Relative weathering intensity of calcite versus dolomite in carbonate-bearing temperate zone watersheds: Carbonate geochemistry and fluxes from catchments within the St. Lawrence and Danube river basins

Kathryn Szramek

Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan 48109, USA

Now at Department of Geology, Washington and Lee University, Lexington, Virginia 24450, USA (kszramek@umich.edu)

Jennifer C. McIntosh

Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan 48109, USA

Now at Department of Hydrology and Water Resources, University of Arizona, Tucson, Arizona 85716, USA

Erika L. Williams

Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan 48109, USA

Now at ARCADIS U.S., Inc., Millersville, Maryland 21108, USA

Tjasa Kanduc and Nives Ogrinc

Department of Environmental Sciences, "J. Stefan" Institute, Jamova 39, 1000 Ljubljana, Slovenia

Lynn M. Walter

Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan 48109, USA

[1] Calcite and dolomite solubilities in open weathering environments are proportional to pCO_2 and inversely proportional to temperature, and dolomite solubility is progressively greater than calcite below 25°C. The continent-scale weathering budget reveals the significance of the Northern Hemisphere (NH) to globally integrated riverine fluxes of Ca^{2+}, Mg^{2+}, and HCO_3^-. The NH contributes 70% of the global HCO_3^- flux while only 54% of the riverine discharge. We present results of a comparative hydrogeochemical study of carbonate mineral equilibria and weathering fluxes in two NH carbonate-rich river basins. Surface water geochemistry and discharge were determined for headwater streams in Michigan and Slovenia within the St. Lawrence and Danube river basins. Michigan watersheds are established atop carbonate-bearing glacial drift deposits derived from erosion of Paleozoic strata with thick soil horizons (100–300 cm). Slovenia watersheds drain Mesozoic bedrock carbonates in alpine and dinaric karst environments with thin soil horizons (0–70 cm). Carbonate weathering intensity is a parameter that normalizes river runoff and HCO_3^- concentration to catchment area (meq HCO_3^- km^{-2} s^{-1}), summing calcite and dolomite contributions, and is used to gauge the effects of climate, land use, and soil thickness on organic-inorganic carbon processing rates. Importantly, Michigan riverine discharge is one-tenth of Slovenian rivers, providing the opportunity to evaluate the kinetics of carbonate mineral equilibration. The study rivers are HCO_3^- − Ca^{2+} − Mg^{2+} waters, supersaturated for calcite at pCO_2 values in excess of the

atmosphere. As discharge varies, HCO_3^- concentrations differ by less than 20% for any location, and Mg^{2+}/Ca^{2+} remains relatively fixed for Michigan (0.5) and Slovenia streams (0.4), requiring that dolomite dissolution exceed calcite on a mole basis. The ability of calcite and dolomite dissolution to keep pace with increased discharge indicates carbonate weathering is limited only by water flux and temperature-dependent solubility in these watersheds. Carbonate weathering intensity in Michigan and Slovenia exceeds the world average by factors between 2 and 20, and dolomite weathering intensity, estimated from riverine Mg^{2+} fluxes, exceeds the world average by factors between 2 and 15. Thus global fluxes of carbonate-related weathering products appear heavily skewed toward carbonate-bearing environments at higher latitudes with relatively low mean annual temperatures and high discharge.

1. Introduction

[2] Mineral weathering is an important regulator of global atmospheric CO_2 concentrations. During silicate weathering, riverine HCO_3^- is derived entirely from the atmosphere and is a net long-term sink for CO_2. Carbonate weathering draws down even greater amounts of atmospheric CO_2, but the withdrawal is relatively short term because CO_2 is then returned to the atmosphere by carbonate precipitation in the oceans. The sequestration of atmospheric CO_2 stored in freshwater and shallow oceans thus can be significant on timescales of hundreds of years making the carbonate system dynamics of surface waters germane to the increasing anthropogenic perturbations to the global carbon cycle. As CO_2 levels increase, riverine chemical fluxes (e.g., dissolved organic and inorganic carbon, nutrients) may be influenced by local changes in organic-inorganic carbon transformation rates, vegetation, and rainfall. Watershed adjustments, in response to climate change, will likely be most evident in the smaller headwater streams. Herein, we present a hydrogeochemical database of the headwater reaches of two major northern hemisphere drainage basins, the St. Lawrence and the Danube, which we use to better quantify the processes controlling rates and pathways of carbonate mineral weathering in carbonate-dominated watersheds of very different geologic and climatic settings.

