wet and very dry  │
│             saturation deficit  │       │          conditions         │
└─────────────────────────────────┘       └─────────────────────────────┘
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Get daily bounds for interpolation
Using daily average saturation deficit,
Determine tension for driest spot in
catchment for each day. For that
day, all tensions within the catchment
will scale between zero and
this value.

Interpolate spatial soil tension, daily
For each pixel on each day, linearly scale
the saturation deficit for each pixel with the
tension bounds.
For each day, the lowest saturation deficit (wettest spot)
in the catchment will have a tension of 0,
and the highest saturation deficit (driest spot)
will have a tension as defined in the box above.

Figure 2. Flowchart showing process for determining spatially distributed soil tension values from saturation deficits produced by TOPMODEL and limited field data.

stormflow zone is extremely transient and remains wet only during and immediately following storms, after which there is no long term drainage.

We first used the weekly spatially distributed measurements of volumetric water content of the soil (converted to tension through the soil characteristic curve) to determine the highest and lowest maximum daily tension values seen in the catchment during the study period. The highest maximum tension can be thought of as the tension measured at the driest spot in the simulation on a very dry day, and the lowest maximum tension can be considered to be the tension measured at that same spot on a very wet day. The maximum tension possible for each day is scaled linearly with the daily catchment average saturation deficit, such that wet days have a lower maximum tension, and the tension approaches the highest maximum tension as the catchment dries out. Once the tension at the driest site in the catchment for each day is known, the tension at each location in the catchment is determined through linear interpolation with the local saturation deficit calculated by TOPMODEL. The lower bounds for the interpolation are tension = 0 when saturation deficit = 0. The upper bound for tension is the calculated maximum tension described above. Therefore, the minimum saturation deficit (always 0, in the stream channel) will have a tension of zero and the maximum saturation deficit will have a tension equivalent to the maximum tension determined based on the

average saturation deficit of the catchment on that particular day. That soil tension is assumed to represent the profile being simulated, as our field observations show that below the first couple centimeters of soil and litter, soil moisture is relatively uniform with depth.

Soil CO$_2$ production and transport model

In order to describe the concentration of CO_2 in soil air, both the production of CO_2 (respiration) and transport of CO_2 need to be simulated. We use a modified version of the model developed by Fang and Moncrieff (1999) where production and transport are simulated in one dimension through the soil profile, assuming horizontal exchange is negligible. The basic equation for the model is

$$\frac{\partial C_t}{\partial t} = -\frac{\partial}{\partial z}(F_{dg} + F_{ag} + F_{dw} + F_{aw}) + S \qquad (5)$$

where F_{dg} and F_{dw} are dispersive/diffusive fluxes in the gaseous and liquid phases of the soil, respectively, F_{ag} and F_{aw} are the advective fluxes resulting from gas convection and vertical water movement, respectively, C_t is the total CO_2 in both gas and liquid phases, and S is a depth-dependent term defining sources and sinks of CO_2 in the soil. The S term in (5) is the sum of root and microbial respiration. Working under the assumption that all organic matter will ultimately be oxidized to CO_2, and that we can express organic matter as an equivalent amount of fine roots, the microbial respiration rate R_m is

$$R_m = \gamma_m M' \qquad (6)$$

where γ_m is the microbial respiration rate parameter (mg CO_2 m^{-2} s^{-1}) of the fine root fraction, and M' is the amount (g dry mass m^{-2}) of labile organic matter given as an equivalent amount of fine roots. Because of the variation in the respiration rates of microbes on dead roots of different sizes, dead root biomass is simplified to an equivalent mass of fine roots, thus only requiring one rate constant (Fang and Moncrieff 1999). Root respiration is a function of specific root respiration rate and the root biomass. Root respiration (R_r) can be described by

$$R_r = \sum \gamma_{r_i} B_i \qquad (7)$$

where γ_{ri} (mg CO_2 m^{-2} s^{-1}) is the respiration rate parameter for root size class i and B_i is the biomass (g dry mass m^{-2}) of size class i. Equations 6 and 7 can be added together and integrated through the soil profile to determine the total CO_2 production.

