

Seasonality of bedrock weathering chemistry and CO₂ consumption in a small watershed, the White River, Vermont

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Abstract

The draw down of CO₂ from the atmosphere during mineral weathering plays a major role in the global budget of this greenhouse gas. Silicate minerals remove twice the CO₂ of carbonate minerals per mole of calcium in runoff during weathering. Bedrock weathering chemistry was investigated in the White River watershed of northeastern USA to investigate whether there are seasonal differences in carbonate and silicate weathering chemistry. Geographic Information Systems analyses of bedrock geology were combined with major element concentrations in river waters to gain an understanding of the consistency of mineral weathering during three seasons. The percent of carbonate mineralogy comprising the bedrock in tributaries of the White River varied from less than 5% to 45% by area. A mass balance calculation using major element concentrations in waters was applied to estimate the seasonal relationships between bedrock geology and bicarbonate flux. In all tributaries and the main stem of the White River the highest calculated percent of bicarbonate from carbonate mineral weathering was measured in the late fall. The results suggest that carbonate and silicate bedrock weathering processes are seasonally controlled. Thus single season sampling could not accurately represent an entire year's geochemical budget. In the White River, water samples obtained solely during the summer would consistently underestimate the total yearly source of bicarbonate from carbonate bedrock weathering. The same sample set would also provide data that would lead to an underestimation of the yearly atmospheric CO₂ draw down by bedrock weathering in the watershed. For example at four of the seven locations studied there was an almost two-fold difference between summer and spring calculated atmospheric CO₂ consumption rates.

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1. Introduction

Geochemical investigations at sites worldwide have sought to distinguish the chemical signatures of silicate and carbonate bedrock weathering in river systems. These studies, from the high Himalayan crystalline terrain (Blum et al., 1998; Jacobson and Blum, 2000), major rivers in Canada (Cameron et al., 1995; Yang et

al., 1996), watersheds in tropical environments (Tardy et al., 1993; Dupré et al., 1996; Viers et al., 2000; Négrel and Lachassagne, 2000), rivers in northern latitudes (Gaillardet et al., 2003; Millot et al., 2003) and catchments in mountains of the western United States (Garrels and Mackenzie, 1967; Reynolds and Johnson, 1972; Mast et al., 1990; Horton et al., 1999) have greatly added to our knowledge of river geochemistry. All of these investigations rely on the spatial assessment of bedrock geology to relate bedrock mineral weathering with river chemistry. Taken in total, these and many

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other studies formulate our understanding of the chemical and isotopic inputs from river systems to the world's oceans and facilitate calculation of the global flux of atmospheric CO₂ consumption attributable to bedrock weathering (Berner et al., 1983; Brady, 1991; Gaillardet et al., 1999; Quade et al., 2003; Amiotte-Suchet et al., 2003; Jacobson and Blum, 2003).

Many river chemistry studies rely on sampling programs that were only active during summer months. It is often logistically impossible to obtain multiple samples from a watershed over the course of multiple seasons or years, especially in locations that experience heavy snowfall, in regions dominated by mountainous terrain, or at remote sites where access is limited by snow or ice covers. Scientists attempting to extrapolate yearly estimates of weathering fluxes from single timeframe sampling are not able to address well-established seasonal and climatic controls on bedrock weathering rates (Bluth and Kump, 1994; White and Blum, 1995; Millot et al., 2003). The effect of seasonal controls on mass balance calculations of river fluxes may be substantial. As such, there is a need to better understand the seasonal aspects of silicate and carbonate weathering geochemistry in catchments before accurate yearly flux assessments can be extrapolated from single season sampling campaigns.

A year long geochemical investigation was undertaken in the White River watershed, a small watershed (1766 km²) in east central Vermont that flows into the Connecticut River. The goal was to quantify the seasonality of river chemistry in the White River and to compare the results to a detailed investigation of the Connecticut River (Douglas et al., 2002). The White River watershed contains a wide range of carbonate-bearing bedrock geology ranging from less than 5% to 45% of exposed bedrock with silicates comprising the remaining bedrock. As a consequence of this range in bedrock lithology, the White River is well suited for a detailed investigation of the seasonal aspects of carbonate and silicate bedrock weathering controls on river chemistry.

This study quantified the geochemistry of the White River during three different seasons that are associated with a unique geochemistry in the watershed: summer, late fall and spring runoff. The goal was to answer whether there were similarities or differences in water chemistry during these different times. Results from such a comparative analysis could be used to determine the applicability of discrete sampling events toward representing yearly average river chemistry in a watershed. Mass balance calculations of river chemistry, combined with Geographic Information Systems (GIS)

analyses, were used to distinguish the relationships between bedrock geology and carbonate weathering geochemistry in subcatchments during these three different seasons. The goal of this aspect of the study was to quantify the percent of carbonate versus silicate weathering in the watershed. The different fractions of silicate and carbonate weathering components can be used to calculate the yearly atmospheric CO₂ draw down by bedrock weathering in this or any other watershed.

2. Sampling and analytical methods

2.1. The White River watershed

The White River flows 89 km northwest to southeast across central Vermont from its source in the Green Mountains to its outlet into the Connecticut River at White River Junction (Fig. 1). The main stem of the White River is free of dams and the watershed ranges from ~75% to 90% forested (Harrington et al., 1998; Douglas et al., 2002; this study). Forest cover consists of coniferous and deciduous second-growth species. Land use is predominantly comprised of agriculture including row crops, hay farming and pasture (Harrington et al., 1998). The White River is free of any urban centers or major development.

GIS was used to quantify the percent coverage of bedrock geology within the White River watershed. Coordinates for the outline of the watershed were used to create a "cookie cut" that was separated from the most detailed bedrock geology at 1:125,000 scale (Robinson et al., 1999). The resulting map was used to quantify the percent coverage of the major bedrock types and the percent of the total White River watershed represented by flows at each sample location.

The White River drains predominantly metamorphosed carbonate and silicate sediments on the west side of the Ammonoosuc fault, a normal fault juxtaposing calcareous-bearing metasediments of Vermont against metapelitic and plutonic terrain of New Hampshire (Moench et al., 1995). The bedrock geology of the watershed can be separated into four distinct units (Fig. 1). The western boundary is comprised of small pockets of Proterozoic granite and gneiss with amphibolite facies metasediments. To the east lie Early Paleozoic graywacke, slate, phyllite, schist, amphibolite, granofels and mafic gneiss with minor metavolcanics, sulfides and carbonate. The Cambrian–Ordovician Hartland–Rowe–Hawley belt of granofels, schist, amphibolite, mafic gneiss and minor sulfides lies further east. The Connecticut River corridor is underlain by the

