

# Carbon Dioxide Variation in a Hardwood Forest Stream: An Integrative Measure of Whole Catchment Soil Respiration

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## ABSTRACT

The concentration of CO<sub>2</sub> in stream water is a product of not only instream metabolism but also upland, riparian, and groundwater processes and as such can provide an integrative measure of whole catchment soil respiration. Using a 5-year dataset of pH, alkalinity, Ca<sup>2+</sup>, and Mg<sup>2+</sup> in surface water of the West Fork of Walker Branch in eastern Tennessee in conjunction with a hydrological flowpath chemistry model, we investigated how CO<sub>2</sub> concentrations and respiration rates in stream, bedrock, and soil environments vary seasonally and interannually. Dissolved inorganic carbon concentration was highest in summer and autumn ( $P < 0.05$ ) although the proportion as free CO<sub>2</sub> ( $p\text{CO}_2$ ) did not vary seasonally ( $P > 0.05$ ). Over the 5 years,  $p\text{CO}_2$  was always supersaturated with respect to the atmosphere ranging from 374 to 3626 ppmv (1.0- to 10.1-fold greater than atmospheric equilibrium), and CO<sub>2</sub> evasion from the stream to the atmosphere ranged from 146 to 353 mmol m<sup>-2</sup> d<sup>-1</sup>. Whereas  $p\text{CO}_2$  in surface water exhibited little intra-annual or interannual variation, distinct seasonal patterns in soil and bedrock  $p\text{CO}_2$  were revealed by the catchment CO<sub>2</sub> model. Seasonally, soil  $p\text{CO}_2$  in-

creased from a winter low of 8167 ppmv to a summer high of 27,068 ppmv. Driven by the seasonal variation in gas levels, evasion of CO<sub>2</sub> from soils to the atmosphere ranged from 83 mmol m<sup>-2</sup> d<sup>-1</sup> in winter to 287 mmol m<sup>-2</sup> d<sup>-1</sup> in summer. The seasonal variation in soil CO<sub>2</sub> tracked soil temperature ( $r^2 = 0.46$ ,  $P < 0.001$ ) and model-derived estimates of CO<sub>2</sub> evasion rate from soils agreed with previously reported fluxes measured using chambers (Pearson correlation coefficient = 0.62,  $P < 0.05$ ) supporting the model assumptions. Although rates of CO<sub>2</sub> evasion were similar between the stream and soils, the overall rate of evasion from the channel was only 0.4% of the 70,752 mol/d that evaded from soils due to the vastly different areas of the two subsystems. Our model provides a means to assess whole catchment CO<sub>2</sub> dynamics from easily collected and measured stream-water samples and an approach to study catchment scale variation in soil ecosystem respiration.

**Key words:** carbon dioxide; ecosystem metabolism; organic matter decomposition; trace gas evasion; catchment scale; Tennessee.

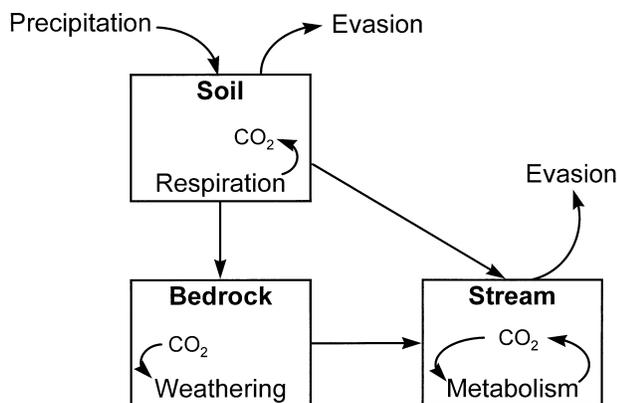
## INTRODUCTION

Respiration is a central process in ecosystems regulating organic matter decomposition, detrital storage, nutrient cycling, and evasion of CO<sub>2</sub> to the

atmosphere. In light of concerns of environmental degradation and climate change, the need for larger-scale studies of ecosystem respiration has become apparent (Mooney and others 1987; Schneider 1989). Most studies of ecosystem metabolism, however, are conducted at relatively small spatial scales [see, for example, Hedin (1990), Pusch and Schw-

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**Figure 1.** Conceptual model of linkages and processes governing  $\text{CO}_2$  concentrations in soil, bedrock, and surface waters. See the text for details.

erbel (1994) and Jones and others (1995)]; spatially and temporally, variation in ecosystem respiration (Solomon and Cerling 1987; Howard and Howard 1993; Piñol and others 1995) restricts efforts to extrapolate results from studies conducted at small spatial scales to larger areas (Raich and Potter 1995). New approaches are needed to characterize respiration over larger areas and time scales.

The chemical composition of stream water is a product of not only instream processes but also is regulated by upland, riparian, and groundwater processes that determine solute and gaseous inputs into aquatic habitats [see, for example, Bormann and Likens (1970, 1979) and Hynes (1975)]. Free  $\text{CO}_2$  ( $p\text{CO}_2$ ) and total dissolved inorganic carbon (DIC) concentrations in streams result from the interplay between inorganic carbon fixation via aquatic primary production, organic matter decomposition, diffusion to the atmosphere, and groundwater inputs (Kling and others 1991, 1992; Cole and others 1994; Hope and others 1994; Dawson and others 1995). If the contribution of instream processes to stream  $p\text{CO}_2$  concentration is known, stream-water  $p\text{CO}_2$  can be used as a tool to assess contributions of  $p\text{CO}_2$  from upland soil respiration via groundwater inputs. Groundwater  $p\text{CO}_2$  can, in turn, be used to quantify carbonate weathering in bedrock environments and the concentration of  $\text{CO}_2$  in soils (Robson and others 1991). Stream-water  $p\text{CO}_2$  is an easily measured parameter, thus allowing for extensive spatial and temporal sampling.

To use stream-water chemistry to study  $p\text{CO}_2$  in bedrock and soil environments, we began with a conceptual model in which catchments are viewed as three interacting subsystems (soil, bedrock, and stream) linked by hydrologic flows (Figure 1). Rates

within and hydrologic fluxes between subsystems regulate stream-water  $p\text{CO}_2$ . Most water initially enters basins through the soil subsystem as precipitation and has an initial  $p\text{CO}_2$  in equilibrium with the atmosphere [360 ppmv (Keeling and Whorf 1994)]. Pore spaces in soils almost always have elevated  $p\text{CO}_2$  levels with respect to the atmosphere, because of root respiration and organic matter decomposition (Figure 1) (Castelle and Galloway 1990; Rebsdorf and others 1991; Piñol and others 1995), which elevates the  $p\text{CO}_2$  content of soil water. From soils, water potentially percolates deeper into a bedrock zone [herein referred to as bedrock water (Mulholland 1993)] where cation exchange and dissolution of bedrock can result in a decline of  $p\text{CO}_2$  and production of bicarbonate (Stumm and Morgan 1981). Water emerging as stream and river water is composed of  $p\text{CO}_2$  mostly derived from soils but reduced from soil levels as a result of bedrock weathering (Skiba and Cresser 1991). Within streams, biotic and abiotic processes such as metabolism, atmospheric evasion, and precipitation of carbonates further modify  $p\text{CO}_2$  (Figure 1). Thus, because stream-water  $p\text{CO}_2$  is a product of processes occurring in both aquatic and upland soil ecosystems, it provides an indication of the rates within and the linkages between these two environments.

Using 5 years of stream-chemistry data from Walker Branch in eastern Tennessee and a hydrologic flowpath model, we investigated temporal variation in stream  $p\text{CO}_2$ , and calculated  $p\text{CO}_2$  concentrations in bedrock and soil environments and  $\text{CO}_2$  evasion rates from soils and stream to the atmosphere. In this way, our analysis provided a means to describe seasonal and interannual variations in  $\text{CO}_2$  flux to the atmosphere from soils at whole catchment scales.

## METHODS

### Site Description

The study was conducted in the West Fork of Walker Branch, a first-order stream (38.4-ha catchment) on the US Department of Energy's Oak Ridge National Environmental Research Park (latitude  $35^{\circ}58'N$ , longitude  $84^{\circ}17'W$ ) in eastern Tennessee. The climate is typical of the humid southern Appalachia region, with mean annual temperature of  $14.5^{\circ}\text{C}$  and mean annual rainfall of 140 cm, distributed fairly evenly throughout a year.

