



Controls of streamwater dissolved inorganic carbon dynamics in a forested watershed

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Abstract. I investigated controls of stream dissolved inorganic carbon (DIC) sources and cycling along a stream size and productivity gradient in a temperate forested watershed in northern California. Dissolved CO₂ (CO_{2(aq)}) dynamics in heavily shaded streams contrasted strongly with those of larger, open canopied sites. In streams with canopy cover > 97%, CO_{2(aq)} was highest during baseflow periods (up to 540 μM) and was negatively related to discharge. Effects of algal photosynthesis on CO_{2(aq)} were minimal and stream CO_{2(aq)} was primarily controlled by groundwater CO_{2(aq)} inputs and degassing losses to the atmosphere. In contrast to the small streams, CO_{2(aq)} in larger, open-canopied streams was often below atmospheric levels at midday during baseflow and was positively related to discharge. Here, stream CO_{2(aq)} was strongly influenced by the balance between autotrophic and heterotrophic processes. Dynamics of HCO₃⁻ were less complex. HCO₃⁻ and Ca²⁺ were positively correlated, negatively related to discharge, and showed no pattern with stream size. Stable carbon isotope ratios of DIC (i.e. δ¹³C DIC) increased with stream size and discharge, indicating contrasting sources of DIC to streams and rivers. During summer baseflows, δ¹³C DIC were ¹³C-depleted in the smallest streams (minimum of -17.7‰) due to the influence of CO_{2(aq)} derived from microbial respiration and HCO₃⁻ derived from carbonate weathering. δ¹³C DIC were higher (up to -6.6‰) in the larger streams and rivers due to invasion of atmospheric CO₂ enhanced by algal CO_{2(aq)} uptake. While small streams were influenced by groundwater inputs, patterns in CO_{2(aq)} and evidence from stable isotopes demonstrate the strong influence of stream metabolism and CO₂ exchange with the atmosphere on stream and river carbon cycles.

Introduction

In stream ecosystems, the amount and form of dissolved inorganic carbon (i.e. DIC) plays a key role in stream biogeochemistry (Neal et al. (1998a, 1998b); Pinol and Avila 1992), as a resource for autotrophs (e.g. Raven et al. (1982) and Sand-Jensen and Frost-Christensen (1998)), and as an influence on environmental conditions for animals (Allan 1995). Carbon in aquatic ecosystems is largely derived from processes occurring in terrestrial ecosystems, and the flux of dissolved carbon from terrestrial ecosystems to surface waters plays a significant role in terrestrial carbon and element cycles (Kempe 1992; Kling et al. 1992; Hope et al. 1994). Terrestrial ecosystems influence stream DIC directly through hydrologic transport of CO₂ produced in soils and groundwater via plant root and microbial respiration and

HCO_3^- generated via weathering. Inputs of terrestrial organic carbon from land to water dominate organic carbon budget of small streams in forested watersheds (Webster and Meyer 1997), and metabolism of these inputs appears to be greater than in situ primary production for large rivers, resulting in higher riverine dissolved CO_2 (i.e. $\text{CO}_{2(\text{aq})}$) than in the atmosphere (Cole et al. 1994; Cole and Caraco 2001).

However, the strength of terrestrial influences relative to other variables affecting stream DIC have rarely been examined at multiple scales within small watersheds. Typically, studies have focused on very small streams (i.e. 0.2 to 5 km^2 watershed area) or large rivers ($> 10000 \text{ km}^2$) where the influence of terrestrial ecosystems may be greatest. Stream carbon cycles may also be influenced by evasion of CO_2 to the atmosphere, algal $\text{CO}_{2(\text{aq})}$ uptake, and, for Ca^{2+} rich waters, precipitation of CaCO_3 (Lorah and Herman 1988; Spiro and Pentecost 1991; Dawson et al. 1995; Pinol and Avila 1992; Jones and Mulholland (1998a, 1998b)). Thus, processes affecting stream DIC may be expected to vary with stream geomorphology, discharge and landscape position or productivity, as well as with terrestrial ecosystem structure and productivity, and watershed geology.

The goal of this study was to understand the controls of the sources and cycling of stream DIC in a temperate forested watershed. Inferences from both stream chemistry and stable carbon isotope ratios of DIC were used across a large gradient in stream size and productivity to assess how the sources and cycling of inorganic carbon changed spatially within the watershed during summer baseflow conditions, and temporally within 6 streams and rivers. This approach revealed strong contrasts between inorganic carbon dynamics of small streams and rivers.

Methods

General approach and site description

Physical and chemical variables that potentially influence DIC were measured monthly (bimonthly in the winter) for 2 years at the South Fork (SF) Eel River and 5 tributary stream and river sites in the Coast Range of northern California. Sampling was conducted to characterize seasonal changes in inorganic carbon cycling rather than the dynamics of individual rainfall events. The 6 sites were located near the forested headwaters of the SF Eel River in Mendocino County, California, USA. These sites (hereafter “monitoring sites”) were chosen to represent a gradient in stream size that included three small headwater streams and three larger streams and rivers (Table 1). All tributary streams have similar aspect, draining from the east into the north-flowing SF Eel River along a 5 km reach near the town of Branscomb.

To examine a greater range of variables, a larger number of streams in northern California were surveyed during mid summer 1998 (hereafter “survey sites”) in addition to the monitoring sites (Table 1). Most of the survey sites were tributaries of

Table 1. Site descriptions from monitoring and survey sites. Sites in bold indicate seasonal sampling (i.e. monitoring sites). Temperature and DOC data are from duplicate samples collected on one day in mid summer 1998. Sampling at survey sites took two weeks to complete and there was no rainfall during the sampling period. The two smallest sites in terms of watershed area were sampled at headwater springs where water emerged from the ground.

Stream or River	Watershed area (km ²)	Slope (%)	Temperature (°C)	Canopy Cover (%)	DOC (μM)
Sugar (left fork)	0.4		12.3	98.2	
Sugar (right fork)	0.4		12.3	98.2	143.3
Sugar	0.8		12.8	98.2	
McKinley	1.0		15.3	98.1	53.7
Skunk	1.4		13.3	97.0	54.3
Dark Canyon	1.7	4.2	16.3	98.4	88.6
Barnwell	1.8	12.7	15.8	98.7	
Fox	2.6	8.4	17.1	97.5	70.5
Deer	3.0	2.6	16.3	98.7	80.2
Redwood	7.8	1.3	15.8	92.0	143.3
Jack of Hearts	10.2		15.2	88.4	77.4
Elk	10.3		20.7	70	
Elder	17.0		18.8	86.1	89.0
Rattlesnake	57.9		22.1	52.3	107.8
South Fork Eel	130.0		23.5	39.4	88.7
Ten Mile	180.0		24.4	6.9	78.3
Middle Fork Eel	1907.2		27.0	0	
Trinity	7303.7		22.1	0	
Klamath	21696.0		23.1	0	

the SF Eel River along a 15 km length of river near the monitoring sites. All but two of these sites were sampled near their confluence with the SF Eel River so that there were minimal elevational gradients between sites. Several other larger rivers were also sampled (i.e. the Middle Fork Eel, Trinity, and Klamath Rivers). In 1999, 6 seeps draining directly into the SF Eel River were sampled along a 5 km reach of river to assess the contribution of groundwater to river CO₂ (aq).

The region has a Mediterranean climate and almost all precipitation to the watershed falls as rain between October and May. Discharge declines to stable summer and fall baseflows after winter and spring rains (Power 1992). The small tributary streams are heavily shaded, with gradients ranging from 2 to 12%. Algal biomass and photosynthesis in the tributary streams is low due to heavy shading by old growth forests (unpublished data). In contrast, the larger streams and rivers have wide channels and sunlit streambeds, and are highly productive during summer (Power 1992). During the baseflow period, turbidity is low, and water clarity high at all sites. Streamwater is undersaturated with respect to calcite.