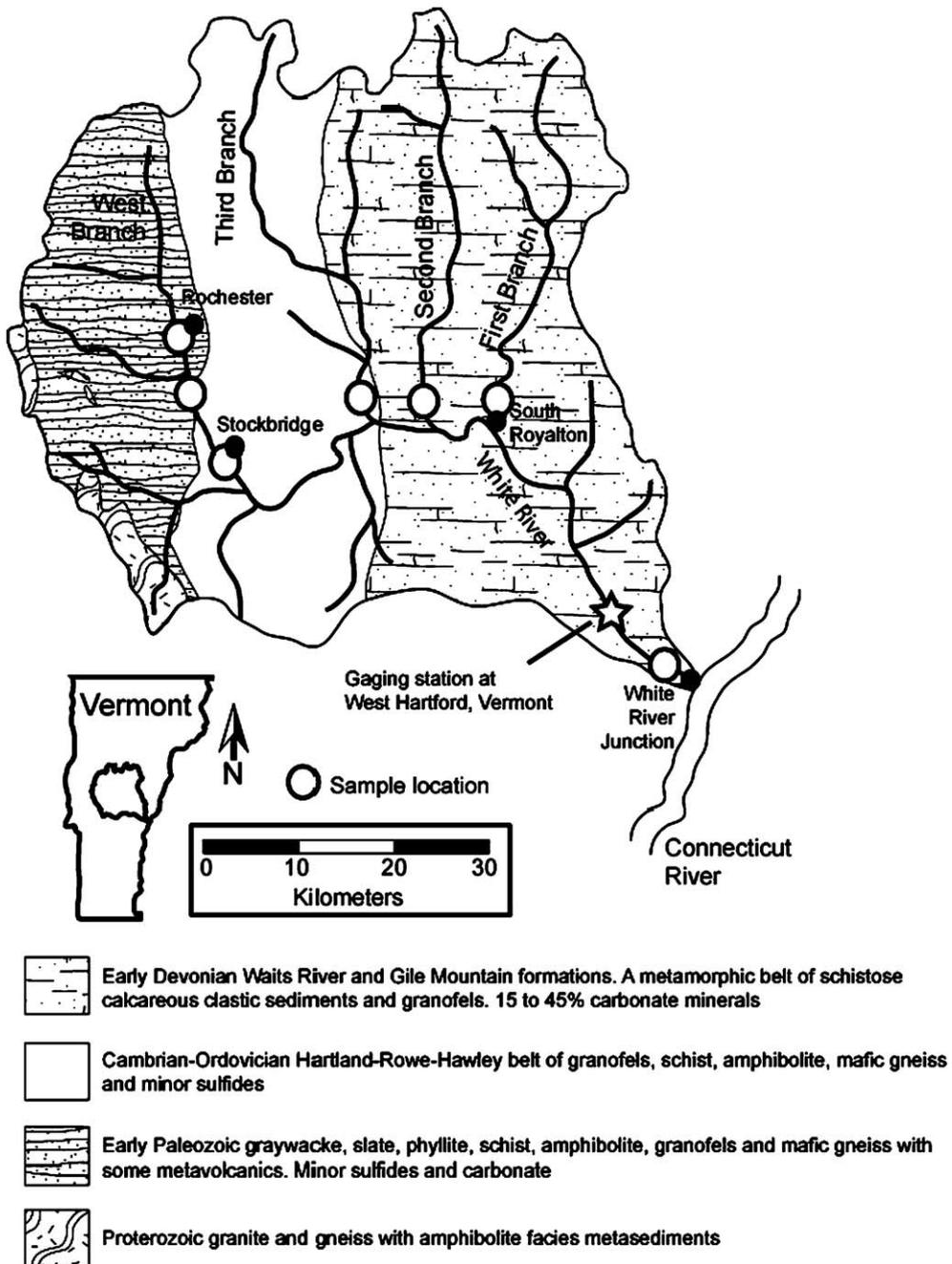


Fig. 1. A map of the White River watershed, Vermont including the seven sample locations in this study and the bedrock geology within the watershed based on Robinson et al. (1999).

Waits River and Gile Mountain formations, an Early Devonian metamorphic belt of schistose calcareous clastic sediments and granofels. Only the Waits River and Gile Mountain formations contain bedrock with an appreciable carbonate-bearing composition (up to 45%).

The entire northeastern United States was extensively covered by ice during the Pleistocene Epoch.

Glaciofluvial deposits are common throughout the White River watershed (Caissie et al., 1996) though cliff faces and hilltops of exposed bedrock are common. Till depths over bedrock at the Sleepers River Experimental Watershed 60km to the north generally range from 1 to 3 m in most areas but tills be thicker in some areas (Shanley et al., 2002). Glacial deposits and

fractured bedrock provide the majority of groundwater storage in the region. The presence of glacial till in the area could affect the relationship between bedrock geology and river chemistry. For example, a carbonate-rich till overlying a silicate bedrock could affect the geochemistry of runoff in that area. However, Douglas et al. (2002) found a strong correlation between silicate and carbonate bedrock and river chemistry in eleven tributaries of the Connecticut River including the White River. The different lithologies represented in the White River, their linear relationship to one another and the ease of road access throughout the watershed make the study area well suited for an investigation of the seasonal controls on bedrock lithology and stream geochemistry.

2.2. Field and laboratory methods

Sites representative of stream geochemistry were selected from three tributaries of the White River and from the White River at four locations within the watershed (Fig. 1). Samples were collected during three different seasons from 1998 to 1999. Sampling times were selected based on their ability to represent three different seasonal flow regimes. Two hydrographs of the White River from the gaging station at West Hartford, Vermont are included in Fig. 2: daily averaged discharge from 1930 to 1999 and daily discharge from the summer of 1998 to the summer of 1999. The historical hydrograph indicates the lowest discharge typically occurs during the warm summer months from the end of July until late September. These low flow conditions are generally followed by a slight increase in discharge during the late fall from early November through December. The highest

discharge is associated with spring snowmelt from mid-March to mid-May.

Based on the historical stream flow record the White River and its tributaries were visited on September 4, 1998 to represent low flow summer conditions, on December 5, 1998 to represent late fall flow conditions, and on April 21, 1999 to coincide with peak spring melt runoff. At each sample site separate 60 mL samples were obtained for cation and anion analysis. The electrical conductivity, pH, temperature and alkalinity (by Gran titration) were measured in the field. Samples for major element analyses were filtered through acid washed 0.45 μm polypropylene filters. Cation samples were acidified to $\text{pH} < 2$ with ultra pure HNO_3 in the field and cation concentrations were measured using a Spectro Analytical Instruments SpectroFlame inductively coupled plasma optical emission spectrometer (ICP-OES). Anions were measured using a Dionex DX 120 ion-chromatograph (IC). Multiple analyses of laboratory standards yielded an analytical uncertainty of $\pm 2\%$ for ICP-OES analyses and $\pm 5\%$ for IC analyses.