Walker Branch drains a hardwood-forested catchment underlain by the Knox Group, a 610-m-thick sequence of Cambrian and Ordovician siliceous dolomite that weathers rapidly to form deep soils

with abundant chert (McMaster 1963). Soils are primarily Ultisols, with small areas of Inceptisols found in alluvial valleys adjacent to streams (Peters and others 1970). Surface infiltration rates are very rapid, and rainfall infiltrates completely even during the greatest-intensity storms (Luxmoore 1983). Surface soils have high hydraulic conductivity because of high macroporosity (Wilson and Luxmoore 1988). Hydraulic conductivity, however, declines rapidly with depth because of increasing clay content (Wilson and others 1989), and zones of perched saturation develop in upper soil layers, producing rapid lateral flow during larger storms (Mulholland and others 1990). During most periods, however, soils are unsaturated, and the permanent groundwater level remains at considerable depth, just above the bedrock zone (Mulholland and others 1990; Mulholland 1993). The surface soils are acidic (pH 4.2–5.0) and low in exchangeable bases, nitrogen, and phosphorus.

#### Sampling Protocol, Frequency, and Analytical Methods

The stream was sampled 300 m downstream from several headwater springs weekly from 1991 through 1995. Samples were collected between 0900 and 1200 h on Mondays prior to 30 March 1992 and on Tuesdays thereafter. Unfiltered samples were collected for alkalinity and pH determination by sealing bottles under water to prevent exposure to the atmosphere, placed on ice, returned to the laboratory, and refrigerated until analysis. Samples for cation analysis were collected in polyethylene bottles, filtered immediately upon returning to the laboratory (within 3 h), and acidified until analysis (0.5% HNO<sub>3</sub>). Water temperature was measured with an Orion (Boston, USA) model 122 conductivity meter. *p*CO<sub>2</sub> and DIC were determined from alkalinity (titration with 0.1 N HCl to a fixed end-point pH of 4.5) and pH by using temperature-adjusted dissociation constants [*K<sub>h</sub>*, *K<sub>1</sub>*, and *K<sub>2</sub>* (Stumm and Morgan 1981)] and were adjusted for the ionic strength of solution (*K<sub>1</sub>* and *K<sub>2</sub>*). Activity coefficients were calculated from the ionic strength estimated from Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations by using Davies' equation (Loewenthal and Marais 1976). The alkalinity of stream water in Walker Branch is highly correlated with the sum of Ca<sup>2+</sup> and Mg<sup>2+</sup> equivalents (linear regression, *r*<sup>2</sup> = 0.90, *P* < 0.001), with a slope of 1.00 indicating that most acid-neutralizing capacity is from carbonates derived from the weathering of the parent bedrock dolomite. Ca<sup>2+</sup> and Mg<sup>2+</sup> were measured by inductively coupled plasma-emission spectrometry.

#### Model Description

Using *p*CO<sub>2</sub>, Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations in stream surface water, we developed a model describing *p*CO<sub>2</sub> concentration in bedrock and soil environments. To back calculate *p*CO<sub>2</sub> in bedrock and soils, we began with a series of equations describing the mean concentration of *p*CO<sub>2</sub> in groundwater discharge to Walker Branch. Surface-water *p*CO<sub>2</sub> concentration is a function of concentration in groundwater input, instream metabolism, and diffusion to the atmosphere,

$$pCO_{2 \text{ STREAM}} = pCO_{2 \text{ GW}} - pCO_{2 \text{ NEP}} - pCO_{2 \text{ EVAS}} \quad (1)$$

where *p*CO<sub>2</sub> STREAM is the concentration in stream water (ppmv), *p*CO<sub>2</sub> GW is the average *p*CO<sub>2</sub> in groundwater discharging into the stream (ppmv), *p*CO<sub>2</sub> NEP is the input or uptake from instream metabolism (ppmv), and *p*CO<sub>2</sub> EVAS is loss to the atmosphere (ppmv).

The uptake or release of CO<sub>2</sub> by instream metabolism (*p*CO<sub>2</sub> NEP) is

$$pCO_{2 \text{ NEP}} = \frac{NEP \times A}{Q} \quad (2)$$

where NEP is net ecosystem production (mol m<sup>-2</sup> d<sup>-1</sup>), A is the area of the wetted channel (m<sup>2</sup>), and Q is discharge (L/s). NEP was estimated by using data collected in the West Fork of Walker Branch (Marzolf and others 1994; Mulholland and others 1997, unpublished data). NEP data were recalculated from the originally presented values by using a modified algorithm to calculate re-aeration flux as presented by Young and Huryn (forthcoming; Marzolf and Mulholland forthcoming). NEP was measured on a total of seven dates spread throughout spring, summer, and autumn during which NEP varied from -2.7 to -6.8 g O<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup>. Lacking any apparent seasonal pattern, we assumed for the purposes of our model that NEP was constant at -4.7 g O<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> (the mean rate). Metabolism was converted to carbon units by using a respiratory quotient of 1. Wetted channel area was assumed to remain constant at 1000 m<sup>2</sup> (Mulholland 1997). Walker Branch arises from several discrete springs and exhibits little longitudinal expansion or contraction with change in discharge. Similarly, the stream channel is incised, and only highest flows spill out onto the floodplain, resulting in little variation in stream width.

The loss of CO<sub>2</sub> to the atmosphere through evaporation is

$$pCO_{2 \text{ EVAS}} = k_{CO_2}(pCO_{2 \text{ STREAM}} - pCO_{2 \text{ ATM}})R_T \quad (3)$$

where  $k_{\text{CO}_2}$  is a diffusion constant ( $\text{d}^{-1}$ ),  $p\text{CO}_2_{\text{ATM}}$  is the atmospheric equilibrium concentration of  $\text{CO}_2$  (ppmv), and  $R_T$  is the mean residence time of surface water in Walker Branch ( $\text{d}^{-1}$ ). The troposphere mean concentration of 360 ppmv was used for  $p\text{CO}_2_{\text{ATM}}$ .  $k_{\text{CO}_2}$  was estimated from propane injections to the stream conducted during the metabolism studies of Marzolf and others (1994) and Mulholland and others (1997, unpublished data). Measurements of  $k_{\text{propane}}$  were made over a range of flows and related to discharge by

$$k_{\text{propane}} = \frac{155.3 Q}{2.41 + Q} \quad (4)$$

where  $Q$  is discharge ( $\text{L/s}$ ;  $r^2 = 0.57$ ). The ratio of  $k_{\text{CO}_2}$  to  $k_{\text{propane}}$  was estimated as 1.3 by using

$$\frac{k_{\text{CO}_2}}{k_{\text{propane}}} = \left( \frac{D_{\text{CO}_2}}{D_{\text{propane}}} \right)^n \quad (5)$$

where  $D_{\text{CO}_2}$  and  $D_{\text{propane}}$  are the aqueous diffusion coefficients for  $\text{CO}_2$  and propane, respectively, and  $n$  ranges from 0.5 to 1 (Bennett and Rathbun 1972).  $D_{\text{CO}_2}$  was calculated by using relationships described by Jähne and others (1987) (assuming a temperature of  $20^\circ\text{C}$ ),  $D_{\text{propane}}$  was set equal to  $2.3 \times 10^{-5} \text{ cm}^2/\text{s}$  (Wise and Houghton 1966), and  $n = 0.7$  (Genereux and Hemond 1990, 1992).  $R_T$  was calculated by using a series of relationships developed by Genereux and others (1993) to describe the longitudinal input of groundwater into Walker Branch as a function of total discharge. Briefly, Genereux and others (1993) partitioned the 300-m channel of Walker Branch into four sections and measured groundwater discharge into each section at a range of flows by using conservative solute tracers. Groundwater discharge into each section was linearly related to surface flow with correlation coefficients ranging from 0.94 to 0.99. Using the four resulting equations, we calculated the proportion of surface flow entering Walker Branch through each of the four stream sections:

$$R_T = \frac{\sum g_i x_i}{v} \quad (6)$$

where  $g_i$  is the proportion of surface flow derived from section  $i$ ,  $x_i$  is the mean distance upstream from the sampling station for section  $i$  (m), and  $v$  is the mean water velocity ( $\text{cm/s}$ ). Water velocity was calculated from discharge as

$$v = 3.552 \ln Q - 2.066, \quad (7)$$

which was derived from unpublished data for Walker Branch ( $r^2 = 0.95$ ).