The respiration rate terms in (6) and (7) are controlled by soil temperature, soil tension, and soil O_2 concentration. That is, the parameters γ_x in (6) and (7) are given by $\gamma_x = f(T)f(W)f(O)\gamma_{x0}$ where γ_x represent the maximum respiration

rate of roots and microbes under a given temperature (10 °C) at optimal conditions. Factors for soil water ($f(W)$) and for soil O_2 content ($f(O)$) are scaling factors and have a value between 0 and 1. The influence of soil temperature on respiration rate can be defined using an Arrhenius relationship of the form

$$f(T) = \exp\left(\frac{-E}{RT}\right) \tag{8}$$

where E is the activation energy for respiration, R is the universal gas constant, and T is the absolute temperature (Lloyd and Taylor 1994). The influence of soil water on respiration is two-fold. First, water enhances the metabolic processes of both roots and microbes. However, if the soil is too wet, gas exchange with the atmosphere is reduced and O_2 levels drop, inhibiting respiration. Therefore, we use a series of equations similar to those used by Šimůnek and Suarez (1993) to describe the influence of soil tension on respiration rate:

$$f(W) = \frac{\log|h| - \log|h_1|}{\log|h_2| - \log|h_1|} \quad h \in (h_2, h_1) \tag{9a}$$

$$f(W) = \frac{\log|h| - \log|h_3|}{\log|h_2| - \log|h_3|} \quad h \in (h_3, h_2) \tag{9b}$$

$$f(W) = 0 \quad h \in (-\infty, h_3) \cup (h_1, +\infty) \tag{9c}$$

where h_2 is the tension where CO_2 production is optimal, h_3 is the tension where respiration ceases because conditions are to dry, and h_1 is the tension where respiration ceases because soils are to wet.

A Michaelis–Menten relationship can be used to model the influence of oxygen concentration on respiration in the form of

$$f(O_2) = \frac{1}{1 + K_M/[O_2]} \tag{10}$$

where K_M is the Michaelis–Menten constant and $[O_2]$ is the concentration of oxygen in the soil air. O_2 content rapidly increases respiration when O_2 concentrations are low, but eventually a plateau is reached beyond which increasing O_2 concentration has little effect on respiration.

Streamwater chemistry model

MAGIC is a lumped-parameter model of intermediate complexity, developed to predict the long-term effects of acidic deposition on surface water chemistry (Cosby et al. 1985a, 2001). The model simulates soil solution chemistry and surface water chemistry to predict the monthly and annual average concentrations of the major ions in these waters. MAGIC consists of: (1) a section in which the concentrations of major ions are assumed to be governed by

simultaneous reactions involving sulfate adsorption, cation exchange, dissolution–precipitation–speciation of aluminum and dissolution–speciation of inorganic carbon; and (2) a mass balance section in which the flux of major ions to and from the soil is assumed to be controlled by atmospheric inputs, chemical weathering, net uptake and loss in biomass and losses to runoff.

At the heart of MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from this pool change over time owing to changes in atmospheric deposition, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry. The degree and rate of change of surface water acidity thus depend both on flux factors and the inherent characteristics of the affected soils.

Cation exchange is modeled using equilibrium equations with selectivity coefficients for each base cation and aluminum (Gaines and Thomas 1953). Sulfate adsorption is represented by a Langmuir isotherm. Aluminum dissolution and precipitation are assumed to be controlled by equilibrium with a solid phase of aluminum trihydroxide. Aluminum speciation is calculated by considering hydrolysis reactions as well as complexation with sulfate and fluoride. Effects of carbon dioxide on pH and on the speciation of inorganic carbon are computed from equilibrium equations. Organic acids are represented in the model as tri-protic analogues. First-order rates are used for retention (uptake) of nitrate and ammonium in the catchment. N uptake rates are assumed to be constant through time in this application. Weathering rates are also assumed to be constant. A set of mass balance equations for base cations and strong acid anions are included. Given a description of the historical deposition at a site, the model equations are solved numerically to give long-term reconstructions of surface water chemistry. All equations, parameters, and coefficients used in MAGIC are detailed in Cosby et al. (1985b).