3. Results

3.1. Geologic classification by GIS

Four north–south trending tributaries drain the northern half of the White River watershed (Fig. 1). The First and Second Branches drain catchments underlain completely by the Connecticut River Valley metamorphosed calcareous clastic sediments (Table 1). The Third Branch drains an area underlain 34% by the Connecticut River Valley metamorphic belt of schistose calcareous clastic sediments and granofels and 66% by

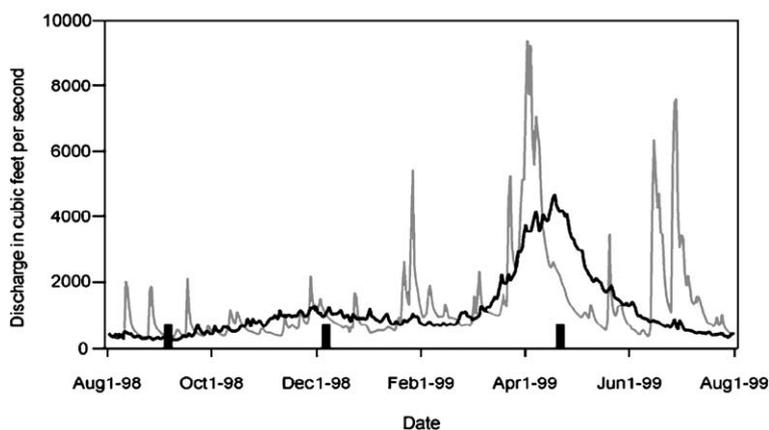


Fig. 2. Hydrographs of average daily flow from 1930 to 1999 (black) and once daily flow from August 1, 1998 to August 1, 1999 (gray) for the White River at West Hartford, Vermont. Vertical bold lines denote sample times.

Table 1

The percent of the White River watershed land area represented by each tributary, the percent coverage of the four major rock types in each tributary, and the percent of carbonate mineralogy in the watershed above each sample site

Sample location	Percent of White River watershed land area	Percent of Proterozoic crystalline and gneiss	Percent of Early Paleozoic metapelite	Percent of Hartland–Rowe–Hawley metapelite	Percent of Early Devonian calcareous metasediments	Percent of carbonate mineralogy
West Branch at Rochester	10		56	44		<5
West Branch below Rochester	15	2	57	41		<5
West Branch at Stockbridge	19	5	46	49		<5
Third Branch	19			66	34	5 to 15
Second Branch	9				100	15 to 45
First Branch	11				100	15 to 45
At White River Junction	100	4	23	31	42	~20

the Hartland–Rowe–Hawley granofels, schist, amphibolite and mafic gneiss. The northwest section of the West Branch drains an area underlain by schist, slate, phyllite and greywacke and minor pockets of Proterozoic granite, gneiss and granofels.

3.2. Major cation and anion chemistry

Results from analyses of 21 water samples from the White River watershed, representing seven locations collected during three different seasons, suggest a strong control on stream water chemistry attributable to bedrock weathering. The geochemical results from this study are included in Table 2. Electrical conductivity is a proxy for the total content of dissolved ions in a watershed (Meybeck, 1986). Measured specific conductance values range from $\sim 40 \mu\text{S}/\text{cm}$ in the tributaries hosted in non-calcareous bearing rocks to over $330 \mu\text{S}/\text{cm}$ in the First and Second Branches, two tributaries containing roughly 90% calcareous bedrock. The largest specific conductance values for each of the seven samples sites are from the summer samples when the watershed is experiencing its lowest yearly discharge (Fig. 2).

The total base cationic charge ($Tz^+ = [\text{Na}^+] + [\text{K}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}]$) for the water samples ranges from over $3500 \mu\text{eq}/\text{L}$ for the carbonate-hosted tributaries of the First and Second Branches to less than $1000 \mu\text{eq}/\text{L}$ for the other tributaries that are underlain by crystalline gneisses and metapelitic rocks. The White River at White River Junction, at $2172 \mu\text{eq}/\text{L}$ in the summer, has a significantly greater cationic charge than world average river waters ($1200 \mu\text{eq}/\text{L}$; Meybeck, 1979). In the fall ($1360 \mu\text{eq}/\text{L}$) and spring ($1272 \mu\text{eq}/\text{L}$) the White River in White River Junction has a cationic charge close to world average rivers.

A comparison of the sum of cationic charge with the sum of anionic charge ($Tz^- = [\text{HCO}_3^-] + [\text{Cl}^-] + 2[\text{SO}_4^{2-}]$)

indicates a relatively consistent charge balance in all samples (Table 2). Bicarbonate accounts for a majority of the anionic load in most tributaries of the White River. However, in waters carrying higher total ionic loads (those draining the predominantly carbonate terrains of the First and Second Branches) the ratio of cations to bicarbonate is slightly greater. Elevated sulfate and chloride concentrations balance out the bulk of the anionic load in these waters. River water ionic concentrations are highest in the summer followed by the fall and then the spring.

Waters draining carbonate-bearing rocks of the First and Second Branches have elevated Si, Ca, Na and K concentrations compared to waters draining the other locations in the watershed (sample locations denoted by the numbers 1 and 2 in Fig. 3A, B, and C, respectively). The concentrations of these species are highest in the summer samples followed by the fall and spring. A plot of alkali Earth ratio versus alkali ratio (Fig. 3D) indicates the First Branch of the White River has the highest alkali Earth ratio of all the sites sampled. The First Branch is characterized by the highest Ca and K concentrations of all the tributaries. There is a slight seasonal control on alkali Earth ratio concentrations in most waters where the $\text{K}/(\text{K} + \text{Na})$ value is lowest in the summer samples. The White River at White River Junction plots within the same alkali ratio as all tributaries but the First Branch. However, the alkali Earth ratio at White River Junction appears to be a mixture between the First Branch and the other tributaries sampled.

The relationship between cation concentrations in waters from the White River watershed is further explored in Fig. 4. The First and Second Branches have the highest concentrations of Na, Mg, K, Sr and Ca in all three seasons with the highest concentrations of all ions occurring in the summer followed by the fall and then spring. The White River in White River Junction in