After calculating the mean  $p\text{CO}_2$  content of groundwater, we determined the proportion derived from soil and bedrock environments by using a hydrologic end-member mixing model in conjunction with the chemical equation for dolomite dissolution, the parent bedrock of the Walker Branch watershed. The mean  $p\text{CO}_2$  of groundwater is a weighted average of  $p\text{CO}_2$  in bedrock and soil water entering the stream:

$$p\text{CO}_2_{\text{GW}} = f_{\text{BED}} p\text{CO}_2_{\text{BED}} + f_{\text{SOIL}} p\text{CO}_2_{\text{SOIL}} \quad (8)$$

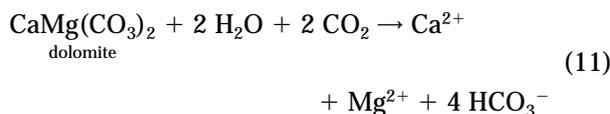
where  $f_{\text{BED}}$  and  $f_{\text{SOIL}}$  are the proportion of stream flow originating from bedrock and soil environments, and  $p\text{CO}_2_{\text{BED}}$  and  $p\text{CO}_2_{\text{SOIL}}$  are concentrations in bedrock and soils, respectively.  $f_{\text{BED}}$  and  $f_{\text{SOIL}}$  were determined by using  $\text{Ca}^{2+}$  in a two-end-member mixing model in which the fraction of total stream discharge contributed by each water reservoir (end-member) at any time is computed by simultaneously solving the following set of equations:

$$f_{\text{BED}} + f_{\text{SOIL}} = 1 \quad (9)$$

$$[\text{Ca}^{2+}]_{\text{BED}} f_{\text{BED}} + [\text{Ca}^{2+}]_{\text{SOIL}} f_{\text{SOIL}} = [\text{Ca}^{2+}]_{\text{STREAM}} \quad (10)$$

where  $[\text{Ca}^{2+}]$  is the calcium concentration in bedrock, soil, or stream environments. Mulholland (1993) measured  $\text{Ca}^{2+}$  in bedrock water (springs) and soil water (subsurface lateral flow, soil lysimeters) from 1988 to 1991 across a broad range of flows.  $\text{Ca}^{2+}$  in bedrock and soil water exhibited little temporal fluctuation, averaging 778 and 85  $\mu\text{M}$ , respectively.

The final two unknowns in Eq. (8) ( $p\text{CO}_2_{\text{BED}}$ ,  $p\text{CO}_2_{\text{SOIL}}$ ) were solved based upon the stoichiometric dissolution of dolomite. All water entering bedrock was assumed to originate from soils and thus has an initial  $\text{CO}_2$  content in equilibrium with soil atmosphere. As dolomite weathers,  $p\text{CO}_2$  is converted to  $\text{HCO}_3^-$  according to the following,



and therefore  $p\text{CO}_2_{\text{SOIL}}$  and  $p\text{CO}_2_{\text{BED}}$  are related by

$$p\text{CO}_2_{\text{SOIL}} = p\text{CO}_2_{\text{BED}} + \text{Ca}_{\text{BED}}^{2+} + \text{Mg}_{\text{BED}}^{2+} \quad (12)$$

where  $\text{Ca}_{\text{BED}}^{2+}$  and  $\text{Mg}_{\text{BED}}^{2+}$  are the molar quantities generated by dissolution.  $\text{Ca}_{\text{BED}}^{2+}$  and  $\text{Mg}_{\text{BED}}^{2+}$  were estimated as the difference between stream-water concentrations and the background concentrations in soil water.

Lastly, using  $p\text{CO}_2 \text{ SOIL}$  we estimated  $\text{CO}_2$  evasion from soils to the atmosphere ( $\text{CO}_2 \text{ EVAS}$ ;  $\text{mol cm}^{-2} \text{ s}^{-1}$ ) by

$$\text{CO}_2 \text{ EVAS} = \frac{D_{\text{CO}_2} dp}{R T dz} \quad (13)$$

where  $D_{\text{CO}_2}$  is the effective molecular diffusion of  $\text{CO}_2$  in a porous medium ( $\text{cm}^2/\text{s}$ ),  $R$  is the ideal gas constant ( $82.057 \text{ ml atm K}^{-1} \text{ mol}^{-1}$ ),  $T$  is soil temperature (K), and  $dp/dz$  is the pressure gradient of  $\text{CO}_2$  with soil depth [ppmv/cm (Lerman 1979)].  $T$  was assumed equal to stream temperature. Soil depth ( $z$ ) was estimated as 100 cm, the approximate depth to soil water measured in wells located along the East Fork of Walker Branch (unpublished data). The  $dp$  was calculated as the difference between  $p\text{CO}_2 \text{ SOIL}$  and an atmospheric concentration of 360 ppmv.  $D_{\text{CO}_2}$  is

$$D_{\text{CO}_2} = \text{CO}_2 \text{ MOL DIFF} \phi^{4/3} \quad (14)$$

where  $\text{CO}_2 \text{ MOL DIFF}$  is the molecular diffusion rate of  $\text{CO}_2$  ( $\text{cm}^2/\text{s}$ ) and  $\phi$  is soil porosity [unitless (Millington 1959)].  $\text{CO}_2 \text{ MOL DIFF}$  in turn was estimated after (Lerman 1979) as

$$\text{CO}_2 \text{ MOL DIFF} = 0.0009 T - 0.11 \quad (15)$$

As a final note regarding our model, all estimates of  $p\text{CO}_2$  in bedrock and soil environments are derived from stream-water chemistry and temperature and do not rely upon measurements of soil chemistry.

### Error Analysis

To characterize the error in calculations of soil and bedrock  $\text{CO}_2$  water concentrations, and  $\text{CO}_2$  evasion to the atmosphere, we conducted an uncertainty analysis in which the six parameters we estimated or derived for the simulation were randomly varied over reasonable ranges and the model repeatedly rerun. Specifically, we randomly varied instream NEP (from  $-2.7$  to  $-6.8 \text{ g O}_2 \text{ m}^{-2} \text{ d}^{-1}$ ), wetted channel area ( $800$ – $1200 \text{ m}^2$ ), soil porosity ( $10\%$ – $60\%$ ), gas gradient across the soil surface ( $10$ – $150 \text{ cm}$ ), rate of diffusion from the stream to atmosphere ( $\pm 25\%$  of estimated rate), and the hydrologic residence time of water on the stream surface ( $\pm 25\%$  of estimated time). All parameters were independently varied at the start of a simulation and then held constant while the response variables were calculated for the 5 years of data. The simulation was run 10,000 times. Following each run, seasonal means were calculated and, following the full analysis of 10,000 runs, coefficients of variation (CV) were calculated for the seasonal means to describe the uncertainty of the model results.

### Statistical Analysis

Seasonal and interannual differences were assessed with two-way analysis of variance. Significant differences ( $P < 0.05$ ) were further evaluated by using Tukey's multiple comparison.

## RESULTS

### Climate and Hydrology

Mean daily air temperature in Walker Branch exhibited a distinct seasonal pattern ranging from an average winter value of  $4.8^\circ\text{C}$  to average summer temperature of  $23.5^\circ\text{C}$  (Table 1). Temperature also varied significantly between years from annual means of  $13.5^\circ\text{C}$  during 1992 and 1994 to  $14.8^\circ\text{C}$  in 1991 (Table 2). In contrast to the seasonal and interannual variability in air temperature, precipitation was fairly uniform over the 5 years, averaging  $3.8 \text{ mm/d}$  (Tables 1 and 2).

Although precipitation varied little, flow out of the basin significantly varied seasonally and interannually, as did discharge from soil and bedrock environments to the stream surface. Seasonally, surface flow declined an average of  $70\%$  from the average winter rate of  $19.4 \text{ L/s}$  to only  $5.8 \text{ L/s}$  in summer (Figure 2 and Table 1). Interannually, stream flow varied twofold from an annual mean of  $8.8 \text{ L/s}$  in 1992 to  $17.9 \text{ L/s}$  in 1991 (Table 2).

Most stream flow ( $76\%$ ) was fed by discharge from bedrock (Tables 1 and 2), although the contribution ranged from a low of  $56\%$  during winter to  $90\%$  in summer (Table 1). Flow from bedrock exhibited two distinct intra-annual regimes, with a high flow period during winter–spring ( $Q = 7.9$ – $8.3 \text{ L/s}$ ) and a low flow period during summer–autumn ( $Q = 4.8$ – $5.0 \text{ L/s}$ ). Discharge from soils was considerably more variable, ranging nearly 16-fold from only  $0.7 \text{ L/s}$  during summer to  $11.1 \text{ L/s}$  in winter (Table 1).

### Weathering, Alkalinity, and pH

The weathering of dolomite and export of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from the Walker Branch watershed were regulated by the absolute rate of flow from bedrock. During the higher-flow winter–spring period, export of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  was greatest, averaging  $1106$ – $1254 \text{ mol/d}$  (Figure 3 and Table 1). As flow from bedrock declined from a mean of  $8.1 \text{ L/s}$  in winter–spring to  $4.9 \text{ L/s}$  in summer–autumn,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  flux dropped  $42\%$  to  $669$ – $705 \text{ mol/d}$ . Interannually, weathering was highest during 1991 and 1994 (Figure 3 and Table 2), the years of greatest discharge from bedrock.