[3] Chemical weathering in the terrestrial environment is often quantified by using dissolved elemental riverine fluxes. Early studies attempted to quantify solute fluxes to the world's oceans and therefore focused on the largest drainage basins, typically greater than 1×10^6 km^2, such as the Amazon, Congo, and Mississippi Rivers [e.g., *Kempe*, 1982; *Meybeck*, 1979, 1987]. Such large river basins integrate varying climates, lithology, soil composition, soil depth and land use types (e.g., agricultural, urban, and forested). In order to examine these individual factors, which can have a large influence on river chemistry, previous studies in smaller scale catchments attempt to control for lithology [*Bluth and Kump*, 1994; *Gaillardet et al.*, 1999; *Jacobson et al.*, 2002], others for lithology in specific climates [*White and Blum*, 1995; *Huh et al.*, 1998; *Huh and Edmond*, 1999; *Hélie et al.*, 2002; *Millot et al.*, 2003], while a few studies investigate a link between soil and land use type [*Telmer and Veizer*, 1999; *Finlay*, 2002].

[4] On a global scale, the importance of mineral weathering on different landmasses is determined by the runoff and the proportions of silicate versus carbonate rock within the drainage basins [e.g., *Gibbs and Kump*, 1994; *Amiotte Suchet and Probst*, 1995; *Ludwig et al.*, 1998; *Amiotte Suchet et al.*, 2003]. The average continental, riverine HCO_3^- concentrations (in meq L^{-1}) in ascending order are: S. America, 0.40; Africa 0.45; Oceania, 1.10; Asia, 1.10; N. America, 1.20; and Europe

1.40 [e.g., *Berner and Berner*, 1996]. Bicarbonate values of <0.5 meq L^{-1} are generally observed in pure silicate catchments while higher values reflect the increasing contribution of carbonate weathering. The continental HCO$_3^-$ fluxes are influenced by both lithology and runoff. The Asian continent contributes the highest total annual flux of HCO$_3^-$ (15 × 10^{15} meq HCO$_3^-$ year^{-1}), while N. America, S. America, Europe and Africa contribute, in descending order, 6.5 × 10^{15}, 5.6 × 10^{15}, 4.3 × 10^{15} and 2.3 × 10^{15}, respectively. Abundant carbonate available for weathering coupled with high annual precipitation contributes to Asia having the highest HCO$_3^-$ flux. Aridity and silicate cratonic bedrock contribute to the low African HCO$_3^-$ flux.

[5] The normalization of HCO$_3^-$ fluxes to drainage area allows for a comparison of weathering "intensities" between drainage basins [see *Amiotte Suchet and Probst*, 1993]. The weathering "intensity" is a proxy for lithology (e.g., silicate versus carbonate), age and development of bedrock/soils (e.g., how deeply weathered), land type/use, and climate. For a given lithology, high runoff values are associated with increasing weathering fluxes [*White and Blum*, 1995; *Ludwig et al.*, 1998; *Millot et al.*, 2003]. *Amiotte Suchet and Probst* [1993] note that rivers draining carbonate terrain have a HCO$_3^-$ flux 17 times higher than that for silicate lithologies at the same runoff value. These relations are illustrated in Figure 1a, which shows carbonate weathering intensity (meq HCO$_3^-$ km^{-2} s^{-1}) versus specific runoff (L km^{-2} s^{-1}) for the different continents. The areas dominated by carbonate mineral weathering (N. America, Asia, Europe) have the highest carbonate weathering "intensities", while those draining silicate-dominated terrains (Africa and S. America) have lower carbonate weathering intensity.