Table 2
Geochemical results from this study without precipitation correction

	Sample name	Temp. °C	pH	Specific Conductance μS/cm	Ca μM/L	Mg μM/L	Na μM/L	K μM/L	Si μM/L	HCO ₃ ⁻ μM/L	Cl ⁻ μM/L	SO ₄ ²⁻ μM/L	Tz ⁺ μeq/L	Tz ⁻ μeq/L	δD ‰	
September 4, 1998 (summer)																
	West Branch in Rochester	ro	18.1	6.83	88.3	191.6	48.2	160.4	13.1	65.9	330.0	101.6	53.8	719	539	-100.2
	West Branch below Rochester	br	18.2	7.02	68.2	136.9	44.1	115.5	10.6	67.7	256.7	98.9	51.3	556	458	-101.2
	West Branch at Stockbridge	st	17	6.81	69.5	185.3	45.8	142.2	10.4	63.8	363.3	79.2	54.2	679	551	-100.6
	Third Branch	3	17.4	6.66	160	547.7	109.9	310.9	23.2	86.6	1076.7	236.5	71.8	1736	1457	-93.8
	Second Branch	2	19	7.92	333	1340.0	207.4	509.4	54.4	112.0	2746.7	448.8	112.3	3771	3420	-94.7
	First Branch	1	18.4	7.46	318	1503.6	127.8	323.3	74.5	105.1	3073.3	226.2	95.4	3766	3490	-94.7
	At White River Junction	wr	20.3	7.43	199	773.3	116.2	370.3	35.8	79.5	1610.0	290.9	82.7	2265	2066	-96.0
December 5, 1998 (late fall)																
	West Branch in Rochester	ro	4.8	5.55	50.9	146.9	42.8	83.5	8.4	55.3	256.0	44.2	52.9	527	406	-96.3
	West Branch below Rochester	br	4.4	5.74	41.2	125.8	40.2	65.4	9.9	57.7	318.0	28.2	49.2	465	445	-101.6
	West Branch at Stockbridge	st	5.8	5.31	47.5	154.2	41.4	74.9	8.1	53.4	260.0	32.7	51.7	528	396	-106.6
	Third Branch	3	5	5.63	99.8	362.5	79.2	160.8	13.9	72.1	806.0	114.1	62.4	1130	1045	-96.1
	Second Branch	2	4.8	6.6	284	1227.4	188.8	390.9	44.7	111.2	2544.0	374.1	128.0	3379	3174	-101.6
	First Branch	1	4.1	7.3	278	1450.3	118.1	190.5	57.5	99.5	2696.0	135.1	107.7	3484	3046	-103.0
	At White River Junction	wr	6.1	6.61	129.4	506.0	82.8	173.9	22.0	68.8	1256.0	126.7	71.1	1442	1525	-98.4
April 21, 1999 (spring)																
	West Branch in Rochester	ro	6.3	6.8	44.2	99.2	30.9	83.7	8.2	40.4	200.0	77.0	45.4	392	368	-103.9
	West Branch below Rochester	br	6.8	6.72	35.7	79.2	26.5	63.4	7.9	41.2	202.5	58.2	42.2	324	345	-100.6
	West Branch at Stockbridge	st	5	6.76	41.2	106.7	30.3	70.3	5.9	37.8	195.0	64.6	44.8	388	349	-97.5
	Third Branch	3	6.5	6.55	100.4	279.7	61.9	164.4	11.2	56.0	667.5	147.7	57.1	915	929	-100.0
	Second Branch	2	7.6	6.51	229	962.0	144.6	337.1	35.9	83.9	2017.5	331.1	104.8	2670	2558	-96.8
	First Branch	1	7.6	6.88	216	956.0	75.6	141.5	41.9	73.1	2042.5	158.6	88.5	2320	2378	-94.5
	At White River Junction	wr	9.9	6.98	141	473.5	69.6	175.8	22.8	59.8	947.5	174.0	67.3	1345	1256	-98.6
Precipitation																
	Average monthly value at Hubbard Brook from May 1997 to May 1998 ^a					2.8	1.1	4.3	2.6	2.1		6.2	19.5			

^a Data from the Hubbard Brook Experimental Forest January 1997 through May 1998.

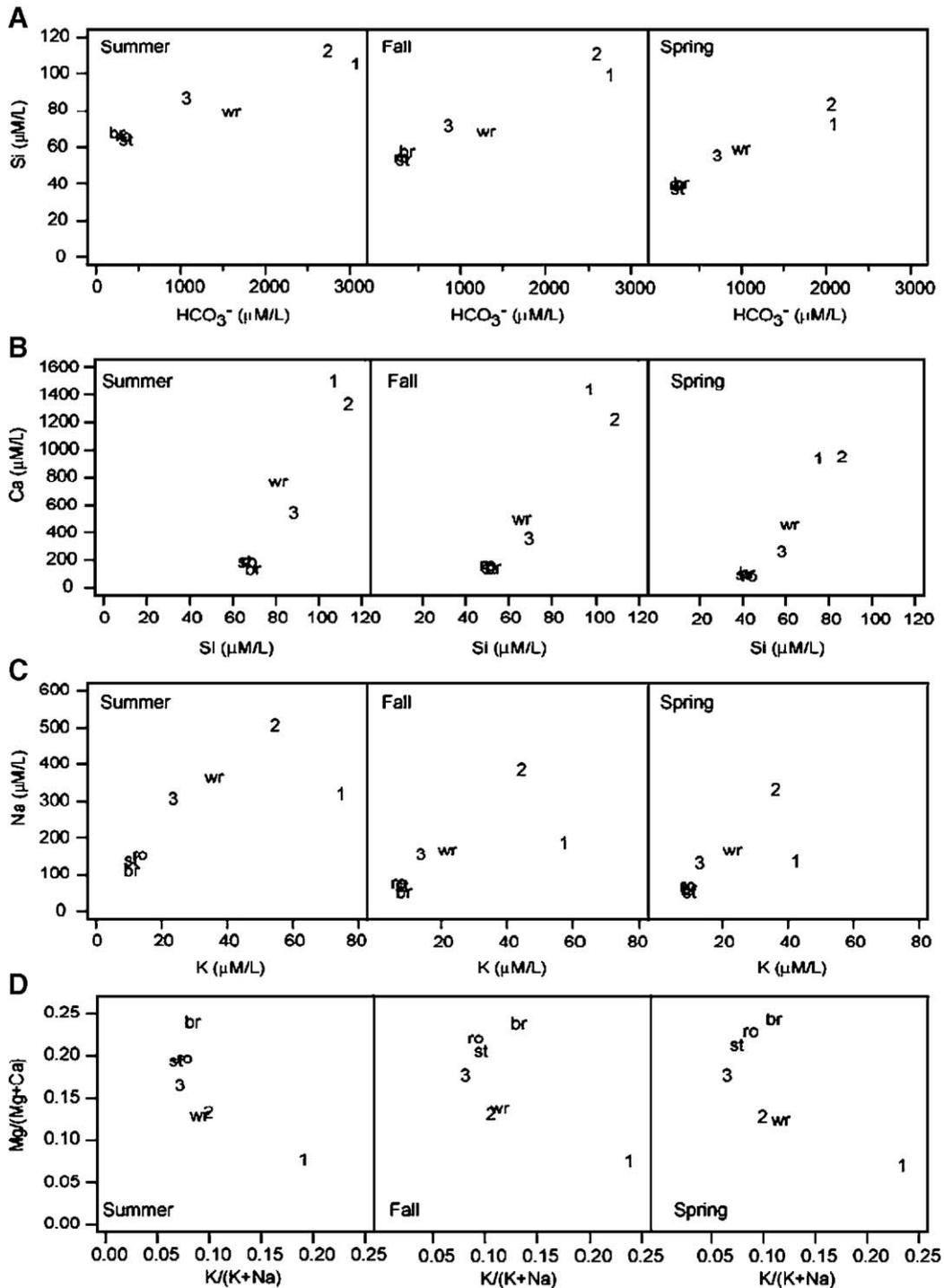


Fig. 3. (A) Silica (µM/L) versus bicarbonate (µM/L), (B) calcium (µM/L) versus silica (µM/L), (C) sodium (µM/L) versus potassium (µM/L), and (D) alkali Earth ratio versus alkali ratio. Values are corrected for precipitation input at the Hubbard Brook Experimental Forest for all species except bicarbonate (see Table 2). Sample marker text corresponds with the second column in Table 2.