Whereas the weathering of dolomite was related to the rate of discharge from bedrock, the resulting

**Table 1.** Seasonal Means and Coefficients of Variation (CV) of Climate, Hydrology, Bedrock Weathering, Stream Chemistry, and Stream, Soil, and Bedrock CO<sub>2</sub> Concentrations and Evasion Rates in Walker Branch, Tennessee, for 1991–1995

	Winter		Spring		Summer		Autumn	
	Mean	CV	Mean	CV	Mean	CV	Mean	CV
Mean air temperature (°C)	4.8 <sup>a</sup>	1.11	17.3 <sup>b</sup>	0.31	23.5 <sup>c</sup>	0.11	10.2 <sup>d</sup>	0.60
Mean daily precipitation (mm)	4.2	2.34	3.8	2.56	3.1	2.57	3.9	2.69
Surface discharge (L/s)	19.4 <sup>a</sup>	1.19	13.3 <sup>a,b</sup>	0.85	5.8 <sup>c</sup>	0.35	9.5 <sup>b,c</sup>	2.11
Soil discharge (L/s)	11.1 <sup>a</sup>	1.98	5.3 <sup>a,b</sup>	1.75	0.7 <sup>b</sup>	1.86	4.7 <sup>a,b</sup>	4.22
Bedrock discharge (L/s)	8.3 <sup>a</sup>	0.28	7.9 <sup>a</sup>	0.31	5.0 <sup>b</sup>	0.24	4.8 <sup>b</sup>	0.29
$f_{\text{bedrock}}$	0.56 <sup>a</sup>	0.32	0.72 <sup>b</sup>	0.27	0.90 <sup>c</sup>	0.16	0.84 <sup>c</sup>	0.25
$f_{\text{soil}}$	0.44 <sup>a</sup>	0.42	0.28 <sup>b</sup>	0.65	0.10 <sup>c</sup>	1.01	0.16 <sup>c</sup>	1.36
pH	8.00 <sup>a</sup>	0.03	8.05 <sup>a,b</sup>	0.02	8.12 <sup>c</sup>	0.01	8.09 <sup>b,c</sup>	0.03
Alkalinity (mEq/L)	1.74 <sup>a</sup>	0.29	2.16 <sup>b</sup>	0.24	2.73 <sup>c</sup>	0.09	2.58 <sup>c</sup>	0.23
Ca <sup>2+</sup> + Mg <sup>2+</sup> flux (mol/d) <sup>1</sup>	1254 <sup>a</sup>	0.40	1106 <sup>a</sup>	0.37	669 <sup>b</sup>	0.21	705 <sup>b</sup>	0.53
pCO <sub>2</sub> stream (ppmv)	1246	0.67	1406	0.49	1457	0.19	1368	0.29
DIC stream (μM)	1796 <sup>a</sup>	0.29	2238 <sup>b</sup>	0.22	2780 <sup>c</sup>	0.09	2610 <sup>c</sup>	0.23
pCO <sub>2</sub> bedrock (ppmv)	1479	3.24	2279	1.91	2847	0.77	3069	0.89
pCO <sub>2</sub> soil (ppmv)	8167 <sup>a</sup>	1.11	16,506 <sup>b</sup>	0.66	27,068 <sup>c</sup>	0.27	18,648 <sup>b</sup>	0.56
Soil evasion (mmol m <sup>-2</sup> d <sup>-1</sup> )	83 <sup>a</sup>	1.16	173 <sup>b</sup>	0.67	287 <sup>c</sup>	0.27	194 <sup>b</sup>	0.57
Stream evasion (mmol m <sup>-2</sup> d <sup>-1</sup> )	353 <sup>a</sup>	1.31	256 <sup>a,b</sup>	0.69	146 <sup>b</sup>	0.29	243 <sup>a,b</sup>	1.99
DIC from respiration (μM) <sup>2</sup>	1142 <sup>a</sup>	0.28	1355 <sup>b</sup>	0.23	1697 <sup>c</sup>	0.13	1575 <sup>b,c</sup>	0.28
DIC flux (mol/d) <sup>1</sup>	2451 <sup>a</sup>	0.55	2138 <sup>a</sup>	0.32	1351 <sup>b</sup>	0.20	1452 <sup>b</sup>	0.62
Respiratory DIC flux (mol/d) <sup>1</sup>	1685 <sup>a</sup>	0.72	1351 <sup>a</sup>	0.38	864 <sup>b</sup>	0.21	1126 <sup>a,b</sup>	0.89

Superscripts denote means significantly different ( $P < 0.05$ ) as determined by Tukey's multiple comparison.  $N = 65$  samples per season. DIC, dissolved inorganic carbon.

<sup>1</sup>Flux = concentration  $\times$  discharge.

<sup>2</sup>DIC from respiration = DIC stream - Ca<sub>BED</sub><sup>2+</sup> - Mg<sub>BED</sub><sup>2+</sup>; assuming Ca<sub>BED</sub><sup>2+</sup> and Mg<sub>BED</sub><sup>2+</sup> is from dolomite, then dolomite-derived DIC = Ca<sub>BED</sub><sup>2+</sup> + Mg<sub>BED</sub><sup>2+</sup>, given dolomite = CaMg(CO<sub>3</sub>)<sub>2</sub>.

stream-water alkalinity and pH were determined by the proportion of surface flow derived from bedrock. During winter, when the relative contribution of surface flow from bedrock was lowest, alkalinity reached a seasonal minimum of 1.74 mEq/L (Figure 4 and Table 1). As the proportion of flow from bedrock progressively increased from a winter low of 50% to a summer high of 90%, alkalinity concomitantly increased to 2.73 mEq/L. Stream-water pH tracked alkalinity, with a seasonal low of 8.00 during winter when alkalinity was minimal to a high of 8.12 in summer when alkalinity was greatest (Figure 4 and Table 1). Alkalinity, however, did not exhibit significant interannual variation, whereas pH ranged from annual means of 7.99 in 1995 to 8.14 in 1992 (Table 2).

### Stream-Water pCO<sub>2</sub>

Coupled to the seasonal variation in alkalinity, total DIC in stream water varied from mean values of 1796 μM in winter to 2610–2780 μM in summer–autumn (Figure 5 and Table 1). Over the 5 years, pCO<sub>2</sub> was always supersaturated with respect to atmospheric concentration, with levels 1.0- to 17.3-

fold greater than equilibrium [assuming an atmospheric concentration of 360 ppmv (Keeling and Whorf 1994)] and seasonal means ranging from 1246 to 1457 ppmv. In spite of the distinct seasonal patterns in stream DIC, however, pCO<sub>2</sub> in stream water did not exhibit consistent seasonal variation (Figure 5 and Table 1). Both DIC and pCO<sub>2</sub> varied among years, but exhibited different patterns, with mean DIC varying from 2210 μM in 1991 to 2511 μM in 1992, and pCO<sub>2</sub> ranging from 1193 ppmv in 1994 to 1618 ppmv in 1995 (Table 2). Interestingly, stream pCO<sub>2</sub> did not appear to be affected by storm flows, whereas DIC showed distinct storm effects, with lower values during spates (Figure 5).

### Soil and Bedrock pCO<sub>2</sub>

Although pCO<sub>2</sub> in surface water exhibited considerable noise, our model effectively filtered the signal, revealing distinct seasonal patterns in soil and bedrock water pCO<sub>2</sub>. In soils, the presumed source of CO<sub>2</sub> to groundwater, pCO<sub>2</sub> varied from 907 to 35,313 ppmv (Figure 6), 2.5–98 times atmospheric concentration. Soil-water pCO<sub>2</sub> was seasonally variable, ranging over threefold between winter and

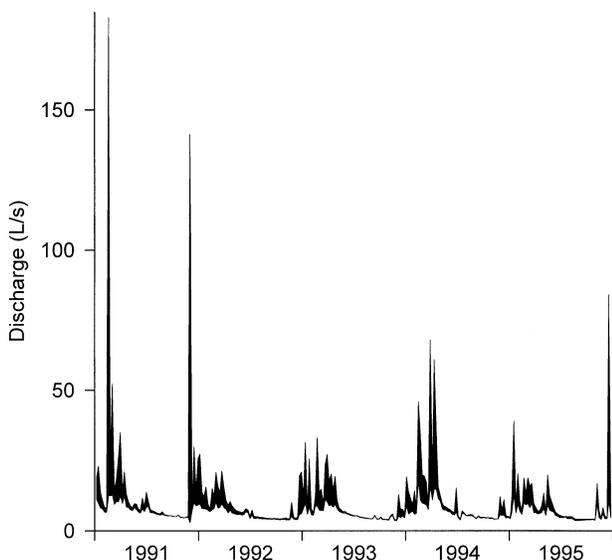
**Table 2.** Annual Means and Coefficients of Variation (CV) of Climate, Hydrology, Bedrock Weathering, Stream Chemistry, and Stream, Soil, and Bedrock CO<sub>2</sub> Concentrations and Evasion Rates in Walker Branch, Tennessee, for 1991–1995