[6] The relations between divalent cations concentrations, Ca^{2+} and Mg^{2+}, for the continents are shown in Figure 1b. The Ca^{2+} and Mg^{2+} concentrations of major world drainages are consistent with the carbonate weathering intensities shown in Figure 1a. The Mg^{2+}/Ca^{2+} ratio for the carbonate-dominated watersheds indicates relative propor-

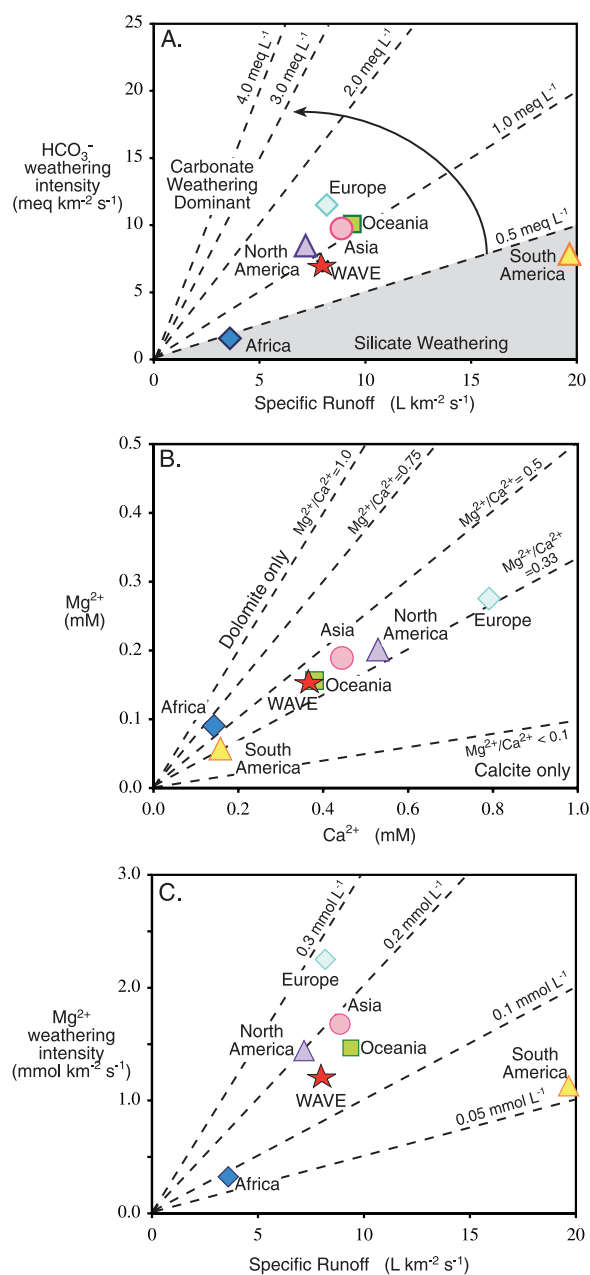**Figure 1.** (a) Carbonate weathering intensity (expressed as HCO$_3^-$ meq km^{-2} L^{-1}) versus specific runoff (L km^{-2} s^{-1}) for the continental landmasses (Europe, N. America, Oceania, Asia, Africa, and S. America). The world average value (WAVE) is calculated from the average world alkalinity concentration and land surface area. Dashed lines indicate the corresponding bicarbonate alkalinity concentration (meq L^{-1}) for the sample. Silicate weathering has HCO$_3^-$ values under 0.5 meq L^{-1}, while increasing values indicate increasing proportions of carbonate mineral weathering. Data from *Berner and Berner* [1996] and plot after *Amiotte Suchet and Probst* [1993]. (b) The average Mg^{2+} versus Ca^{2+} for the continental landmasses. The Mg^{2+}/Ca^{2+} ratio is represented with dashed lines, which indicate the contribution of dolomite and calcite in carbonate mineral weathering. Data from *Berner and Berner* [1996]. (c) Mg^{2+} weathering intensity (mmol km^{-2} L^{-1}) versus specific runoff for the continental landmasses. The dashed lines represent Mg^{2+} (mmol L^{-1}) concentration. Data from *Berner and Berner* [1996].
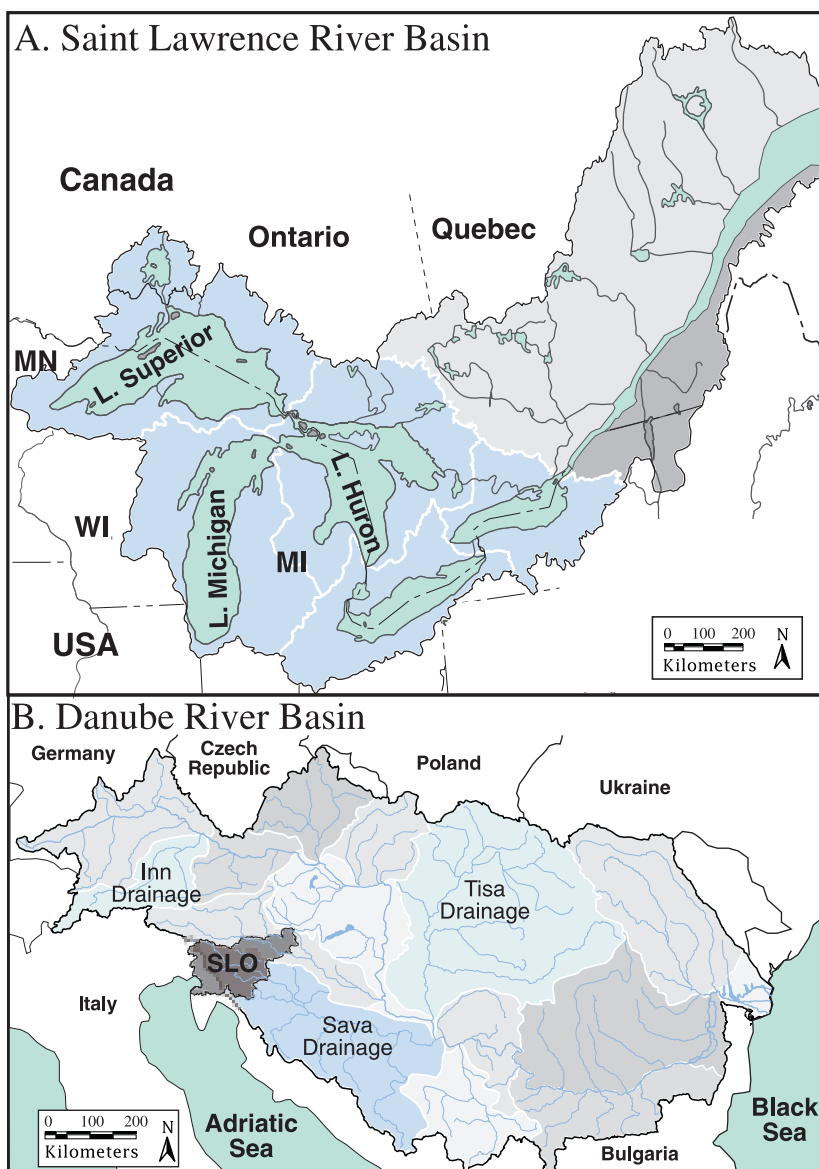