Coastal watersheds of northern California are underlain by sedimentary rocks (shales, greywacke, conglomerates) of marine origin. These watersheds are heavily

forested with C_3 tree species. Uplands are dry in the summer and are occupied by manzanita and madrone (*Arctostaphylos* spp. and *Arbutus menziesii*). Douglas fir, redwoods, and bay laurel (*Pseudotsuga menziesii*, *Sequoia sempervirens*, and *Umbellularia californica*) dominate lower valley areas. Stable carbon isotope ratios ($\delta^{13}C$) of forest foliage and forest floor litter (-28.5 and -27.4‰ , respectively; unpublished data) are similar to average values for C_3 plants (Rounick and Winterbourn (1986); unpublished data). Study areas in the Eel River watershed are lightly impacted by human use except for some ongoing and past timber harvesting.

Physical and chemical variables

Discharge was measured at four of the six monitoring sites. Continuous measurements were made on the SF Eel River at a former USGS gaging station near Branscomb and on Elder Creek at a current USGS gaging station (11475560). Discharge measurements were made when stream chemistry samples were collected on two small tributary streams using a Marsh McBirney (Model 2000) flow meter (Fox Creek) and by collecting water flow from a culvert in a calibrated bucket (McKinley Creek).

Samples for stream solutes were collected from well-mixed areas during mid morning through mid afternoon in small shaded streams, and during mid afternoon at sites with canopy cover $< 95\%$ unless otherwise noted. At one site on each monitoring or survey stream or river, temperature, pH, and conductivity were measured with Orion pH (Model 540A) and conductivity (Model 128) meters. $CO_2(aq)$ was measured by equilibrating well-mixed river water with ambient atmospheric air at ambient stream temperature in a syringe (Kling et al. 1992). The syringe headspace was transferred to a gastight nylon syringe and analyzed with a Shimadzu TCD gas chromatograph analyzer (Model 14A) within 24–36 h. $CO_2(aq)$ was calculated using temperature-corrected values of Henry's constant and measurements of ambient atmospheric $CO_2(gas, g)$ made at each site. The coefficient of variation (CV) of duplicate samples was almost always $< 1\%$.

At one small shaded stream and one more open canopied river, $CO_2(aq)$ was measured diurnally in midsummer. For these samples, $CO_2(aq)$ in excess of atmospheric equilibrium (i.e. excess $CO_2(aq)$) was calculated as measured $CO_2(aq)$ divided by calculated $CO_2(aq)$ in equilibrium with the atmosphere based on measurements of water temperature and ionic strength, and atmospheric $CO_2(g)$.

Samples for DIC (i.e. $\Sigma CO_2(aq) + HCO_3^- + CO_3^{2-}$) and $\delta^{13}C$ DIC were collected in glass bottles without exposure to the atmosphere. Bottles were flushed three times and sealed with Teflon septa after preservation with saturated $HgCl_2$. Samples were refrigerated until analyses. For DIC, known sample volumes were equilibrated with an air or N_2 headspace and headspace samples were injected into the gas chromatograph and analyzed as for dissolved $CO_2(aq)$. The CV of duplicate samples was usually $< 1\%$. Bicarbonate plus carbonate ion concentration (i.e. $HCO_3^- + CO_3^{2-}$) was calculated as the difference between DIC and $CO_2(aq)$. For $\delta^{13}C$ DIC analyses, samples were acidified with 100% phosphoric acid under vacuum and the resulting CO_2 was collected and purified cryogenically (Tan et al. 1973). The purified CO_2

was analyzed on a dual inlet mass spectrometer (Micromass Prism). The analytical standard deviation was usually $\pm 0.1\text{‰}$, and the standard deviation of duplicate samples was $\pm 0.33\text{‰}$. $\delta^{13}\text{C}$ DIC were measured in 1997 and 1998 only.

Samples for Ca^{2+} were filtered through pre-ashed Whatman glass fiber filters (nominal pore size $0.7\text{ }\mu\text{m}$) and acidified with high purity hydrochloric acid. Samples were refrigerated in polyethylene bottles until analysis. Ca^{2+} was determined by inductively coupled plasma (ICP) analyses (Thermo Jerrell Ash Iris HR). Samples for dissolved organic carbon (DOC) were collected and preserved as for Ca^{2+} , and were refrigerated in glass vials until analysis (Kling et al. 1992). DOC was analyzed by high temperature oxidation to CO_2 followed by detection with an infrared gas analyzer (Shimadzu Instruments).

Regression models (linear and polynomial) were used to analyze spatial and temporal influences on streamwater DIC. Significance levels of t -tests for regression slopes was assessed at $p < 0.05$.

Conceptual basis for use of carbon stable isotope ratios to study stream DIC

Measurements of $\delta^{13}\text{C}$ DIC were used to determine sources of DIC to streamwater. $\delta^{13}\text{C}$ DIC are a useful natural tracer of DIC because the potential sources (biogenic, atmospheric and geologic) often have distinct $\delta^{13}\text{C}$. $\text{CO}_{2(g)}$ derived from respiration has a similar $\delta^{13}\text{C}$ to that of the organic carbon source, and thus in watersheds dominated by C_3 plants (average foliar $\delta^{13}\text{C}$ -28‰) respiratory $\text{CO}_{2(g)}$ should have lower $\delta^{13}\text{C}$ than atmospheric $\text{CO}_{2(g)}$ (-8‰). Carbonate minerals have higher mean $\delta^{13}\text{C}$ (ca. 0‰) than atmospheric $\text{CO}_{2(g)}$ (Craig 1953).

Streamwater $\delta^{13}\text{C}$ DIC are determined by the generation of DIC in terrestrial ecosystems and by in-stream processes (reviewed in Kendall et al. (1992) and Pawellek and Veizer (1994)). Briefly, $\delta^{13}\text{C}$ DIC formed in soils and groundwaters are determined by the $\delta^{13}\text{C}$ of soil and groundwater CO_2 , the primary weathering agent in vegetated watersheds, and $\delta^{13}\text{C}$ of mineral carbonates, if present. $\delta^{13}\text{C}$ $\text{CO}_{2(g)}$ in soils of temperate watersheds with C_3 plants generally range between -24 to -18‰ (e.g. Reardon et al. (1979) and Rightmire (1978), Aravena et al. (1992), Bacon and Keller (1998)) and are determined by the $\delta^{13}\text{C}$ of organic matter mineralized by decomposers and respired by plant roots, and by fractionation of $\delta^{13}\text{C}$ $\text{CO}_{2(g)}$ during diffusion of $\text{CO}_{2(g)}$ from soils to the atmosphere (Cerling et al. 1991). HCO_3^- formed by dissolution of carbonate minerals by carbonic acid derived from $\text{CO}_{2(g)}$ should have $\delta^{13}\text{C}$ DIC exactly intermediate between the $\delta^{13}\text{C}$ of $\text{CO}_{2(g)}$ and that of the carbonate source. HCO_3^- derived from silicate weathering should be 7 to 10‰ higher than the $\delta^{13}\text{C}$ of CO_2 (Kendall et al. 1992; Pawellek and Veizer 1994).

When DIC enters streams, $\delta^{13}\text{C}$ DIC may be modified through the addition or removal of $\text{CO}_{2(aq)}$ from streamwater. Addition of CO_2 may increase or decrease $\delta^{13}\text{C}$ DIC depending on the CO_2 source. For example, inputs of CO_2 from heterotrophic respiration would decrease $\delta^{13}\text{C}$ DIC because $\delta^{13}\text{C}$ CO_2 from respiration is similar to the organic matter source and thus is often highly ^{13}C -depleted. By contrast, inputs of atmospheric $\text{CO}_{2(g)}$ at -8‰ would increase $\delta^{13}\text{C}$ DIC.

Removal of CO_2 (aq) by degassing to the atmosphere would increase $\delta^{13}\text{C}$ DIC because at equilibrium CO_2 (aq) is ^{13}C -depleted relative to HCO_3^- by 7 to 10‰ depending on temperature (Mook et al. 1974). Removal of CO_2 (aq) through aquatic plant uptake may also increase $\delta^{13}\text{C}$ DIC through discrimination against ^{13}C relative to ^{12}C during uptake, leaving the remaining pool of DIC ^{13}C -enriched (McKenzie 1985).