	1991		1992		1993		1994		1995	
	Mean	CV	Mean	CV	Mean	CV	Mean	CV	Mean	CV
Mean air temperature (°C)	14.8 <sup>a</sup>	0.58	13.5 <sup>b</sup>	0.60	14.1 <sup>a,b</sup>	0.65	13.5 <sup>b</sup>	0.61	14.0 <sup>a,b</sup>	0.66
Mean daily precipitation (mm)	4.2	2.50	3.1	2.12	3.5	2.80	4.5	2.57	3.4	2.46
Surface discharge (L/s)	17.9 <sup>a,c</sup>	1.72	8.8 <sup>b</sup>	0.63	9.4 <sup>b,c</sup>	0.77	12.6 <sup>a,b</sup>	1.08	11.1 <sup>a,b</sup>	1.16
Soil discharge (L/s)	10.3	2.92	3.0	1.39	3.4	1.69	5.6	1.94	4.9	2.37
Bedrock discharge (L/s)	7.6 <sup>a</sup>	0.32	5.7 <sup>b</sup>	0.32	6.0 <sup>b</sup>	0.36	7.0 <sup>a,c</sup>	0.46	6.3 <sup>b,c</sup>	0.36
$f_{\text{bedrock}}$	0.74	0.34	0.76	0.26	0.77	0.32	0.76	0.31	0.74	0.25
$f_{\text{soil}}$	0.26	0.97	0.24	0.78	0.21	1.04	0.24	0.99	0.26	0.71
pH	8.03 <sup>a,c</sup>	0.03	8.14 <sup>b</sup>	0.02	8.04 <sup>a,c</sup>	0.02	8.11 <sup>a,b</sup>	0.02	7.99 <sup>c</sup>	0.03
Alkalinity (mEq/L)	2.18	0.31	2.45	0.24	2.34	0.26	2.25	0.28	2.28	0.26
Ca <sup>2+</sup> + Mg <sup>2+</sup> flux (mol/d) <sup>1</sup>	1136 <sup>a</sup>	0.51	829 <sup>b</sup>	0.39	831 <sup>b</sup>	0.38	981 <sup>a,b</sup>	0.55	882 <sup>b</sup>	0.44
pCO <sub>2</sub> stream (ppmv)	1388 <sup>a,b</sup>	0.61	1238 <sup>b</sup>	0.32	1441 <sup>a,b</sup>	0.22	1193 <sup>b</sup>	0.30	1618 <sup>a</sup>	0.51
DIC stream (μM)	2210 <sup>a</sup>	0.30	2511 <sup>b</sup>	0.23	2385 <sup>a,b</sup>	0.25	2318 <sup>a,b</sup>	0.26	2313 <sup>a,b</sup>	0.26
pCO <sub>2</sub> bedrock (ppmv)	2626	1.98	1293	1.37	2619	0.96	1821	1.40	3230	1.70
pCO <sub>2</sub> soil (ppmv)	17,079	0.69	15,967	0.77	18,593	0.62	14,708	0.84	17,966	0.60
Soil evasion (mmol m <sup>-2</sup> d <sup>-1</sup> )	179	0.70	167	0.79	195	0.64	153	0.86	188	0.62
Stream evasion (mmol m <sup>-2</sup> d <sup>-1</sup> )	373 <sup>a</sup>	1.61	157 <sup>b</sup>	0.54	229 <sup>a,b</sup>	0.69	184 <sup>b</sup>	0.62	318 <sup>a,b</sup>	1.39
DIC from respiration (μM) <sup>2</sup>	1316 <sup>a</sup>	0.30	1566 <sup>b</sup>	0.25	1429 <sup>a,b,c</sup>	0.25	1328 <sup>a,c</sup>	0.27	1435 <sup>a,b,c</sup>	0.28
DIC flux (mol/d) <sup>1</sup>	2288 <sup>a</sup>	0.68	1645 <sup>b</sup>	0.32	1672 <sup>b</sup>	0.38	1874 <sup>a,b</sup>	0.52	1799 <sup>b</sup>	0.48
Respiratory DIC flux (mol/d) <sup>1</sup>	1693 <sup>a</sup>	0.89	1112 <sup>b</sup>	0.33	1109 <sup>b</sup>	0.41	1298 <sup>a,b</sup>	0.56	1223 <sup>a,b</sup>	0.60

Superscripts denote means significantly different ( $P < 0.05$ ) as determined by Tukey's multiple comparison.  $N = 52$  samples per year. DIC, dissolved inorganic carbon.

<sup>1</sup>Flux = concentration × discharge.

<sup>2</sup>DIC from respiration = DIC stream - Ca<sub>BED</sub><sup>2+</sup> - Mg<sub>BED</sub><sup>2+</sup>; assuming Ca<sub>BED</sub><sup>2+</sup> and Mg<sub>BED</sub><sup>2+</sup> is from dolomite, then dolomite-derived DIC = Ca<sub>BED</sub><sup>2+</sup> + Mg<sub>BED</sub><sup>2+</sup>, given dolomite = CaMg(CO<sub>3</sub>)<sub>2</sub>.



**Figure 2.** Mean daily discharge from the West Fork of Walker Branch, Tennessee. The *black fill* indicates flow from soils, and the *open fill* indicates flow from bedrock.

summer (Figure 6 and Table 1). This seasonal variation closely tracked climate, with soil temperature explaining 46% of the variance in soil CO<sub>2</sub> [ $P < 0.001$  (Figure 6)]. Thus, during winter, when air temperature averaged 4.8°C and soil temperature averaged 7.2°C, soil pCO<sub>2</sub> was only 8167 ppmv (Table 1). As air and soil temperatures increased to seasonal highs of 23.5° and 20.5°C, respectively, in summer, soil pCO<sub>2</sub> increased to a seasonal peak of 27,068 ppmv. Interestingly, soil pCO<sub>2</sub> did not exhibit significant interannual variation, even though stream-water pCO<sub>2</sub> varied between years (Table 2). In contrast to the seasonal variation in pCO<sub>2</sub> in soil water, pCO<sub>2</sub> concentration in bedrock water did not significantly vary seasonally or interannually, averaging 2318 ppmv (Figure 6 and Tables 1 and 2).

### CO<sub>2</sub> Evasion and Stream Export

Evasion of CO<sub>2</sub> from soils ranged nearly fivefold from 83 to 287 mmol m<sup>-2</sup> d<sup>-1</sup> between winter and

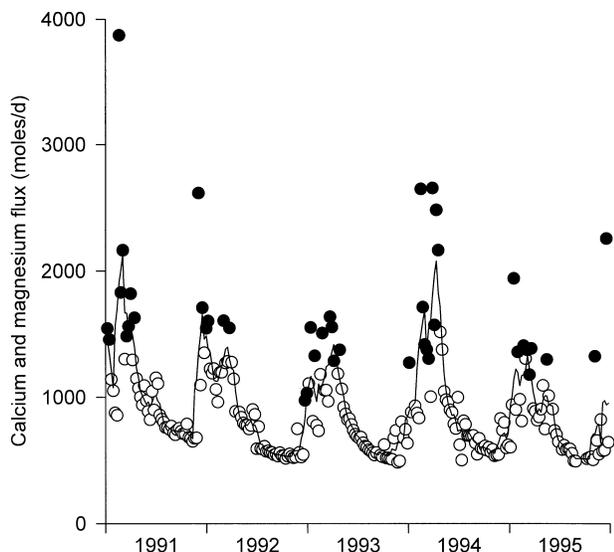


Figure 3. Flux of calcium and magnesium from the West Fork of Walker Branch, Tennessee. The filled circles indicate spates, and the fitted line is a 5-week running average.