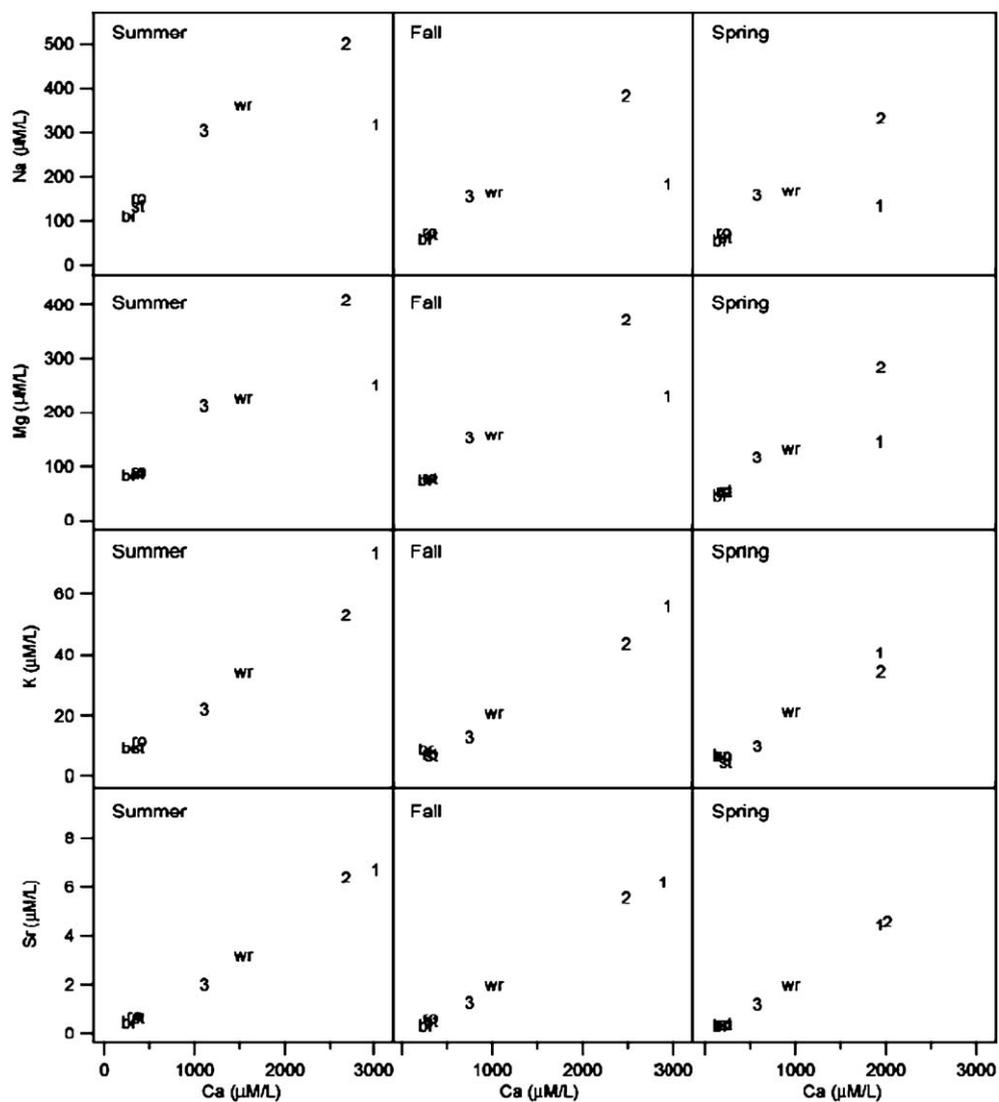


Fig. 4. (A) Sodium ($\mu\text{M/L}$), (B) magnesium ($\mu\text{M/L}$), (C) potassium ($\mu\text{M/L}$) and (D) strontium ($\mu\text{M/L}$) versus calcium ($\mu\text{M/L}$). Values are corrected for precipitation input at the Hubbard Brook Experimental Forest for all species except bicarbonate (see Table 2). Sample marker text corresponds with the second column in Table 2.

the summer plots between the First and Second Branches and the other tributaries in major element concentrations. Na and Mg concentrations are linearly correlated to Ca for all sample locations but the First Branch. The First Branch has particularly elevated Ca concentrations with respect to Mg. The coefficients of determination relating Na and Mg with Ca in all summer samples are 0.70 and 0.76, respectively. Without including the First Branch samples the coefficients of determination relating Na and Mg with Ca in summer samples are 0.92 and 0.98, respectively. K and Sr are strongly linearly related to Ca in all samples (r^2 values of 0.96 and 0.99, respectively).

4. Discussion

The focused objective of this investigation was to measure a suite of geochemical parameters in waters of the White River during three different seasons that are associated with a unique geochemistry in the watershed: summer, late fall and spring runoff. The goal of this part of the study was to answer whether there were similarities or differences in water chemistry during the different seasons. Results from such a comparative analysis could be used to determine the applicability of discrete, single season sampling events toward representing yearly average river chemistry in a watershed.

A series of mass balance calculations were applied to the geochemical parameters measured in the watershed to distinguish the relationships between bedrock geology and bicarbonate geochemistry during the three different seasons. The goal of this aspect of the study was to quantify the bicarbonate sources in the watershed. Since silicate mineral weathering draws down twice as much CO₂ as carbonate weathering there is a need to determine the seasonal aspects of these two different weathering regimes.

4.1. Seasonal influences on river geochemistry

Historically the lowest flow conditions in the White River occur in the summer and early fall (Fig. 2). During this investigation the summer does have the lowest flow conditions but summer rainstorms cause rapid increases in discharge. On a stream hydrograph the elevated rainfall inputs yield rapid increases in discharge over a period of a few hours followed by recession to base flow conditions during the following few days. The early peak flows associated with the onset of these events probably flush much of the stored “old water” out of the system (Sklash et al., 1976; Buttle, 1994).

Many investigations of storm runoff indicate that at least half of the stream flow during peak events is comprised of pre-event water (Buttle, 1998). A study at Mink Brook, New Hampshire, 10 km from the White River, shows that the stream component of new, event, water increases relative to that of old, pre-event, water as peak storm flows dissipate and base flow conditions resume (Feng et al., 2002).

In both the historical records and in the fall of 1998 the late fall is characterized by slightly more precipitation and runoff than the summer but with fewer severe storm events. Fall season sampling occurred a few days after a significant precipitation event when the river was undergoing recession to base flow conditions. Other storm events in the White River watershed are characterized by a rapid (~1–2 days) return to base flow conditions.

Peak flows in the White River typically occur during spring runoff between mid-March and early May. During sampling on April 21, 1999 the White River had passed yearly peak flows related to spring runoff and was characterized by decreasing discharge rates. Two hydrologic investigations in the Sleepers River watershed 60 km north of the White River suggest that these conditions should correspond with flow containing a snow melt runoff component with a contribution from groundwater that increases toward the end of peak flow (Shanley, 2000; Shanley et al., 2002). Peak

discharge in the White River during spring melt is generally ten times greater in volume than summer or late fall discharge. As a consequence, though the concentrations of ions are lowest during spring runoff the largest ion flux export out of the White River (and other temperate watersheds) is generally associated with this season.

4.2. Bedrock influences on river geochemistry

Weathering of carbonate minerals largely controls the major cation and anion chemistry of the White River. Tributaries draining carbonate-bearing bedrock in the eastern half of the watershed yield much higher concentrations than tributaries in the western half (Figs. 2, 3 and 4). It has been widely established that the weathering of carbonate minerals, even where they comprise a minor proportion of the bedrock geology, controls river chemistry in many watersheds (Blum et al., 1998; White et al., 1999; Karim and Veizer, 2000; Jacobson and Blum, 2000; Jacobson et al., 2002).