Results

Temporal dynamics

Streamwater CO_2 (aq) at the monitoring sites was influenced by factors related to stream size and discharge. Daytime CO_2 (aq) was similar among sites during high flow winter and spring periods, but increasingly diverged during summer and fall (Figure 1(A)). In the 3 smallest streams, CO_2 (aq) increased with decreasing discharge through the summer, while an opposite pattern was observed in the 3 larger, more open canopied streams and rivers (Figures 1(A) & 2(A)). For two small streams, CO_2 (aq) peaked with minimum discharge, while peak CO_2 (aq) occurred during high flows in winter at two larger rivers (Figure 2(A)). In the three largest rivers, daytime CO_2 (aq) fell below atmospheric equilibrium (e.g. $\sim 14 \mu\text{M}$ at 20°C in the SF Eel River) for much of the summer baseflow periods. pH ranged from a minimum of 7.23 in the tributaries up to 8.4 in the SF Eel and Ten Mile Creek during mid summer. Variation in pH was largely determined by CO_2 (aq) (linear regression model, $\text{pH} = -0.744(\log \text{CO}_2) + 8.99$, $r^2 = 0.78$).

CO_2 (aq) and Ca^{2+} had similar seasonal patterns only in small streams (Figure 1(A & B)) where both Ca^{2+} and CO_2 (aq) were negatively influenced by discharge (Figure 2(A & B)). As a result, CO_2 (aq) and Ca^{2+} were correlated only in small streams (Figure 3(A)).

In contrast to CO_2 (aq), streamwater carbonate ions, predominantly HCO_3^- , showed similar patterns for small streams and rivers. Streamwater HCO_3^- was strongly related to Ca^{2+} (Figure 3(A)). Ca^{2+} and HCO_3^- increased during summer and fall baseflows, and decreased during winter and spring periods (Figure 1(B & D)). Both Ca^{2+} and HCO_3^- were negatively related to discharge, and these relationships were consistent across the range of streams examined (Figure 2(B & D)).

Streamwater $\delta^{13}\text{C}$ DIC followed patterns of CO_2 (aq). Streamwater $\delta^{13}\text{C}$ DIC were similar in streams and rivers during winter and spring (Figure 1(C)). However $\delta^{13}\text{C}$ DIC decreased during summer and fall baseflows in the small tributary streams while an opposite pattern was observed in the larger streams and rivers (Figure 1(C)). Similarly, streamwater $\delta^{13}\text{C}$ DIC increased with discharge in two tributary streams but not in the larger sites (Figure 2(C)). Thus, patterns in $\delta^{13}\text{C}$ DIC corresponded closely to patterns in stream CO_2 (aq) (Figure 1(A)) and not HCO_3^- (Figure 1(D)). Streamwater $\delta^{13}\text{C}$ DIC were more strongly related to CO_2 (aq) than Ca^{2+} (Figure 3(B & C)).

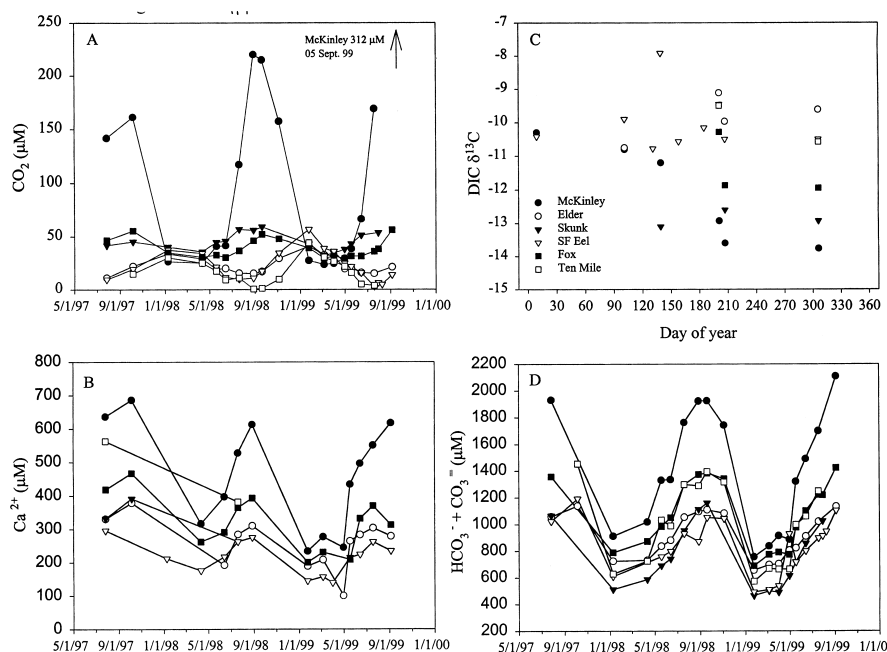


Figure 1. Seasonal patterns in (A) $\text{CO}_2(\text{aq})$, (B) Ca^{2+} , (C) $\delta^{13}\text{C}$ DIC, and (D) HCO_3^- at the six monitoring sites. Each point is usually the mean of duplicate samples collected during the day. The three smallest streams are shown with dark symbols and the three largest streams are shown with open symbols. Combined $\delta^{13}\text{C}$ DIC data from 1997 and 1998 are presented in (C).

Spatial dynamics

Stream survey results showed that streamwater $\text{CO}_2(\text{aq})$ was strongly influenced by factors related to stream size across a broad spatial range (i.e. 0.4 to 21000 km^2 watershed area). Daytime $\text{CO}_2(\text{aq})$ decreased with increasing stream size from up to 540 μM in heavily shaded headwater springs to undersaturation with respect to the atmosphere in the 7 largest streams and rivers (Figure 4(A)). pH ranged from a minimum of 6.00 in one of the smallest tributaries up to 8.5 in the largest rivers. Streamwater $\text{CO}_2(\text{aq})$ strongly influenced pH ($\text{pH} = -1.2(\log \text{CO}_2) + 9.6$, $r^2 = 0.87$).

Streamwater $\text{CO}_2(\text{aq})$ declined with stream size through several mechanisms. First, high $\text{CO}_2(\text{aq})$ in steep headwater streams would rapidly degas to the atmosphere and thereby lower stream $\text{CO}_2(\text{aq})$. Stream slope appeared to play an important role in degassing losses shown by a strong negative relationship between stream gradient and $\text{CO}_2(\text{aq})$ in closed canopied streams of 1.7 to 8 km^2 watershed area (Figure 5). Algal biomass and photosynthesis rates were similar among sites (unpublished data) suggesting that high $\text{CO}_2(\text{aq})$ was due to reduced evasion of $\text{CO}_2(\text{aq})$ from low gradient streams.

Second, the relative contribution of groundwater to streamflow would decline with increasing stream size. Groundwater inputs to streams and rivers in the SF Eel