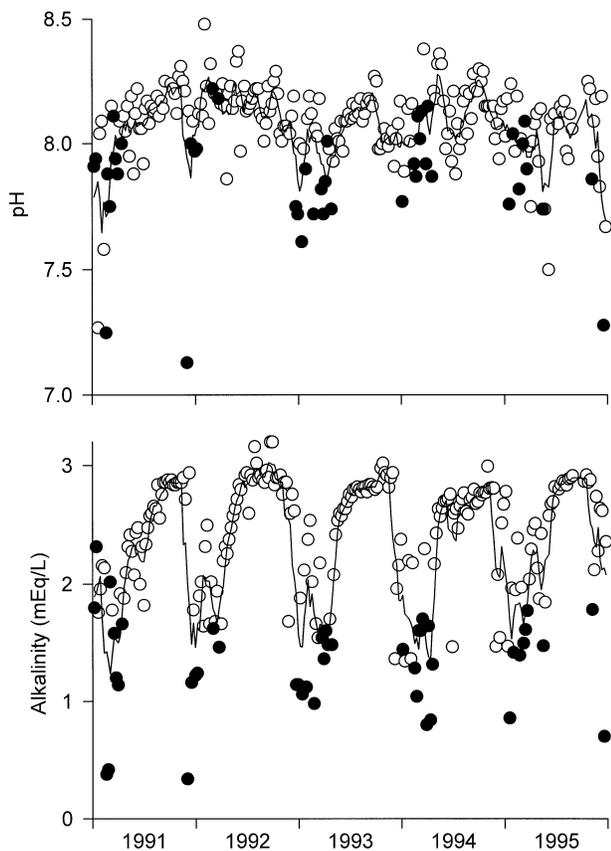


Figure 4. The pH and alkalinity in the West Fork of Walker Branch, Tennessee. The filled circles indicate spates, and the fitted lines are 5-week running averages.

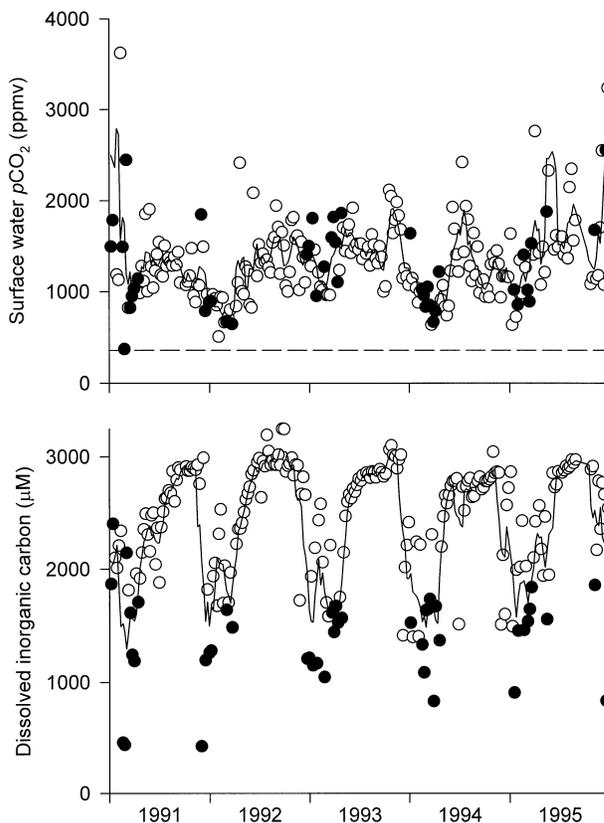
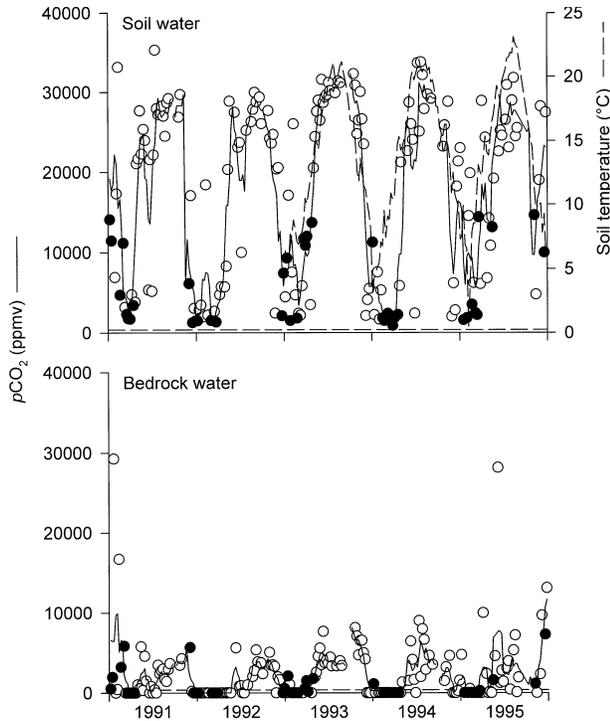


Figure 5. Surface water  $p\text{CO}_2$  and total dissolved inorganic carbon in the West Fork of Walker Branch, Tennessee. The filled circles indicate spates, the dashed line shows atmospheric concentration of 360 ppmv (Keeling and Whorf 1994), and the fitted lines are 5-week running averages.

summer, respectively (Figure 7 and Table 1). Evasion of  $\text{CO}_2$  from soils did not significantly vary among years, averaging  $176 \text{ mmol m}^{-2} \text{ d}^{-1}$  across the 5 years (Figure 7 and Table 2).

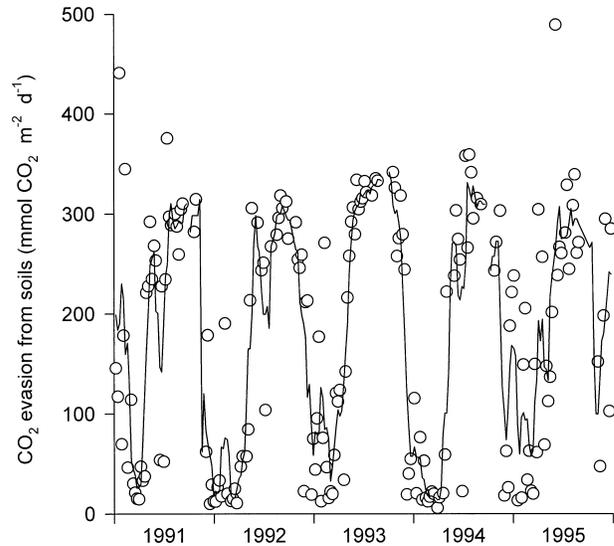
In contrast to the summer peak of  $\text{CO}_2$  evasion from soils, evasion from the stream surface was greatest during winter, averaging  $353 \text{ mmol m}^{-2} \text{ d}^{-1}$  due to higher discharge and increased turbulence (Figure 8 and Table 1). During summer, when soil  $\text{CO}_2$  evasion was greatest, stream flow was lowest, resulting in reduced turbulence and an evasion rate of  $146 \text{ mmol m}^{-2} \text{ d}^{-1}$ , only 41% of winter evasion. In contrast to the lack of interannual variation in evasion from soils,  $\text{CO}_2$  evasion from the stream exhibited significant interannual differences, ranging from annual means of 157 to  $373 \text{ mmol m}^{-2} \text{ d}^{-1}$  (Figure 8 and Table 2). Interestingly, the interannual pattern of  $\text{CO}_2$  evasion did not directly correspond with differences in surface discharge, indicating that factors other than flow and the resulting turbulence influenced stream evasion. Overall, the



**Figure 6.** Soil water  $p\text{CO}_2$ , soil temperature, and bedrock water  $p\text{CO}_2$  in the West Fork of Walker Branch, Tennessee, as determined from the catchment  $\text{CO}_2$  model. Soil temperature data are from Paul Hanson (personal communication; Environmental Sciences Division, Oak Ridge National Laboratory). The *dashed reference line* indicates atmospheric concentration of 360 ppmv (Keeling and Whorf 1994), the *filled circles* indicate spates, and the *fitted lines* are 5-week running averages.

area-specific rate of  $\text{CO}_2$  evasion from the stream surface was 143% greater than from soils, averaging  $252 \text{ mmol m}^{-2} \text{ d}^{-1}$ .

Export of DIC in stream water was sizable, especially compared with  $\text{CO}_2$  evasion from the stream surface. Downstream DIC flux was sevenfold greater than evasion from this headwater stream, averaging  $1856 \text{ mol/d}$  compared with an evasion of  $252 \text{ mol/d}$  (calculated as the product of area-specific rate and stream channel area). Respiration (primarily in soils) contributed 69% of the stream-water DIC flux at  $1287 \text{ mol/d}$ , with the remainder derived from weathering of dolomite. Like the seasonal pattern in evasion from the stream surface, stream-water DIC flux tracked discharge, with lowest and highest rates in summer and winter, respectively (Figure 8 and Table 1). Unlike surface evasion, however, stream-water DIC flux exhibited the same interannual pattern as discharge, although the finding is not unexpected given that flux is calculated from discharge.