Within MAGIC, alkalinity is produced from the dissolution of CO_2 in water, followed by dissociation to bicarbonate and carbonate, with the excess protons consumed in base cation exchange reactions (equation 1a, b, c) (Cosby et al. 1985b). In general, the higher the soil air CO_2, the higher the soil and stream water alkalinity, as long as the protons can be consumed. In systems with low soil base cation status, alkalinity can remain low despite high CO_2 concentrations because bicarbonate is charge balanced by protons rather than by base cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) from the soil.

Model implementation

Atmospheric deposition and net uptake-release fluxes for the base cations and strong acid anions are required as inputs to the model. The stream discharge for the catchment, values for soil and stream temperature, partial pressure of carbon dioxide in the soil and stream water and organic acid concentrations in soil water and stream water must also be provided to the model. As implemented in this project, the model is a two-compartment representation of a catchment. Atmospheric deposition enters the soil compartment and the equilibrium equations are used to calculate soil water chemistry. The water is

then routed to the stream compartment, and the appropriate equilibrium equations are reapplied to calculate stream water chemistry.

Calibration procedure

The aggregated nature of the model requires that it be calibrated to observed data for the modeled stream before it can be used to examine potential system response. Calibration is achieved by setting the values of certain parameters in the model (called 'fixed' parameters). The model is then run (using observed atmospheric and hydrologic inputs) and the output (stream water and soil chemical variables, called 'criterion' variables) are compared to observed values of these variables. If the observed and simulated values differ, the values of another set of parameters in the model (called 'optimized' parameters) are adjusted to improve the fit. After a number of iterations, the simulated-minus-observed values of the criterion variables usually converge to near zero. Tables of MAGIC equations, optimization variables, and input variables are available in Cosby et al.(1985b).

Goodness of fit is determined using the Nash and Sutcliffe (1970) efficiency value, which is simply a ratio of the mean square error between observed and simulated to the variance in the observed data.. Values of 1 are best with large negative values being poor.

Results

Calibration results

The parameter set for soil temperature was determined by manual calibration of the leaf area index (LAI) and the thermal diffusivity of the soil (k_s) to match the model-calculated soil temperatures with data measured in 2001. The model matched the calibration period well where daily measurements were made, giving a Nash–Sutcliffe (1970) efficiency value of 0.93. The model slightly overpredicts soil temperatures greater than 19 °C and slightly underpredicts soil temperatures less than 19 °C. While the calibrated fit to data at one site is good, we are applying the model to a number of points along the stream channel. When the model is run for 10 sites sampled weekly in the catchment, the Nash–Sutcliffe efficiency criterion decreases to 0.48. Calibration was considered successful when the highest efficiency between modeled and observed data for the continuous measurements at site one and spatially distributed weekly measurements was obtained. More details of the calibration are given in Welsch and Hornberger (2004).

Scanlon et al. (2000) calibrated TOPMODEL to measured flow rates at South Fork Brokenback Run; we used their calibrated model. The tension model was calibrated by changing the minimum–maximum and maximum–maximum tensions seen in the catchment throughout the study. The fit of the predicted tension was poor during very dry (day 0–25) and very wet conditions

(day 110–150) periods. During the wet period the model overpredicts tension, resulting in a Nash–Sutcliffe criterion of -0.11. However, if the very wet times occurring mainly in the dormant season are disregarded, the model efficiency increases to 0.65. The large errors in tension during the dormant season are allowable because soil temperatures are low enough to be the controlling factor in respiration during the cold season, rendering tension unimportant during this time (Welsch and Hornberger 2004). Calibration was considered successful when the greatest correlation between observed and simulated soil moisture data was obtained.