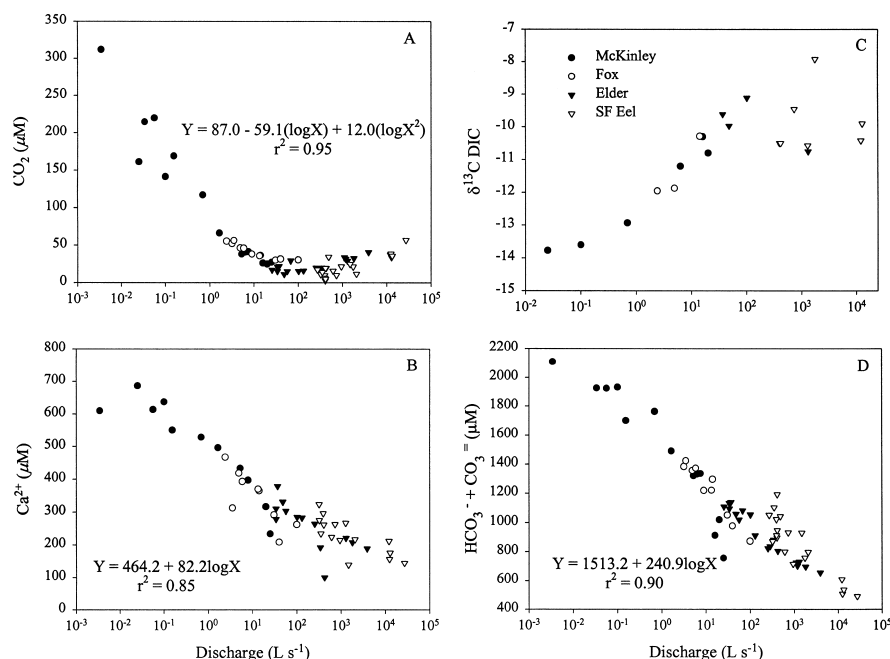


Figure 2. Relationships between discharge and (A) daytime CO_2 (aq), (B) Ca^{2+} , (C) $\delta^{13}\text{C DIC}$ and (D) HCO_3^- for four monitoring sites. Discharge in the SF Eel River was measured approximately 5 km up-river from the point of CO_2 (aq) measurement. Due to very low rainfall from June to October, low discharge points usually correspond to summer and fall, while high discharge points correspond to winter and spring periods. A non-linear regression model (i.e. polynomial model, $p < 0.001$) explained most variation CO_2 (aq) as a function of discharge for all data (results shown on the Figure). Individual polynomial models also explained most variation for McKinley ($r^2 = 0.94$), Fox ($r^2 = 0.96$), and Elder Creeks ($r^2 = 0.72$), and the SF Eel River ($r^2 = 0.70$). Linear regression models were used for Ca^{2+} and HCO_3^- relationships.

River watershed were highly supersaturated with CO_2 (aq) as shown by high CO_2 (aq) in headwater springs, and in riparian seeps draining directly into the SF Eel River. The latter sites were highly supersaturated with CO_2 (aq), averaging $161 \mu\text{M}$ (± 168 standard deviation, $n = 6$). Groundwater inputs relative to stream volume should decrease with stream size, and thus exert a diminishing effect on stream CO_2 (aq).

Finally, decreases in CO_2 (aq) with stream size were due in part to increasing algal photosynthesis in larger streams and rivers. Canopy cover decreased and thus light levels increased with stream size (Table 1). Light levels are a primary control of algal photosynthesis, and algal production typically increases with decreasing canopy cover (Lamberti and Steinman 1997). The importance of algal CO_2 (aq) uptake is shown by the contrast in diurnal patterns of streamwater CO_2 (aq) between a shaded tributary stream (Fox Creek) and the more productive SF Eel River. Minor daytime decreases in CO_2 (aq) occurred in the tributary stream, suggesting that algal uptake was not an important factor in determining CO_2 (aq) at closed canopied sites (Figure 6; see also Finlay et al. (1999)). However, decreases of $20 \mu\text{M}$ during mid-

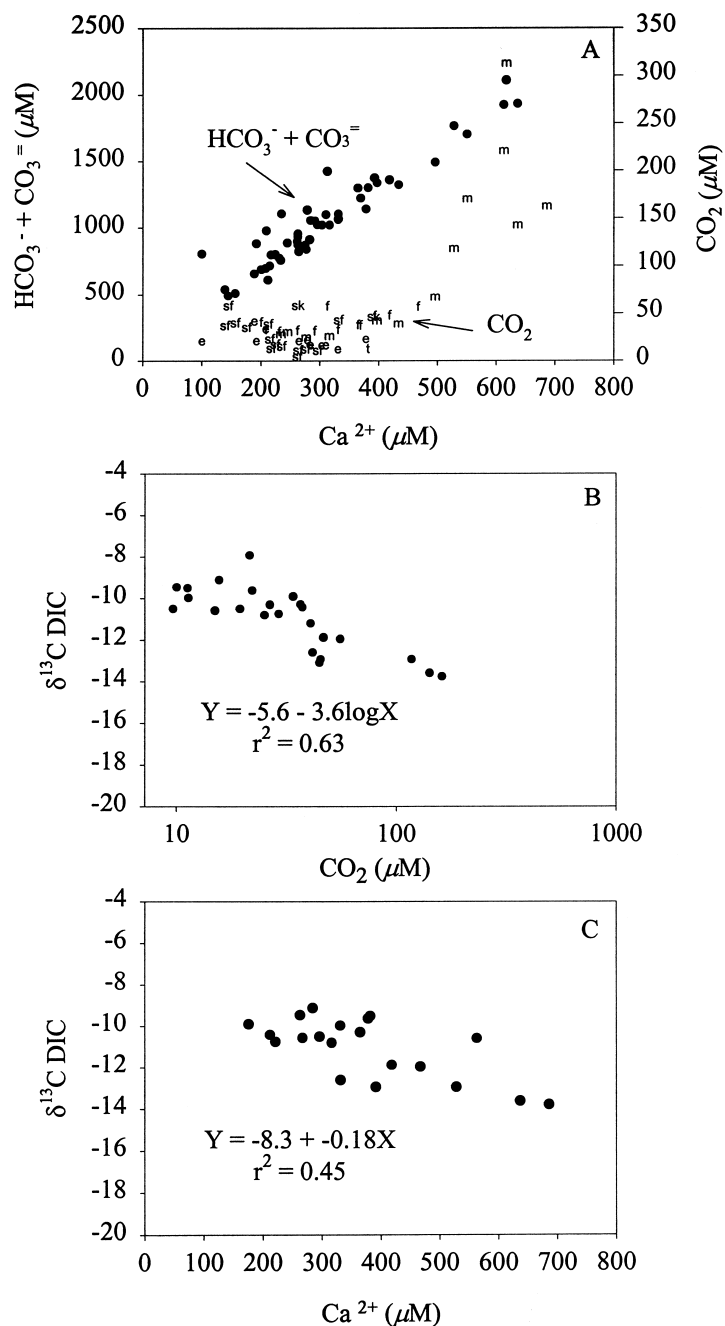


Figure 3. Relationship between (A) DIC and Ca^{2+} , (B) $\delta^{13}\text{C}$ DIC and $\log \text{CO}_2$ (aq), and (C) $\delta^{13}\text{C}$ DIC and Ca^{2+} at the monitoring sites. Linear regression models were used in all cases. For (A), the relationship between HCO_3^- and Ca^{2+} (shown by closed circles) was $Y = 206.8 + 2.8X$ with $r^2 = 0.89$. Letters represent Ca^{2+} and CO_2 (aq) for each stream or river; most data were from McKinley (m), Fox (f), and Elder (e) Creeks and SF Eel River (sf) but several points for Skunk (sk) and Ten Mile Creek (t) were also included. Ca^{2+} and CO_2 (aq) relationships were significant and positive in McKinley ($r^2 = 0.80$) and Fox Creeks ($r^2 = 0.31$), and negative in Elder Creek ($r^2 = 0.12$) and SF Eel ($r^2 = 0.73$). Ca^{2+} and CO_2 (aq) data were log transformed for McKinley Creek but not for other sites.

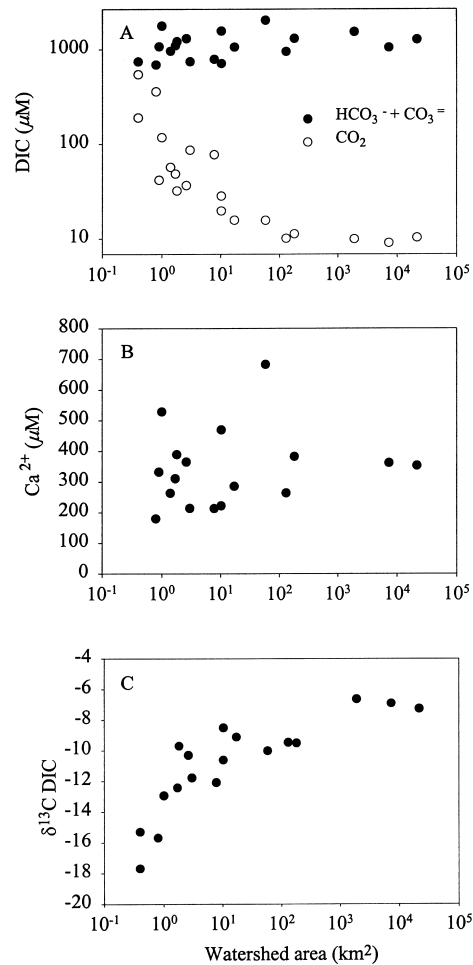


Figure 4. Mid summer longitudinal patterns in (A) DIC, (B) Ca²⁺, and (C) δ¹³C DIC with watershed area in 1998 at survey sites.

day relative to night were observed in the SF Eel River, suggesting that algal uptake was important in reducing CO_{2(aq)} in more open canopied sites.