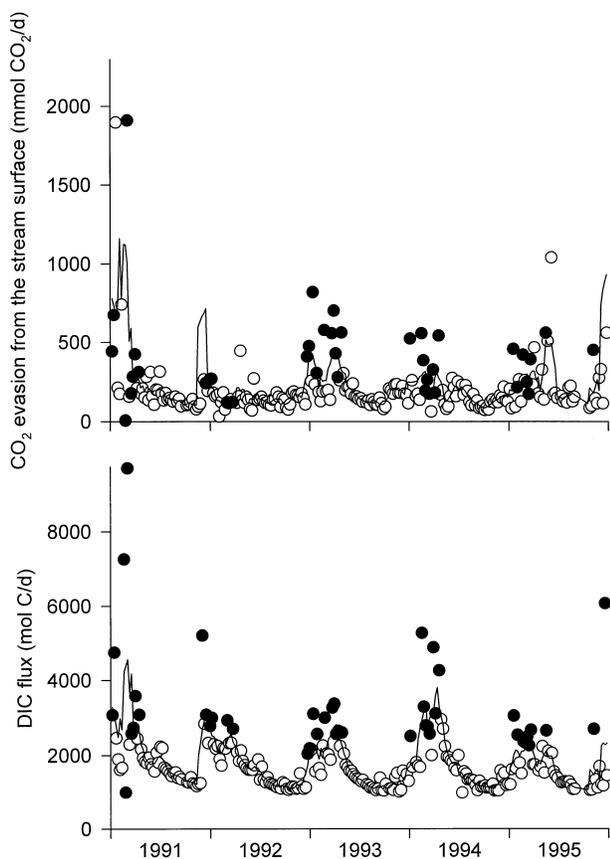
**Figure 7.** Evasion of  $\text{CO}_2$  from soils of the West Fork of Walker Branch watershed, Tennessee. The *fitted line* is a 5-week running average.

Although area-specific evasion rates were similar between the surface water and soils, the total amount of  $\text{CO}_2$  emitted from soils was much greater than from the stream, because of the vastly different surface areas of the two systems. In Walker Branch, the stream surface had an area of approximately  $1000 \text{ m}^2$  compared with  $384,000 \text{ m}^2$  for soils. As a consequence, the total  $\text{CO}_2$  evasion from the stream was only 0.4% of the  $70,752 \text{ mol/d}$  emitted from soils. Even summing stream-water DIC flux and stream-surface evasion, total stream export of inorganic carbon was only  $2100 \text{ mol/d}$  or 3.0% of soil evasion.

### Uncertainty Analysis

Based on the uncertainty analysis, there was little error in estimates of  $\text{CO}_2$  in soils. The CVs for the estimates of seasonal means of soil  $\text{CO}_2$  ranged from 0.15 to 0.21 (Figure 9). For bedrock environment, the CVs of seasonal mean estimates were greater than for soils, ranging from 0.29 to 0.49 (Figure 9).

In contrast to the minimal uncertainty in soil and bedrock water  $\text{CO}_2$ , the error associated with estimates of  $\text{CO}_2$  evasion from soils was much greater. The CVs for estimates of seasonal soil  $\text{CO}_2$  evasion rates varied from 1.01 to 1.15 (Figure 10). During winter, when evasion was low, 50% of the evasion estimates ranged from 67 to  $229 \text{ mmol m}^{-2} \text{ d}^{-1}$ . In summer, however, when evasion was much greater, the range in estimates was threefold greater, with 50% of the estimates between 238 and  $815 \text{ mmol m}^{-2} \text{ d}^{-1}$ .

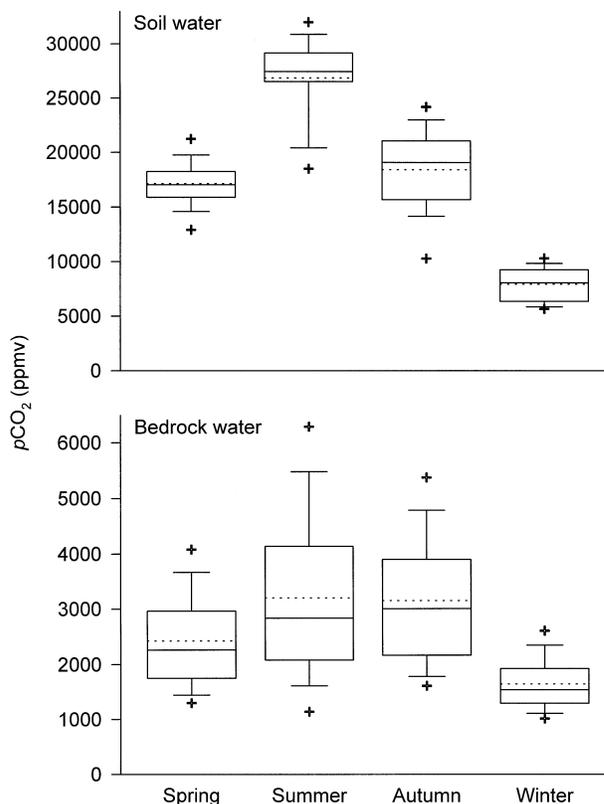


**Figure 8.** Evasion of  $\text{CO}_2$  from the stream-surface and stream-water total dissolved inorganic carbon (DIC) flux from the West Fork of Walker Branch, Tennessee. The filled circles indicate spates and the fitted lines are 5-week running averages.

## DISCUSSION

The subsurface  $\text{CO}_2$  model in conjunction with the 5 years of alkalinity, pH,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  data revealed distinct seasonal patterns in stream-water DIC and in bedrock and soil  $\text{CO}_2$ . In soils,  $\text{CO}_2$  varied from near atmospheric equilibrium of 360 ppmv to nearly 40,000 ppmv, presumably due to seasonal shifts in root and heterotrophic respiration. The hydrologic coupling between soil and deeper groundwater produced a similar summer peak in bedrock  $\text{CO}_2$ , although levels were lower due to consumption by weathering of dolomite. Weathering appears to have a substantial impact on  $\text{CO}_2$ , particularly at times during the winter when all free  $\text{CO}_2$  is apparently consumed by chemical reaction with bedrock (Figure 6).

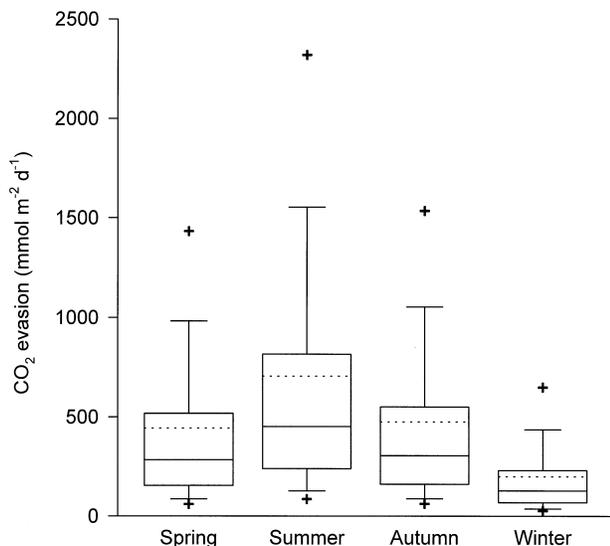
The seasonal patterns in soil and bedrock  $\text{CO}_2$  were revealed even though  $p\text{CO}_2$  of stream water did not exhibit intra-annual variation. The seasonal shift in relative importance of flow from soil and bedrock environments to the stream functions to



**Figure 9.** Results from uncertainty analysis of catchment  $\text{CO}_2$  model on estimates of soil and bedrock water  $p\text{CO}_2$ . The dotted line, solid center line, box extent, error bars, and crosses denote the mean, 50th, 25th and 75th, 10th and 90th, and 5th and 95th percentiles of estimates resulting from the 10,000 model runs.

dampen fluctuations in stream-water  $p\text{CO}_2$ . During summer, when soil  $\text{CO}_2$  is high, stream flow is nearly all derived from bedrock water and, as a consequence, little soil  $\text{CO}_2$  is expressed in stream water. Moving into autumn and winter, as catchment evapotranspiration declines, more stream flow is sustained by discharge from soils. This shift from largely bedrock-derived flow to shallower soil flow-paths has been shown to occur during storms in Walker Branch (Mulholland 1993). Thus, although bedrock  $\text{CO}_2$  declines during winter, the increased contribution of surface flow from soils results in an infusion of water enriched in  $\text{CO}_2$  and counters the drop in bedrock  $\text{CO}_2$  content.