A ternary diagram allowing comparison between the White River samples and waters draining other bedrock types is included as Fig. 5. Potassium likely has multiple sources and sinks in the watershed including inputs from precipitation and both inputs and outputs from biologic activity. Potassium is the only ion investigated in this study for which precipitation concentrations are as much as thirty percent of river water concentrations (Table 2). Additionally, potassium flux both in and out of the soil system can be controlled by seasonal biotic activity (Likens et al., 1994). However, in all but one watershed (the First Branch) the Na concentrations are at least eight times greater than the K concentrations. Thus by combining Na and K in the ternary analysis much of the atmospheric and biotic controls on potassium fluxes are minimized.

All of the samples from this study plot in a region dominated by calcite weathering with minor biotite, feldspar and quartz weathering. The First and Second Branches of the White River plot in a field indicating almost exclusively the weathering of calcite as is expected based on their geology. These tributaries are slightly more enriched in (Ca+Mg) and depleted in Si than waters draining similar carbonate-bearing metasediments in southwestern Montana (Horton et al., 1999). The First and Second Branches contain slightly more (Na+K) than the limestone spring values reported by Quade et al. (2003) but they still suggest that calcite weathering is the source of a majority of the cations in these subcatchments of the White River.

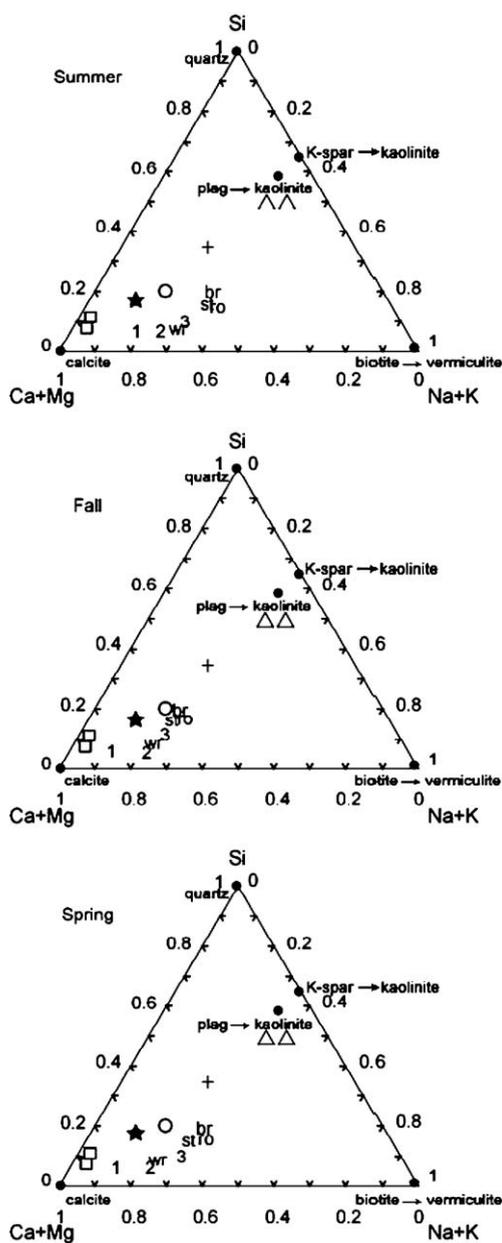


Fig. 5. Mole fractions of the major cations measured in White River water samples each season with fields for mineral weathering reactions. Weathering products of quartz, calcite and biotite plot at the apices. The position of the plagioclase weathering products is based on a Ca–Na ratio of 0.3 for plagioclase reported by Ferry (1992). Sample marker text corresponds with the second column in Table 2. Average water compositions for gneiss and granite from the Raikhot watershed in the Himalaya (circle; Blum et al., 1998), the Loch Vale, Colorado granite with disseminated calcite (plus; Mast et al., 1990), carbonate metasediments from southwestern Montana (star; Horton et al., 1999), limestone springs from Nevada (open box) and silicate springs from the Sierras and Nepal (open triangle; Quade et al., 2003) are plotted for reference.

The West Branch of the White River at Rochester, the West Branch below Stockbridge and the White River below Stockbridge all plot in a region corresponding with more biotite, feldspar and quartz weathering than the other locations in the watershed. These values are close to the water chemistry attributable to granite weathering in the Raikhot watershed of the Himalaya (Blum et al., 1998) but they are more enriched in (Ca+Mg) from calcite weathering than granite with disseminated calcite from Loch Vale, Colorado (Mast et al., 1990).

Seasonal controls on river chemistry in the catchments of the White River are apparent in the results. For example, during low flow summer conditions all of the sample sites exhibit an enrichment in the chemistry associated with the weathering of biotite (with a commensurate depletion in the calcite weathering component) compared to the late fall and spring. The weathering chemistry of quartz and feldspars, represented by the Si apex in the ternary diagram, shows no seasonal relationship, suggesting that quartz and potassium feldspar dissolution (orthoclase, the Si source) is not as seasonally controlled as calcite and biotite weathering.

Strontium isotope values from other rivers in the Connecticut River watershed yield insight into the seasonal sources of Ca in the White River because Sr and Ca have similar ionic radii and charge. $^{87}\text{Sr}/^{86}\text{Sr}$ values from the Ompompanoosuc River, located 20 km north of the White River, varied a total of 0.0003 between summer, late fall and spring samples during this investigation (Douglas et al., 2002). The Ompompanoosuc River is a tributary of the Connecticut River underlain by the carbonate-bearing Waits River and Gile Mountain formations. $^{87}\text{Sr}/^{86}\text{Sr}$ values from the Ammonoosuc River, a silicate-hosted watershed in New Hampshire located 60 km northeast of the White River, varied a total of 0.0002 between summer, late fall and spring samples during this investigation (Douglas et al., 2002). The strontium isotope results from these rivers suggest that the Ca source in both carbonate and silicate terrains (calcite dissolution) remains relatively constant throughout the three seasons sampled.

Based on the ternary plot (Fig. 5) Ca, Mg, and Si do not change proportionally over the three seasons sampled so Na (and/or) K must vary enough seasonally to alter the mass balance calculations of the bicarbonate sources in the watershed. This, in turn, suggests that feldspar and/or biotite dissolution are the dominant factors controlling the seasonal differences in river geochemistry. Lower rates of feldspar and/or biotite weathering compared to carbonate weathering in the fall

samples yield a larger calculated carbonate source of bicarbonate in the fall than in other seasons. Taken in total, the geochemical results (Figs. 3, 4 and 5) suggest that there are higher ionic concentrations in the summer than in the fall and spring. Regardless of the specific mineralogical cause of the seasonal variations in river chemistry the stoichiometric ratios of the major ions to one another are not consistent throughout the three seasons. Thus single season samples could not accurately represent the mineral weathering chemistry of the watershed.