Variation in DOC did not influence streamwater CO_{2(aq)} in the watershed. DOC was low during summer baseflow at all sites (Table 1), and CO_{2(aq)} was not related to DOC (linear regression model, $p > 0.05$, $r^2 = 0.01$; data not shown).

In contrast to CO_{2(aq)}, Ca²⁺ and HCO₃⁻ showed no pattern with stream size (Figure 4(A & B)). As observed for the temporal data, variation in HCO₃⁻ was strongly related to Ca²⁺ (Figure 7(A)).

Streamwater δ¹³C DIC increased with stream size from a minimum of -17.6‰ in the smallest streams to -6.4‰ in the largest rivers (Figure 4(C)). Downstream patterns reflected patterns of CO_{2(aq)} and not HCO₃⁻ (Figure 4(A & C)). As ob-

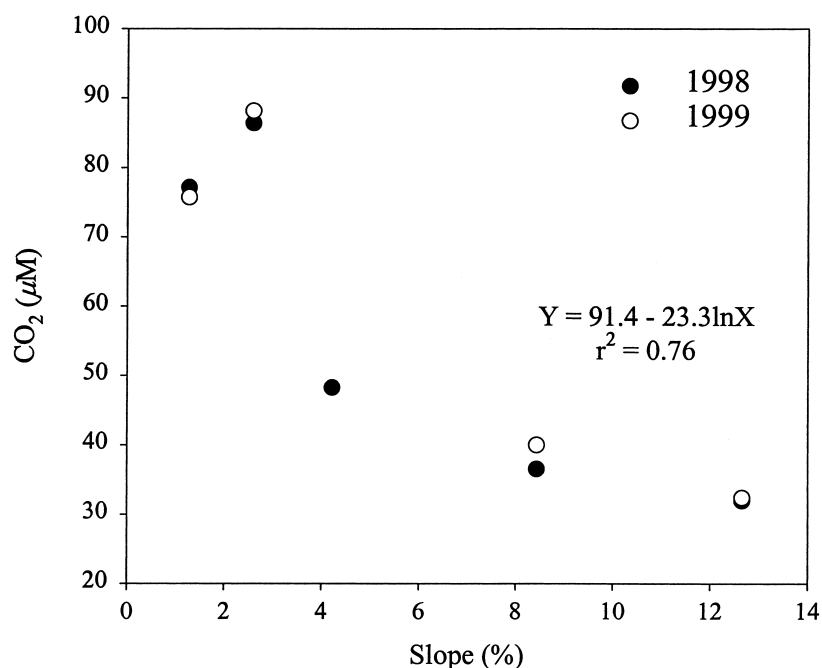


Figure 5. Relationship between stream gradient and CO₂ (aq) for closed-canopied streams (1–5 km²).

served for the monitoring sites, streamwater $\delta^{13}\text{C}$ DIC were strongly related to CO₂ (aq), and not Ca²⁺ (Figure 7(B & C)).

I used streamwater DIC data to estimate the $\delta^{13}\text{C}$ DIC of source groundwater to small streams using inverse concentration analyses (e.g. Hellings et al. (2000)). The Y-intercept of a plot of $\delta^{13}\text{C}$ DIC versus $1/\text{CO}_2$ (aq) indicates the $\delta^{13}\text{C}$ of the groundwater DIC source. I assumed that the increase in $\delta^{13}\text{C}$ DIC with stream size in the small headwater streams was primarily due to degassing loss of CO₂ (aq) since algal photosynthesis did not affect streamwater CO₂ (aq) at these sites (Finlay et al. 1999). I also assumed that the slightly slower diffusion of ¹³C relative to ¹²C through water during CO₂ (aq) degassing should be associated with minimal ¹³C-enrichment of the remaining CO₂ (aq) because of turbulent mixing of water in the steep streams. Using data for the smallest sites that had high canopy cover and similar streamwater temperature (Table 1), my analysis suggests groundwater $\delta^{13}\text{C}$ HCO₃⁻ of -13.0‰ and $\delta^{13}\text{C}$ CO₂ (aq) of -23.3‰ (Figure 8).

Discussion

Study of stream biogeochemistry is a powerful approach for understanding the dynamics of terrestrial ecosystems and for investigating the influence of terrestrial ecosystems on streams (sensu Likens and Bormann (1974)). However, most studies

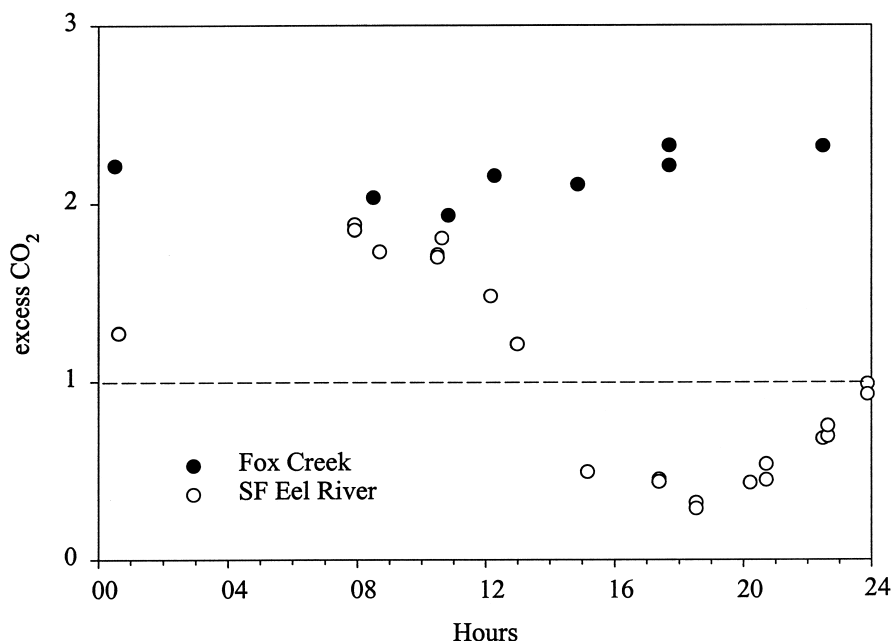


Figure 6. Deviation of measured values of streamwater $\text{CO}_2(\text{aq})$ from calculated values of $\text{CO}_2(\text{aq})$ at equilibrium with the atmosphere (i.e. measured $\text{CO}_2(\text{aq})$ / equilibrium $\text{CO}_2(\text{aq})$) over a 24 h period in a heavily shaded tributary stream (Fox Creek) and the SF Eel River. Streamwater $\text{CO}_2(\text{aq})$ at equilibrium with the atmosphere would have a value of one as shown by the dashed line. Measurements were made on one date in late July in Fox Creek, and on two dates (late July and mid August) in the SF Eel River.

have focused on small streams. As a consequence, the relative influence of basin size and in-stream processes on the composition and amount of DIC in streams are poorly understood. In this study, effects of discharge size on $\text{CO}_2(\text{aq})$, and evidence from stable carbon isotopes, suggest a strong contrast in the sources and cycling of inorganic carbon in small streams compared to larger streams and rivers. Groundwater inputs of DIC clearly dominate small streams, but patterns in streamwater chemistry and $\delta^{13}\text{C}$ DIC suggest increasing importance of in-stream processes such as mixing with the atmosphere and photosynthesis on $\text{CO}_2(\text{aq})$ cycling and HCO_3^- sources with stream size.