The CO_2 portion of the model was calibrated by adjusting two different sets of parameters. The first set is the respiration rate coefficients that define the optimal rates for root and microbial respiration at 10 °C. The second set includes the values used to simulate the effect of moisture on respiration. These values were adjusted so that predicted data matched the measured data as well as possible from the calibration period. The model appears to properly simulate most of the calibration sequence except for an extremely dry period in August. For the entire period, the Nash–Sutcliffe efficiency criterion is -1.87. However, when this dry period during August is disregarded, the efficiency increases to 0.56. For a more detailed discussion of the calibration results, see Welsch and Hornberger (2004).

The stream and soil water chemistry model MAGIC was calibrated by running the model for 132 years beginning in 1850 and ending in 1982, at the beginning of the USGS record of stream chemistry. For each ion measured in stream water and for pH, a flow-weighted average was determined such that each ion had a single value representing the period between 1983 and 1991. Parameters in MAGIC were adjusted until the model output for each ion at the end of the 132 year sequence (1982) equaled the flow-weighted average value for that ion. MAGIC requires as atmospheric inputs estimates of the precipitation volume and the total deposition of eight ions: Ca, Mg, Na, K, NH_4^+, SO_4^{2-}, Cl^-, and NO_3^-. These total deposition data are required for each year of the calibration period. Estimated total deposition data are also required for the 132 years preceding the calibration period as part of the calibration protocol for MAGIC, and for each year of any future scenario that will be run using MAGIC.

Total deposition of an ion at a particular site for any year can be represented as combined wet, dry, and cloud deposition. Inputs to the model are specified as wet deposition (the annual flux in $\mu eq/m^2/year$) and a dry deposition and cloud deposition enhancement factor (DDF, unitless) used to multiply the wet deposition in order to get total deposition: TotDep = WetDep * DDF.

MAGIC was calibrated to the study site using wet deposition data collected at Big Meadows in the nearby Shenandoah National Park, VA, by the National Atmospheric Deposition Program (NADP; http/:nadp.sws.uiuc.edu). Wet deposition input data were averaged for the study site over the calibration period. The dry deposition enhancement factors (DDF) for S and N were calculated using the NADP wet deposition data and dry deposition estimates from CASTNet (http/:www.epa.gov/castnet) data also collected at Big

Meadows. Historical estimates of total deposition of S and N were derived by scaling present day observed deposition of these elements to their present day emissions inventory and then using these scaled values with historical emissions data to estimate past deposition (Office of Technology Assessment 1984). Historical deposition of other ions were assumed to have been constant.

Stream NO_3^- was calibrated by adjusting ecosystem uptake. Stream SO_4^{2-} was calibrated by adjusting the total amount of SO_4^{2-} that could be specifically adsorbed to the soil, and by adjusting the half saturation constant for specific adsorption. Stream Cl^- was adjusted by adding or removing Cl^- in deposition, balanced stochiometricaly by Na^+. Base cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) were calibrated by adjusting the exchangeable fractions on the soil surface and, more importantly, by adjusting the weathering rates of catchment rocks.

Simulation results

For most years in the simulation, alkalinity simulated by MAGIC matches closely with observed alkalinity determined by the USGS. We were able to simulate both summer maximum alkalinity well in most years, and winter minimum alkalinity values well in all years (Figure 4a). Modeled alkalinity is highest in the summer, approaching 120 μeq/l, and lowest in the winter, reaching about 30 μeq/l, matching the measured data well. However, during 1987, 1988, and 1990, growing season alkalinity is significantly overpredicted by the model, reaching about 200 μeq/l, while observed data remained near or below 100 μeq/l (Figure 4a). When all data are considered, the Nash–Sutcliffe criterion is -0.5 (Figure 4b). However, if the data in the 3 years which were climatological anomalies, 1987, 1989, and 1990, are disregarded, the Nash–Sutcliffe criterion is 0.26.