The seasonal shift in hydrologic flowpaths and transport of  $\text{CO}_2$  between subsystems regulates the rate of bedrock weathering, and stream-water pH and alkalinity. During winter and spring, when discharge from bedrock to the stream is greatest (although lower as a proportion of total stream flow), weathering of dolomite is highest, as indicated by the flux of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from the



**Figure 10.** Results from uncertainty analysis of catchment  $\text{CO}_2$  model on estimates of  $\text{CO}_2$  evasion from soil. The dotted line, solid center line, box extent, error bars, and crosses denote the mean, 50th, 25th and 75th, 10th and 90th, and 5th and 95th percentiles of estimates resulting from the 10,000 model runs.

catchment (Figure 3). Interestingly, in spite of increased weathering during winter and spring, alkalinity declined by dilution from increased discharge from soils.

### Controls on Soil Respiration and $\text{CO}_2$ Evasion

Soil respiration and production of  $\text{CO}_2$  are principally governed by temperature and secondarily by soil moisture (Howard and Howard 1993; Raich and Potter 1995). In dry soils, biotic activity and  $\text{CO}_2$  production are limited by water availability. At the other extreme, oxygen diffusion is reduced in saturated soils, which can likewise limit biotic activity (Skopp and others 1990). Walker Branch receives frequent rain and has well-drained soils, which maintains soil moisture at levels of 10%–30% (Hanson and others 1993).

$\text{CO}_2$  generated in soils is emitted to the atmosphere either directly or following hydrologic transport to streams. By far, the dominant pathway for  $\text{CO}_2$  evasion from Walker Branch is by diffusion directly from soils. Stream evasion of  $\text{CO}_2$  and fluvial export of DIC amounts to 2100 mol/d, only 3.0% of evasion from soils to the atmosphere of 70,752 mol/d.

The annual evasion rate of  $\text{CO}_2$  from soils estimated in the present study agrees with a previous study conducted in the Walker Branch catchment. Hanson and others (1993) measured soil  $\text{CO}_2$  efflux

by using chambers from four sites within the Walker Branch watershed from March through mid-November 1991. The annual  $\text{CO}_2$  efflux from their four sites ranged from 168 to 212  $\text{mmol m}^{-2} \text{d}^{-1}$ . The daily evasion rates for soil  $\text{CO}_2$  evasion during 1991 estimated from our model were correlated with chamber-made estimates, with a Pearson correlation coefficient of 0.62 ( $P < 0.05$ ). Moreover, the correlation was particularly high between model estimates and chamber-made measures of  $\text{CO}_2$  evasion from the valley bottom of the Walker Branch watershed (Pearson correlation coefficient = 0.70,  $P < 0.05$ ), the study site of Hanson and others (1993) nearest the stream channel. The similarity of model and chamber estimates of soil  $\text{CO}_2$  evasion, along with the close correlation between soil  $p\text{CO}_2$  and soil temperature (Figure 6), give strong credence to the model assumptions and lend support to its utility as a tool to study soil respiration.

### Catchment Scale Inorganic Carbon Dynamics

Streams and lakes are typically supersaturated with  $\text{CO}_2$  (Cole and others 1994) and, as suggested by Kling and others (1991, 1992), function as conduits for trace gas exchange between terrestrial ecosystems and the atmosphere. The flux of carbon from soils through lakes to the atmosphere is substantial, contributing around  $0.14 \times 10^{15} \text{ g C}$  to the atmosphere per year, a rate about half the global riverine export of organic and inorganic carbon to oceans (Cole and others 1994). The flux through freshwater ecosystems may be much greater when lotic ecosystems are also considered. The annual flux of  $0.14 \times 10^{15} \text{ g C}$  from lakes translates to an area-specific rate of 16  $\text{mmol m}^{-2} \text{d}^{-1}$ .  $\text{CO}_2$  evasion from surface water of Walker Branch averaged 252  $\text{mmol m}^{-2} \text{d}^{-1}$ , 16-fold greater than the mean lentic efflux. Moreover, evasive loss of  $\text{CO}_2$  from the stream surface to the atmosphere was small compared with riverine export. The total respiratory flux of  $\text{CO}_2$  from Walker Branch averaged 1509  $\text{mmol m}^{-2} \text{d}^{-1}$  (sum of  $\text{CO}_2$  evasion and respiratory DIC flux in stream flow), 94-fold greater than the evasion rate from lakes. Further, most of the  $\text{CO}_2$  flux (90%) was from soil water, given the assumption that instream respiration is  $-4.7 \text{ g O}_2 \text{ m}^{-2} \text{d}^{-1}$  or 147  $\text{mmol m}^{-2} \text{d}^{-1}$ , further supporting the contention that streams and other freshwater ecosystems are pathways for  $\text{CO}_2$  efflux from terrestrial sources.

The hydrologic linkage between catchments and streams generates marked gradients in stream-water inorganic carbon. In a lateral dimension, floodplain waters are commonly enriched in  $p\text{CO}_2$  relative to the main channel (Hamilton and others 1995). As floodplains are inundated,  $p\text{CO}_2$  increases

as a result of contact of surface water with metabolically active soils (Pulliam 1993). Similarly,  $p\text{CO}_2$  commonly declines from headwaters to downstream reaches (Hoffer-French and Herman 1989; Dawson and others 1995; Jones and Mulholland 1998) as connectivity between streams and their catchments declines. Headwaters have high  $p\text{CO}_2$  concentration because of large inputs of typically  $\text{CO}_2$ -rich groundwater. Moving downstream, outgassing to the atmosphere coupled with reduced importance of groundwater discharge (as a proportion of stream flow) diminishes stream-water  $p\text{CO}_2$ .

Catchment-stream linkage effects on inorganic carbon not only influence the partial pressure of  $\text{CO}_2$  in solution but also alkalinity and pH. The effect of catchment geology and weathering on stream alkalinity has garnered attention in light of concerns about acid precipitation. Commonly, alkalinity declines with increased flow that results from reduced contact time of groundwater with mineral-rich bedrock (Piñol and Avila 1992; Reynolds and others 1986; Rustad and others 1986; Neal 1988; Neal and others 1990). Under low discharge, groundwater residence time is increased, enriching subsurface waters in rock-weathering products. The water ultimately discharged as surface flow can have a high acid-neutralizing capacity. With higher flows, in contrast, enrichment of groundwater in rock-weathering products is reduced due to limited contact time; a greater proportion of subsurface flow is via shallow pathways and bypasses the bedrock subsystem and is not exposed to mineral augmentation (Neal and others 1990; Robson and Neal 1990).

Spatial gradients of surface water  $\text{CO}_2$  can have profound impacts on stream chemistry and the physical structure of the stream channel, particularly if groundwater is rich in calcite. The solubility of calcite is indirectly related with pH. As  $\text{CO}_2$  outgasses and pH rises, calcite can become supersaturated in stream water and precipitate as travertine on the stream bottom (Hoffer-French and Herman 1989). If precipitation and travertine formation are substantial, the subsurface (that is, the hyporheic zone) can be effectively sealed off from the stream surface, which will affect nutrient cycling, ecosystem metabolism, and biotic diversity.

### Future Applications

Our approach and model provides an effective and powerful tool to characterize  $\text{CO}_2$  dynamics in soils of headwater catchments over seasonal and interannual time scales. Samples of stream water for  $p\text{CO}_2$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  determination are easily collected and analyzed. An end-member mixing model can be readily parameterized, allowing the  $\text{CO}_2$  model

presented herein to be applied to a range of catchment types. A difficulty with applying our model to other catchments lies with modeling the consumption of  $\text{CO}_2$  via bedrock weathering particularly for basins with poorly characterized geology or heterogeneous composition of bedrock. Our model, however, could be expanded by coupling it to a geochemical program such as PHREEQC [US Geological Survey (Parkhurst 1995)] and using an inverse-modeling technique to determine the effect of carbonate weathering on the chemistry of water as it flowed through a catchment from precipitation to stream outflow. Further, weekly stream-chemistry sampling provides a dataset on catchment  $\text{CO}_2$  dynamics that is nearly impossible to obtain with other approaches. Studies based on point measurements of soil  $\text{CO}_2$  and evasion are of limited utility for describing catchment scale dynamics, because of high spatial variability and the consequent labor required for adequate data collection. Eddy-diffusion techniques overcome concerns of spatial variability but are economically unfeasible for studies of  $\text{CO}_2$  dynamics in more than one or a few catchments. Stream-water chemistry provides a catchment scale integration of soil respiration that when coupled with an end-member mixing model and knowledge of catchment geology enables cost-effective characterization of soil  $\text{CO}_2$  dynamics. Given the ease and affordability of sampling, our approach can be used for studies examining longer-term soil  $\text{CO}_2$  dynamics (decades and longer), for comparisons between catchment types, and to address questions on the influence of factors such as soil organic matter, climate, and vegetation type on rates of ecosystem respiration.

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