Patterns and controls of streamwater DIC

In small headwater streams underlain by carbonate rocks, $\text{CO}_2(\text{aq})$, Ca^{2+} and HCO_3^- should be strongly related since carbonic acid weathering of carbonate rocks is the dominant reaction producing HCO_3^- in forested watersheds (Holland 1978). In this study, streamwater HCO_3^- and Ca^{2+} were strongly correlated, and both variables were negatively related to discharge. These patterns are consistent with a large contribution of carbonate weathering to streamwater DIC in the watershed, and control of streamwater HCO_3^- by the time of contact between groundwater and carbonate

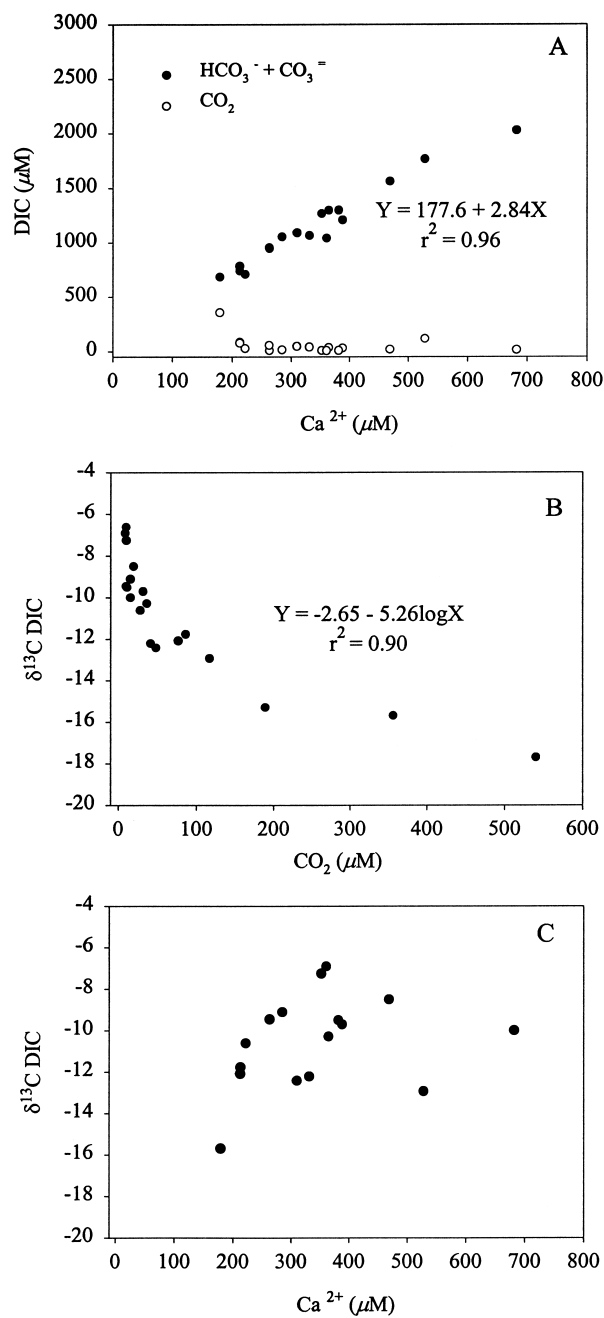


Figure 7. Relationship between (A) DIC and Ca^{2+} , (B) $\delta^{13}\text{C DIC}$ and CO_2 (aq), and (C) $\delta^{13}\text{C DIC}$ and Ca^{2+} for survey sites during mid summer 1998. The relationship in (B) was linear using log transformed values of CO_2 (aq) but is shown untransformed for reference. Relationships between Ca^{2+} and CO_2 (aq) shown in (A) and $\delta^{13}\text{C DIC}$ and Ca^{2+} shown in (C) were not significant (r^2 around 0 in both cases).

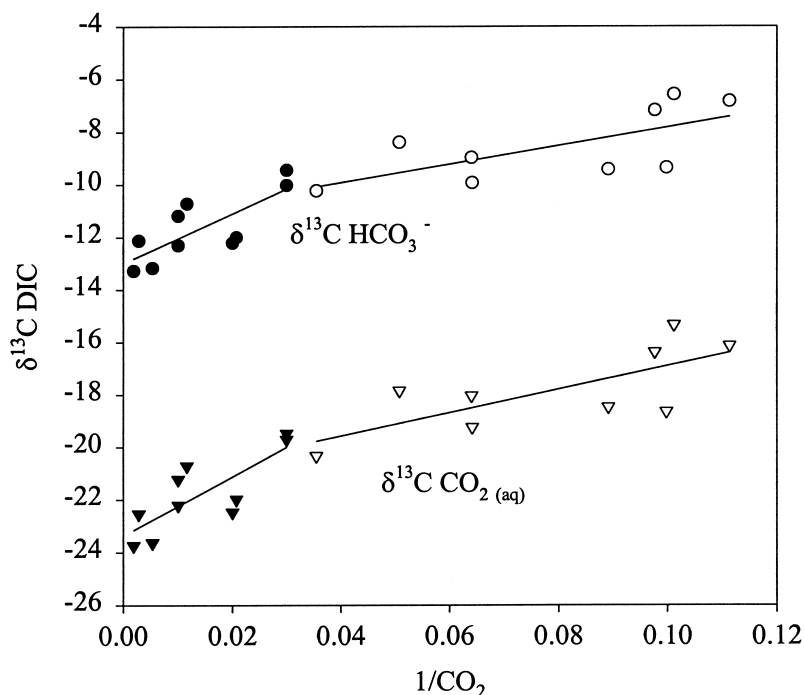


Figure 8. Inverse concentration of $\text{CO}_2(\text{aq})$ versus $\delta^{13}\text{C CO}_2$ and HCO_3^- for survey sites during mid summer 1998. Regression results to estimate source values of $\delta^{13}\text{C CO}_2$ and HCO_3^- were made using data from small ($< 8 \text{ km}^2$ watershed area) heavily shaded tributary streams shown by dark symbols. $\delta^{13}\text{C CO}_2$ and HCO_3^- were calculated from measurements of DIC, $\text{CO}_2(\text{aq})$, $\delta^{13}\text{C DIC}$ and temperature according to Mook et al. (1974). The regression relationship for $\delta^{13}\text{C HCO}_3^-$ and $1/\text{CO}_2(\text{aq})$ was $Y = -13.0 (\pm 0.53 \text{ standard error}) + 91.0X$, $r^2 = 0.47$; the relationship for $\delta^{13}\text{C CO}_2(\text{aq})$ and $1/\text{CO}_2(\text{aq})$ was $Y = -23.3 (\pm 0.60) + 108.1X$, $r^2 = 0.49$.

minerals (Wolock et al. 1997; Johnson et al. 2000). However, $\text{CO}_2(\text{aq})$ was correlated with Ca^{2+} and HCO_3^- only in the smallest streams, suggesting that the dynamics of $\text{CO}_2(\text{aq})$ and HCO_3^- are increasingly decoupled with increasing stream size.

Stream size and discharge explained much of the observed variability in stream-water $\text{CO}_2(\text{aq})$. Decreases in $\text{CO}_2(\text{aq})$ with stream size during summer were a function of several processes including $\text{CO}_2(\text{aq})$ loss to the atmosphere, declining groundwater inputs relative to stream volume, and, in stream with open canopies, algal uptake. Downstream decreases in $\text{CO}_2(\text{aq})$ have been observed elsewhere (Lorah and Herman 1988; Dawson et al. 1995; Jones and Mulholland 1998b) but the relative importance of the mechanisms responsible for this apparently general pattern is not well distinguished. However, one potential mechanism to account for downstream decreases in $\text{CO}_2(\text{aq})$ under baseflow conditions did not appear to be important in northern California. Several studies have suggested that increased contact time between groundwater and minerals with basin size may promote greater weathering of base cations, leading to increases in weathering products in

streams as stream size increases (Wolock et al. 1997; Jones and Mulholland 1998b; Johnson et al. 2000). Since weathering consumes soil and groundwater CO_2 , groundwater contributions to streams lower in watersheds could have lower CO_2 (aq) than inputs to headwater streams. However, in this study there were no downstream trends for Ca^{2+} (Figure 4(B)) or other base cations (unpublished data), suggesting that stream CO_2 (aq) was not influenced by increasing weathering with basin size. Such effects appear to most pronounced in streams smaller than the ones examined here (e.g. Johnson et al. (2000)).