Given that the alkalinity simulations are the product of simulations of soil temperature, soil moisture, and soil air CO_2, it is appropriate to briefly discuss the results from these sub-models. All three models show a typical seasonal trend, with low values in the winter or dormant season, and high values in summer or growing season (Figure 3). Average winter low CO_2 concentrations for the simulated period is about 0.3%, and the average summer peak of CO_2 is about 5%. The deep soil air CO_2 concentration averages 0.7% greater than the shallow concentrations. The greatest differences between shallow and deep concentrations occur during the summer and the concentrations are most similar during the winter. During the summers of 1987, 1989, and 1990, the simulated deep CO_2 concentrations are about 2.5% greater than the simulated shallow concentrations (Figure 3a, b).

Measured air temperature follows a seasonal pattern with average summertime highs reaching about 28 °C and winter lows reaching about −8 °C, except for the winters of 1984 and 1985, which had temperatures approaching −13 °C. The summer of 1988 was warmer than the rest of the series with summer peak temperatures reaching 32 °C (Figure 3c). Even though the
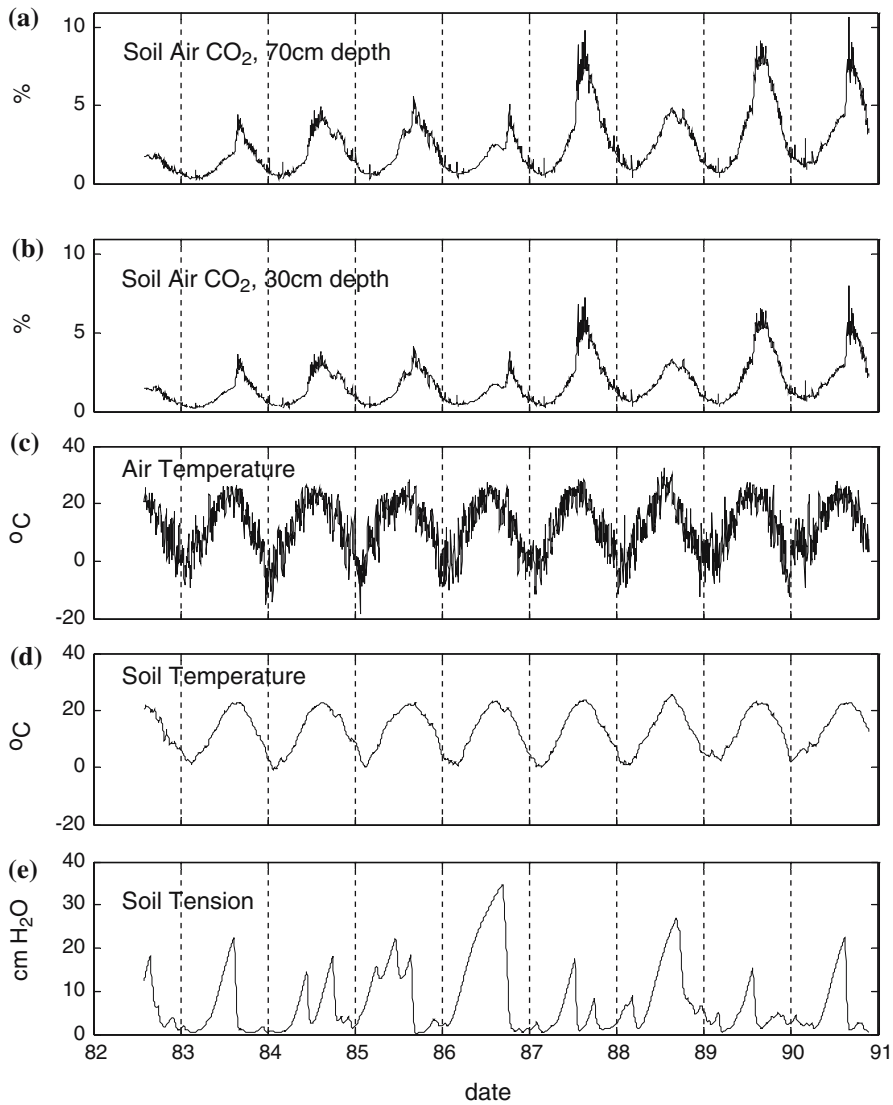
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Figure 3. Modeled and input parameters through time for the South Fork Brokenback Run watershed. Soil CO_2 concentrations (a, b) are model output. Air temperature (c) is model input, determined form a composite of two nearby NOAA NWS weather stations. Soil temperature (d) is output from the soil temperature model and is then input into the CO_2 production and transport model. Soil tension (e) is output from the soil tension model and is then input into the CO_2 production and transport model.