4.3. Carbonate and silicate weathering as a source of bicarbonate

In an attempt to distinguish the seasonal controls on the relative weathering contributions attributable to the major rock types within the White River watershed mass balance calculations were used to quantify the relative ion fluxes from silicate and carbonate mineralogies following Blum et al., 1998. The calculation procedure is designed to simplify the most dominant geochemical reactions in a system to allow calculation of the bicarbonate source in the system. The series of calculations assume weathering reactions in soils and bedrock control river water chemistry and that the bedrock at a given location provides the majority of material undergoing weathering. In the White River watershed the presence of glacial tills from regional Pleistocene glaciation may challenge this assumption, however, the predominant weathering material is assumed to be either bedrock or overlying soils derived from the local bedrock. The calculations account for precipitation inputs to the system, however, a few important assumptions must be made in regard to other solute sources. The reactions do not take into account the potential effect of incongruent aluminosilicate dissolution at mineral surfaces (Blum and Lasaga, 1991) the presence of organic acids in weathering fluids (Chin and Mills, 1991; Bennett et al., 1988) input of ions to the soil surface via throughfall (Likens et al., 1994) and watershed acidification by organic acids (Zhang and Bloom, 1999).

The six step process in calculating the bicarbonate source is outlined in detail in Blum et al. (1998) and was applied to the Connecticut River watershed by Douglas et al. (2002). Stoichiometric relationships of the weathering reactions can be used to calculate the contribution of each weathering reaction to stream water chemistry. The dominant minerals in the rocks in the White River watershed include potassium feldspar, plagioclase feldspar, biotite, muscovite and calcite.

First, ionic concentrations are corrected for atmospheric input. Precipitation information from the Hubbard Brook Experimental Watershed, located 80 km northeast of White River Junction, Vermont (Table 2), was used. Second, all Na is attributed to the weathering of albite to kaolinite. For this 2 mol of Si and 1 mol of HCO_3^- are subtracted for each mole of Na. Third, the presence of Ca, due to the weathering of anorthite to kaolinite, is assumed to be proportional to the Ca/Na ratio in plagioclase. A Ca/Na ratio in plagioclase feldspars of 0.3 was used because it is within the range of values reported for Vermont rocks (0.17–0.38; Ferry, 1992). For this correction 2 mol of HCO_3^- are subtracted for each mole of Ca. The average deposition of Ca in 18 months of precipitation at Hubbard Brook Experimental Forest was $2.8 \mu\text{M/L}$. Thus precipitation is not a major source of Ca to the system. Fourth, the remaining Si is attributable to the weathering of orthoclase to kaolinite. For this reaction, 0.5 mol of K and 0.5 mol of HCO_3^- are subtracted for each mole of Si. Fifth, the remaining K is attributable to the weathering of biotite to vermiculite. Thus 1 mol of HCO_3^- is subtracted for each mole of K. Sixth, the excess Ca and Mg are attributed to carbonate dissolution. For this 2 mol of HCO_3^- are subtracted for each mol of Ca+Mg.

Two important results emerge from the calculation of the source of bicarbonate to the White River (Fig. 6). First, though calcareous metasediments comprise little to no mapped bedrock in the western White River basin, carbonate minerals are the predominant source of bicarbonate to the tributaries in this part of the watershed. These minerals may be present in both carbonate and silicate rocks. More than 60 percent of the bicarbonate in tributaries draining Early Paleozoic metapelites, Proterozoic crystalline rocks and gneisses and Hartland–Rowe–Hawley metapelites is attributable to the weathering of carbonate minerals. This supports the work of Douglas et al. (2002) who found that though calcareous metasediments comprise roughly 10% of the overall bedrock in the Connecticut River watershed the weathering of carbonates accounts for up to 60% of the bicarbonate at the river's mouth. These results suggest that all of the bedrock units in the White River contain at least minor carbonate mineralogy and that the dissolution of this mineralogy preferentially influences river chemistry by releasing elevated ionic strength waters into the watershed. However, the percent of the bedrock comprised of carbonate minerals such as calcite, dolomite or siderite cannot be ascertained from these calculations.

Second, there is a strong seasonal control on the percent of bicarbonate attributable to the weathering of

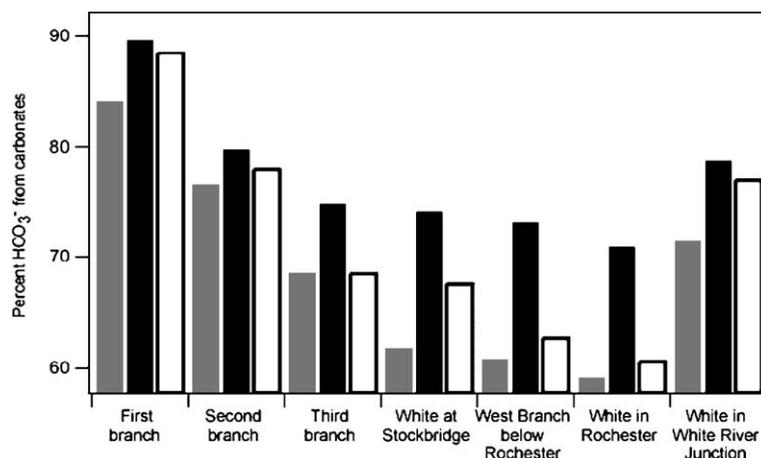


Fig. 6. A category plot of the percent bicarbonate attributable to carbonate mineral weathering by season for each of the locations in the White River watershed sampled in this study. The summer, fall and spring seasons are represented by gray, black and white, respectively.

carbonate minerals. At all seven sample sites the highest calculated carbonate weathering values are from the late fall samples while the lowest values are from the summer. A comparison of means for the three seasons indicates that the late fall values are statistically significantly greater than the summer values ($\alpha=0.05$). This suggests that there is a distinct seasonality to the ratios of ions in the tributaries of the White River.

The strong seasonal control on the weathering of carbonate mineralogy is not unique to the White River watershed. In all eleven of the major tributaries of the Connecticut River investigated by Douglas et al. (2002) the late fall samples, obtained within a week of the White River samples during the same seasons, yielded a higher calculated percent of bicarbonate attributable to carbonate weathering than the summer or spring waters.

4.4. Atmospheric CO₂ consumption in the White River watershed

Discharge data, basin characteristics and the seasonal major element concentrations were combined to quantify the relationship between seasonal flow regimes and the atmospheric CO₂ draw down related to bedrock weathering geochemistry in the White River watershed. The calculations follow the detailed steps outlined in Jacobson et al. (2003) and Jacobson and Blum (2003). In summary, major ion values are combined with runoff rates to calculate the atmospheric CO₂ consumption, in moles per square kilometer per year, attributable to silicate weathering ($W_{\text{silicate-CO}_2}$) and carbonate weathering ($W_{\text{carbonate-CO}_2}$). Silicate weathering rates are scaled by a factor of two because

that is the stoichiometric ratio of Ca involved with the reaction between carbonic acid and plagioclase.