Discharge was the second major influence on stream CO_2 (aq). In small tributary streams, negative relationships between CO_2 (aq) and discharge were probably related to reduced degassing of CO_2 (aq) at low flows. For a given site, higher flows increases water turbulence, enhancing evasion of CO_2 (aq) from streamwater to the atmosphere (Genereux and Hemond 1992). Such effects of discharge on CO_2 (aq) degassing in tributary streams should be similar for larger streams and rivers. However, low flow periods corresponded with periods of high algal productivity and biomass at such sites (Power 1992), strongly reducing CO_2 (aq) (Figures 1(A) & 2(A)); (Finlay et al. 1999). Thus, in contrast to the tributary streams, peak CO_2 (aq) was observed during high flows in larger streams and rivers during periods when CO_2 (aq) loss from streamwater to the atmosphere should have been greatest. This suggests effects of reduction of algal CO_2 (aq) uptake and increased heterotrophic metabolism of organic matter transported from terrestrial ecosystems during winter periods in rivers.

Opposite patterns of CO_2 (aq) with discharge for small streams versus rivers suggests a contrast in the sources of CO_2 (aq) to these sites. In small streams, large inputs of CO_2 from soils and groundwater, and lower rates of mixing with the atmosphere during summer baseflow periods may account for the negative relationship with discharge. High CO_2 (aq) during baseflows may also be the result of increased retention and subsequent decomposition of terrestrial organic matter within streams. In either case, heterotrophic sources of CO_2 appear to dominate during baseflows. By contrast, CO_2 (aq) was often below atmospheric concentrations during baseflows in larger streams and rivers, indicating high rates of invasion of atmospheric CO_2 (g) at these sites. Increasing CO_2 (aq) with discharge in larger streams and rivers indicates that heterotrophic sources of CO_2 (aq) dominate during winter and spring due to increased metabolism of labile organic carbon from terrestrial ecosystems in downstream areas (e.g. Devol et al. (1995) and Hinton et al. (1997), Butturini and Sabater (2000)).

Baseflow patterns in CO_2 (aq) may be significant for the ecology of these ecosystems. For example, CO_2 (aq) may influence growth rates or distributions of freshwater plants since some taxa, such as bryophytes and some red algae, may only use CO_2 (aq) as an inorganic carbon source (Raven et al. 1985). Many aquatic plants that can use HCO_3^- preferentially use CO_2 (aq) because of lower energetic costs associated with CO_2 (aq) acquisition. Finally, the strong influence of CO_2 (aq) on streamwater pH may be significant for the distribution of aquatic animals in the watershed since pH is an important environmental variable for biota.

Stable carbon isotope ratios of DIC

Stable carbon isotopes of DIC further revealed sources and cycling of DIC in the SF Eel River watershed. In the smallest headwater streams, high $\text{CO}_2(\text{aq})$ and low $\delta^{13}\text{C}$ DIC were consistent with contributions of both $\text{CO}_2(\text{aq})$ derived from respiration in soils and groundwater and a carbonate weathering source of HCO_3^- . Assuming a $\delta^{13}\text{C}$ value for soil $\text{CO}_2(\text{g})$ of -23‰ (Figure 8) and a typical value for carbonate rocks (i.e. 0‰), the $\delta^{13}\text{C}$ HCO_3^- value determined for groundwater (-13.0‰ ; Figure 8) is consistent with carbonate weathering of the marine sedimentary bedrock of the watershed as the main source of HCO_3^- to streams (Kendall et al. 1992).

In larger streams and rivers, stable carbon isotopes ratios showed extensive effects of $\text{CO}_2(\text{aq})$ cycling on streamwater DIC. $\delta^{13}\text{C}$ DIC consistently increased with stream size and the strong correlation between $\delta^{13}\text{C}$ DIC and $\text{CO}_2(\text{aq})$ suggests the importance of at least two processes in stream DIC cycling. First, removal of $\text{CO}_2(\text{aq})$ through degassing in the tributary streams increased $\delta^{13}\text{C}$ DIC. The amount of the DIC that is present as $\text{CO}_2(\text{aq})$ relative to HCO_3^- directly affects $\delta^{13}\text{C}$ DIC because at isotopic equilibrium, $\text{CO}_2(\text{aq})$ is ^{13}C -depleted by 7 to 10‰ depending on temperature (Mook et al. 1974). However, the strong ^{13}C -enrichment at low $\text{CO}_2(\text{aq})$ suggests that simple degassing of $\text{CO}_2(\text{aq})$ cannot completely account for the relationship between $\text{CO}_2(\text{aq})$ and $\delta^{13}\text{C}$ DIC observed in Figure 7(B). $\text{CO}_2(\text{aq})$ loss from streamwater by degassing alone would result in a linear increase in $\delta^{13}\text{C}$ DIC. In contrast, increases in $\delta^{13}\text{C}$ DIC at low $\text{CO}_2(\text{aq})$ were greater than would be expected by degassing alone revealing the importance of a second process on stream carbon cycles.

The observed increase in $\delta^{13}\text{C}$ DIC at low $\text{CO}_2(\text{aq})$ indicates extensive mixing and exchange of atmospheric $\text{CO}_2(\text{g})$ with stream DIC. In circumneutral waters, atmospheric $\text{CO}_2(\text{g})$ in isotopic equilibrium with stream HCO_3^- should yield $\delta^{13}\text{C}$ DIC around 0‰ (Mook and Tan 1991). High $\delta^{13}\text{C}$ DIC (up to -6.4‰) indicated that river DIC was approaching isotopic equilibrium with the atmosphere in larger streams and rivers. The increase in DIC derived from the atmosphere at downstream sites was driven by invasion of $\text{CO}_2(\text{g})$ into streamwater. This process would be accelerated by the undersaturated daytime $\text{CO}_2(\text{aq})$ at these sites due to algal uptake (Schindler et al. 1972). Since river pH did not exceed 8.5, the effect of large fractionation of $\delta^{13}\text{C}$ associated with invasion of atmospheric $\text{CO}_2(\text{g})$ into water at high pH (Herczeg and Fairbanks 1987) was not a factor. Thus, the high $\delta^{13}\text{C}$ DIC observed in larger rivers suggests that a large proportion (i.e. at least half) of DIC was atmospheric in origin due to mixing of atmospheric $\text{CO}_2(\text{g})$ with streamwater.

While degassing of excess $\text{CO}_2(\text{aq})$ and atmospheric mixing are the most likely processes increasing $\delta^{13}\text{C}$ DIC in rivers, several other mechanisms could potentially influence $\delta^{13}\text{C}$ DIC along a gradient of stream size and $\text{CO}_2(\text{aq})$. First, effects of algal photosynthesis should increase streamwater $\delta^{13}\text{C}$ DIC through discrimination against ^{13}C during carbon uptake (McKenzie 1985). In small streams with high canopy cover, photosynthesis did not affect streamwater $\text{CO}_2(\text{aq})$ suggesting that discrimination would not significantly influence $\delta^{13}\text{C}$ DIC. However, in larger

streams and rivers where photosynthesis rates were higher, discrimination may have increased $\delta^{13}\text{C}$ DIC. However, algal discrimination was low at such sites (i.e. 0 to 7‰, Finlay (2000)) suggesting that this effect would be reduced at sites where the increases in $\delta^{13}\text{C}$ DIC were largest.