observed temperature extremes seen in 1984, 1985, and 1988 are short lived, their influence can still be seen in the soil temperature simulation results (Figure 3d). The lowest simulated soil temperatures (about −1 °C) occurred in

the winter of 1983–1984. In all other years simulated, soils do not freeze below the top few centimeters. Maximum summer soil temperatures are about 23 °C with the exception of 1988, when soils reached a temperature of 25.6 °C during the very hot summer.

Simulated soil tension values averaged for the nearstream contributing cells (Figure 1) are highest in summer (dry soils) and lowest in winter (wet soils) (Figure 3e). Typical winter low tensions are around 2.5 cm of water, while summer high tensions in these riparian soils reach about 23 cm on an average year. The summer of 1986 was very dry, with tensions reaching up to 35 cm of water, and the summers of 1987, 1989, and 1990 were quite wet, with tensions not exceeding 20 cm for more than a few days.

Discussion

One of the most useful purposes that a model can serve is as a hypothesis testing tool. In this case, we have constructed the series of models according to our hypothesized understanding of how alkalinity is generated in forested watersheds, and what impacts that generation, principally from the perspective of CO_2 production and subsequent reactions with water in the soil. From these simulations, we have learned that many of our hypotheses are correct, but a few still need work. Of principal interest is the relationship between soil temperature and soil moisture as the controlling factors on CO_2 production. In constructing the model, we have hypothesized that soil temperature is limiting seasonally, but when soils are warm, soil moisture becomes limiting. This hypothesis was based on observations of our calibration data set, which was obtained during one of the worst drought years in Virginia's history (2001). We have found support for this hypothesis through the simulations presented here, however the extent of this effect still needs investigation as we overpredict summer alkalinity during wet years (Figure 4a). The years in which simulated alkalinity concentrations are significantly