The 1998–1999 discharge data shown in Fig. 2 was used to calculate runoff rates based on the cumulative discharge measured during the three seasons represented by the samples. The percent of the White River watershed represented by each sample location was used as a correction factor for the discharge measured at the White River gaging station at Hartford, Vermont (Figs. 1 and 2). The results from this calculation (Fig. 7) support the earlier finding that the dominant source of the mineral weathering signature in waters of the White River is attributable to carbonates. More importantly, the results from a calculation of atmospheric CO₂ consumption rates suggest that at all seven sample locations the spring season is associated with the largest CO₂ consumption. The spring is characterized by the largest discharge and discharge volumes are included in the atmospheric CO₂ consumption rate calculations so this finding is not a surprise. Despite lower overall ionic concentrations in spring waters the elevated flow makes the spring season the greatest period of export of ions from the watershed. At three locations (the First Branch, the West Branch below Rochester and the White River at Rochester) there were no major seasonal differences in calculated atmospheric CO₂ consumption. However, at four other locations (the Second Branch, the Third Branch, the White at Stockbridge and the White in White River Junction) there was an almost two-fold difference between summer and spring calculated atmospheric CO₂ consumption rates. The seasonal controls on weathering chemistry do not appear to be related to watershed bedrock geology or land area. Based on this result, selecting one sampling time during

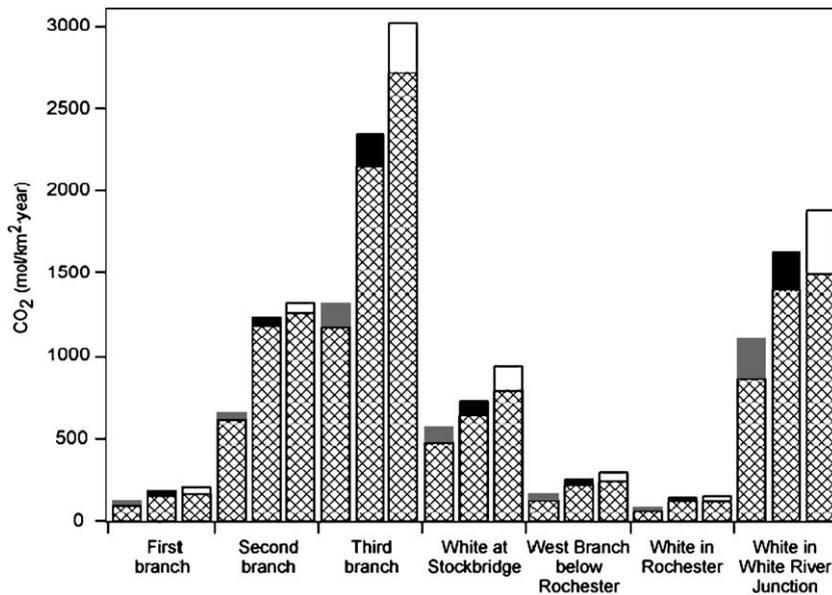


Fig. 7. A category plot of atmospheric CO₂ consumption rates calculated for the White River. The total fraction of CO₂ consumption from bedrock weathering ($W_{\text{carbonate-CO}_2} + W_{\text{silicate-CO}_2}$) for the summer, fall and spring seasons are represented by gray, black and white, respectively. The fraction of CO₂ from carbonate minerals ($W_{\text{carbonate-CO}_2}$) for each sample site and season is represented by the hashed design.

a single season to accurately represent the yearly flux of atmospheric CO₂ consumption in the White River watershed would be impossible.

5. Conclusions and implications

This geochemical investigation was undertaken to assess the relationship between bedrock geology and weathering geochemistry in a small watershed (~2000 km²) during three different seasons. The White River was selected because it experiences minimal anthropogenic disturbance and its subcatchments contain bedrock carbonate coverage ranging from less than 5% to almost 45%. In addition, the White River is situated in a northern temperate climate where peak flows during spring runoff often yield ten times the discharge of base flow conditions. Two important conclusions emerge from this work.

First, the weathering of carbonate minerals, accounting for at most twenty percent of the bedrock mineralogy in the White River watershed, accounts for roughly 75% of the total ionic load in all seasons sampled. In addition, tributaries comprising roughly forty percent of the land area in the White River watershed provide a majority of the total ionic load in the White River. Numerous similar investigations of silicate and carbonate weathering have shown that trace amounts of carbonate mineralogy in a watershed can be the source of a majority of the ionic load (Blum et al.,

1998; Horton et al., 1999; Jacobson and Blum, 2000; Douglas et al., 2002). The White River has a carbonate weathering dominated geochemical signature as a consequence of this preferential carbonate weathering. However, carbonates are not the predominant rock type in the watershed.

Second, there is a significant seasonal control on river geochemical fluxes and the subsequent estimates of bicarbonate sources and atmospheric CO₂ consumption rates calculated from these fluxes. The highest carbonate to silicate weathering ratio is found in the late fall and the lowest carbonate to silicate weathering ratio is measured in the summer. If this seasonal shift in silicate versus carbonate weathering is due to elevated Na:HCO₃⁻ and K:HCO₃⁻ ratios in summer waters then this would indicate that silicate weathering is most active in the summer season. Calculated atmospheric CO₂ consumption rates are lowest in the summer due to low flow conditions and are highest in the spring because of high flow conditions. However, the relationship between CO₂ consumption during bedrock mineral weathering and seasons appears to be unpredictable. Some subcatchments of the White River exhibit a marked variation in atmospheric CO₂ consumption over the three seasons sampled while others show consistent CO₂ consumption in all three seasons sampled.

Many investigations have sought to estimate the relationship between mineral weathering rates and

environmental factors such as precipitation (White and Blum, 1995), temperature (Meybeck, 1986, 1994; Sverdrup, 1990) and climate (Peters, 1984; Bluth and Kump, 1994; Millot et al., 2003). These environmental factors affect the residence time of waters in soils and bedrock aquifers. The longer the residence time the more concentrated ions become in soil waters that eventually comprise river flows. April et al. (1986) report that the amount of glacial till in a watershed regulates the residence time of water and thus controls weathering fluxes out of the soil and into surface waters. Stallard (1985) reports that soil thickness plays an important role in regulating the water residence time.

The higher silicate weathering component present in the summer samples implies that elevated summer temperatures are associated with increased silicate weathering rates. However, results from strontium isotopes and major element concentrations suggest that the carbonate weathering regime in the White River is consistent throughout the year. Investigations of the climatic controls on silicate and carbonate weathering in northwestern Canadian watersheds suggest that carbonates have the highest weathering rates of major rock types (Gaillardet et al., 2003) and that silicate weathering rates increase with elevated summer temperatures (Millot et al., 2003). Without detailed knowledge of soil temperature, thickness, aquifer types and bedrock fracture connectivity in the White River watershed the issues of summer soil temperatures or water residence times in the different catchments sampled cannot be addressed.

Taken in total, the results from this study irrefutably suggest that stoichiometric relationships between dissolved ions in river waters are significantly seasonally variable. Estimates of river compositions or mineral weathering rates relying on single season sampling campaigns thus may not accurately represent the annual flux of ions through a watershed. For example at four of the seven locations studied there was an almost two-fold difference between summer and spring calculated atmospheric CO₂ consumption rates. This has ramifications on relating carbonate and silicate bedrock weathering to global bicarbonate fluxes and the atmospheric CO₂ reservoir.

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