Second, methane (CH_4) production from CO_2 reduction could increase $\delta^{13}\text{C}$ CO_2 through kinetic fractionation (LaZerte 1981). In strongly reducing environments, such as lake, wetland, or estuarine sediments, CH_4 production may increase $\delta^{13}\text{C}$ CO_2 enough to increase $\delta^{13}\text{C}$ DIC (e.g. Hellings et al. (2000)). However, effects of CH_4 cycling on $\delta^{13}\text{C}$ DIC seem unlikely given the absence of wetlands in the study watersheds. Further, such effects are likely to be accompanied by increases in CO_2 and DIC (LaZerte 1981) and this was not observed in the larger streams and rivers studied here (Figure 4(A)).

A final mechanism to explain correlations between stream size, $\text{CO}_{2(\text{aq})}$ and $\delta^{13}\text{C}$ DIC is increases in groundwater $\delta^{13}\text{C}$ DIC with stream size. While groundwater inputs to larger streams should be relatively small, such waters may have longer residence times in contact with weatherable minerals (e.g. Wolock et al. (1997) and Johnson et al. (2000)). This effect could increase the amount of carbonate weathering contributing to the DIC pool or could be accompanied by changes in the $\delta^{13}\text{C}$ of soil $\text{CO}_{2(\text{g})}$ reacting with carbonate minerals. Thus, increased contact times could potentially increase stream $\delta^{13}\text{C}$ DIC in larger streams and rivers. However, as noted previously, there was no trend in Ca^{2+} or HCO_3^- with stream size. Further, the study watersheds were dominated by C_3 forests throughout suggesting that $\delta^{13}\text{C}$ of soil $\text{CO}_{2(\text{g})}$ would not change with basin size.

The relative importance of these mechanisms cannot be fully assessed without measurements of groundwater inputs, stream metabolism, and air-water gas exchange rates. However, $\delta^{13}\text{C}$ DIC was most strongly correlated with $\text{CO}_{2(\text{aq})}$ and not pH, watershed area, or Ca^{2+} , providing compelling evidence for effects of $\text{CO}_{2(\text{aq})}$ cycling on stream DIC sources.

Additional evidence for the importance of $\text{CO}_{2(\text{aq})}$ cycling in streamwater DIC dynamics is shown in a summary of literature $\delta^{13}\text{C}$ DIC data from groundwater and streamwater (Figure 9). Literature data show large increases in $\delta^{13}\text{C}$ DIC in the transition from groundwater to streamwater in agreement with the results from the SF Eel River. This increase is consistent with high $\text{CO}_{2(\text{aq})}$ in groundwaters compared to streams (References cited in Figure 9), and declining $\text{CO}_{2(\text{aq})}$ with increasing stream size. Thus, strong effects of $\text{CO}_{2(\text{aq})}$ degassing and mixing of atmospheric $\text{CO}_{2(\text{g})}$ with stream DIC appear to be common in temperate watersheds during baseflows.

The patterns in $\delta^{13}\text{C}$ DIC for the SF Eel River watershed and elsewhere clearly show the influence of in-stream processes on stream DIC, but these results are also significant with respect to the use of streamwater $\delta^{13}\text{C}$ DIC to infer terrestrial weathering processes (Kendall et al. 1992; Telmer and Veizer 1999). Such use of streamwater $\delta^{13}\text{C}$ DIC data assumes no influence of in-stream processes on $\delta^{13}\text{C}$ DIC. However, in the SF Eel River watershed, processes affecting $\text{CO}_{2(\text{aq})}$ loss or gain from streams strongly influence $\delta^{13}\text{C}$ DIC. Thus, $\delta^{13}\text{C}$ DIC measurements in streams may only be used to infer terrestrial weathering if the effects of in-stream

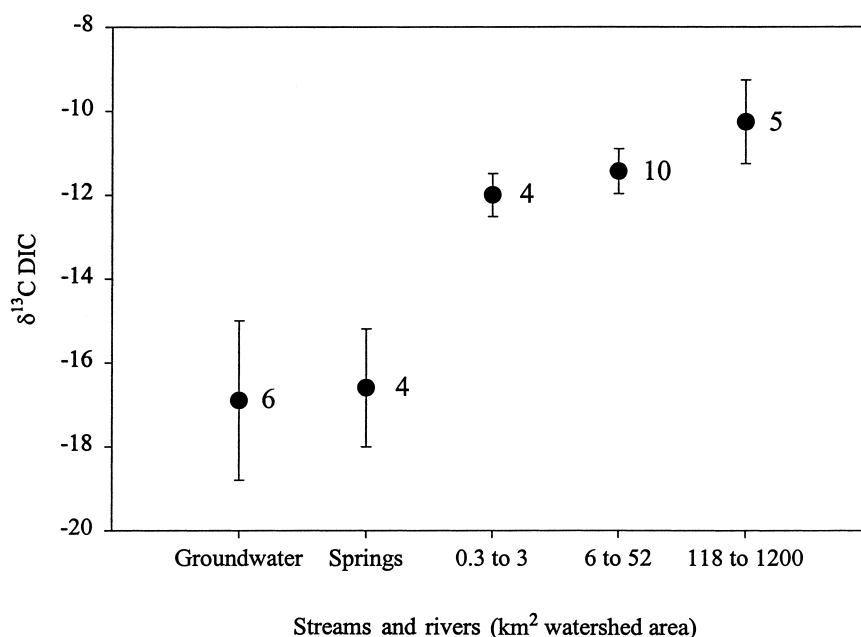


Figure 9. Literature data for $\delta^{13}\text{C DIC}$ of ground and surface waters in temperate watersheds. For groundwaters and springs, data were averaged by region or watershed for studies by Pearson and Friedman (1970) and Deines et al. (1974), Osmond et al. (1981), Rounick and James (1984), Wassenaar et al. (1991a, 1991b), Bacon and Keller (1998), Murphy and Schramke (1998), Amiotte-Suchet et al. (1999). Data from heavily agricultural, urban, or karst areas were not included. Stream values were calculated by averaging summer data for sites with watershed areas of 0.3 to 3, 6 to 52, and 118 to 1200 km² from a previous literature review (cited in Finlay (2001)). Data for the sites in the SF Eel River watershed were not included. Error bars are $\pm$ standard deviation; numbers next to symbols represent the number of ground water studies or surface water sites used to calculate mean values.

processes are accounted for and these effects have rarely been directly examined. As a consequence, $\delta^{13}\text{C DIC}$ measurements in groundwater or very small streams may be much more easily used to study terrestrial weathering than in larger streams and rivers. $\delta^{13}\text{C DIC}$ measurement in rivers may be better suited to understanding carbon cycling within these ecosystems.

Comparisons with other forested watersheds

The strong influence of groundwater CO_2 (aq) on DIC dynamics of headwater streams in the Eel River watershed is consistent with findings for several other small streams (e.g. Usdowski et al. (1979) and Lorah and Herman (1988)). However, there are several key differences between the results of this study and other studies of inorganic carbon dynamics in forested watersheds. First, across the gradient of stream size examined no spatial trends in weathering processes were apparent. Further, precipitation of inorganic carbon with CO_2 (aq) loss from streamwater was not observed. Spatial variation in stream DIC due to effects of landscape position or

carbonate precipitation have been observed in other watersheds, particularly in very small streams.

The most interesting comparisons, however, arise from observations in this study of very low CO_2 (aq) in larger streams and rivers due to algal uptake. This result strongly contrasts with widespread observations of CO_2 supersaturation of freshwaters relative to the atmosphere (Cole et al. 1994; Cole and Caraco 2001). Two explanations may resolve this apparent inconsistency. First, rivers of northern California are affected by a Mediterranean climate characterized by warm summers with very low rainfall. This may limit downstream transport of terrestrial organic carbon and maintain high rates of in-channel production (Young and Huryn 1996). An alternative explanation is that most data for stream CO_2 (aq) come from either very small streams or large rivers; there are relatively few measurements for streams and rivers from 5 to 10000 km² where algal production is expected to be greatest (Vannote et al. 1980; Lamberti and Steinman 1997). In either case, consistent patterns in streamwater $\delta^{13}\text{C}$ DIC for other forested watersheds indicate similar dynamics of carbon cycling in temperate streams and rivers. This suggests an important but poorly known influence of in-stream processes on inorganic carbon cycling in stream ecosystems.

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