higher than observed concentrations correspond to 3 years in which simulated CO_2 in both shallow and deep soils was much higher than in other years (Figure 3a) which we attribute to an incomplete understanding of the relationship between moisture and CO_2 concentrations. For the 3 years in question simulated soil moisture was significantly higher than for other years in the record. During 1987 and 1989, more precipitation fell during the summer months than in normal years (Figure 5), and certainly more than fell during the calibration period (343 mm), explaining why the catchment remained relatively wet during the summer, and why CO_2 concentrations and thus alkalinity concentrations were unusually high, as our data show that soil tension is the dominant control on respiration during the growing season, and thus soil air CO_2 concentration. While the summer of 1990 did not experience above average precipitation values, it did experience low early summer temperatures which depressed evapotranspiration resulting in wetter summer soils and higher respiration and
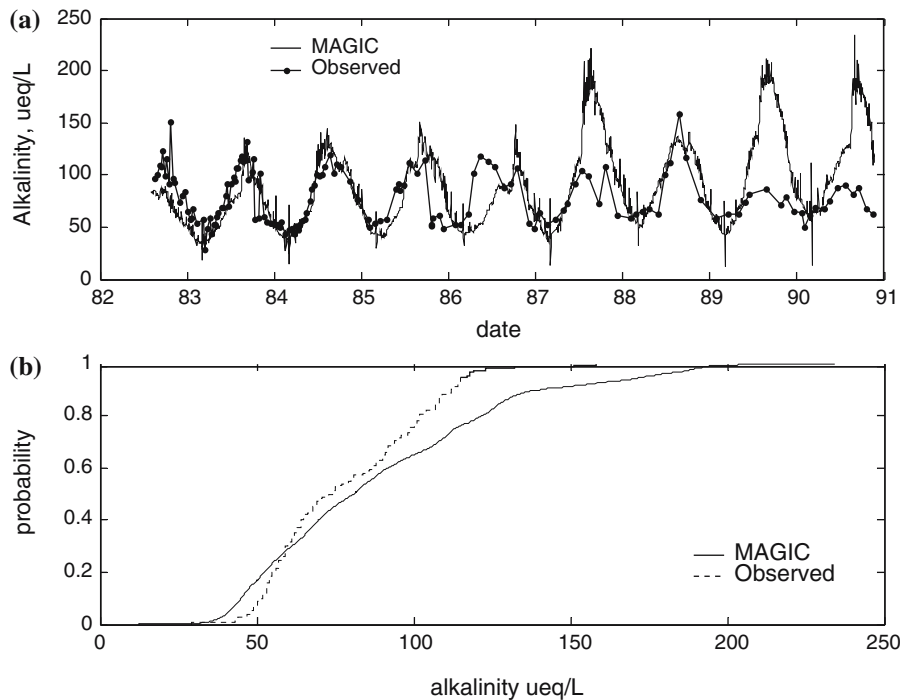
Figure 4. Simulated soil air CO_2 concentrations are output from the soil air CO_2 model and input into MAGIC to produce time series of stream and soil water chemistry for the South Fork of Brokenback Run watershed. (a) Simulated and measured alkalinity concentrations through time. (b) Cumulative distribution function of both the simulated and measured data.

concentration values. For the water year 1990, only 0.75 m of water was evapotranspired, simulated as part of TOPMODEL. For all other years in the simulation, depths of water evapotranspired was between 0.81 and 0.86 m.

Although the CO_2 model accounts for soil wetness, it was calibrated using only six months of data, collected during a very dry late summer and early autumn period when rainfall and streamflows in the mid-Atlantic were at or near record lows. Therefore, the model failure during the relatively wet years may result because it was not calibrated to handle such conditions. During times when soil wetness is more 'normal', such as 1983, the model does an excellent job of predicating stream alkalinity.

It is also possible that different hydrological mechanisms are contributing water to the stream during dry and wet periods, affecting alkalinity. MAGIC is a lumped model, and as such, assumes the same soil properties for all soils in the catchment. During dry periods such as the one during which model calibration data were collected, it is very likely that water draining to the stream is only in contact with soils in the riparian area. However, during wet periods, it is likely that hillslope water flowing through the riparian zone contributes
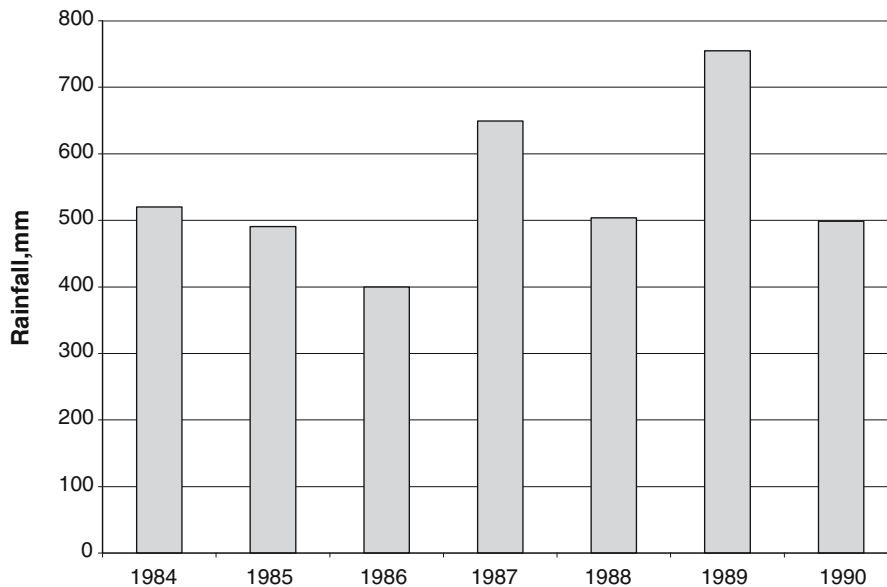
Figure 5. Summer (May–September) precipitation totals showing that 1987 and 1989 are wetter than normal years for the South Fork of Brokenback Run watershed. These years correspond with years where simulated stream water alkalinity is much greater than observed alkalinity.

a significant proportion of water to the stream, and also contributes organic acids (DOC) which act to lower the measured alkalinity in the stream (McGlynn and McDonnell 2003). The concentration–discharge relationship for alkalinity that we used was established for 'normal' conditions when discharge is high in winter and low in summer, and as such may not accurately represent periods with wetter than average summers such as those seen in 1987, 1989, and 1990.

All cells selected using the topographic masks occupy a similar topographic position within the watershed; hillslope hollow or riparian hollow. Because of this, the model is not particularly sensitive to the choice of cells or to the number of cells selected. Analysis of the modeled CO_2 concentrations from the selected cells shows that cell concentrations vary subtly according to changes in moisture and temperature and that the average value input into MAGIC is not skewed by one or several very high or very low concentration cells. Because of this minor variation, a simpler way of aggregating catchment CO_2 response for input into MAGIC is being investigated.

While we were unable to predict the peak summer alkalinity concentration in 3 of the 9 years simulated, we were able to accurately predict the minimum annual stream alkalinity for all years. From a resource management perspective, the minimum values are of most interest as they indicate the minimum ability of the system to buffer acid inputs which may endanger fish populations, particularly during high flow events in the dormant season.

Conclusion

Admittedly, a simple sinusoidal function would have been able to simulate much of the variation seen in the observed catchment CO_2 and stream alkalinity response, and perhaps more accurately. However, the purpose of our investigation was not to simply recreate the data collected by the US Geological survey in the catchment, but to understand the functioning of the catchment systems that we have simulated here. How accurately or inaccurately we are able to recreate the time series of collected data is simply a measure of how well we understand the system and how well we are able to translate that understanding into a mathematical model. The model presented here is probably more complicated then it needs to be. However, we felt it was important to begin with a formalization of the catchment processes in as much detail as we could efficiently manage, and then to pare down and create a more parsimonious model once we have established that our fully detailed model was reasonably accurate and precise.

We have shown that a series of coupled mathematical models of physical processes is capable of simulating stream water alkalinity, within the climatic bounds of the calibration data set. Understanding the factors influencing production and transport of CO_2 in soil, and being able to simulate this mathematically, is critical to understanding carbon exchange through the boundary layer on larger scales. Further, understanding the response of terrestrial and stream ecosystems to changing climates (increasing temperatures, increasing rainfall intensities) is difficult without being able to simulate the acid-base reactions occurring in soils and streams, including the production of acids such as H_2CO_3 (Equation 1). The work presented here is a first step in understanding the influences on soil CO_2 generation and the resultant chemical impacts on catchment streams.

Acknowledgements

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