Figure 2. (a) The St. Lawrence River Basin is separated into two major regions, the Great Lakes subbasin (shaded blue) and watersheds draining Canadian Shield rocks from the north. (b) The Danube River Basin begins on the eastern side of the Alps in Germany. The major subbasins are indicated, including those discussed in the paper, the Sava, Inn, and Tisa drainages in blue. The country of Slovenia (SLO) is highlighted.

tions of calcite and/or dolomite weathering. Ratios much less than 0.1 indicate calcite only, ratios near 1.0 indicate dolomite dominance and ratios of 0.33 indicate equal calcite and dolomite weathering on a mole basis. The contribution of Mg^{2+} from high-Mg calcite would be minimal and account for ratios far less than 0.1 Mg^{2+}/Ca^{2+} [*Mackenzie et al.*, 1983]. In carbonate-bearing regions, the weathering of dolomite contributes the majority of Mg^{2+} in the watershed. Figure 1c shows the relationship between Mg^{2+} weathering intensity (mmol km^{-2} s^{-1}) and the specific runoff (L km^{-2} s^{-1}) of the world

landmasses. Europe clearly has the highest Mg^{2+} weathering intensity, nearly 2 times the world average intensity. Importantly, both the high HCO_3^- and Mg^{2+} concentrations implicate dolomite weathering as a major control on high weathering intensity. The dissolution of carbonates is ultimately limited by the inverse temperature dependence of the absolute solubility of calcite and dolomite, and the progressively greater relative solubility of dolomite at temperatures below 25°C [*Drever*, 1997; *Langmuir*, 1997]. When both dolomite and calcite are present within the weathering
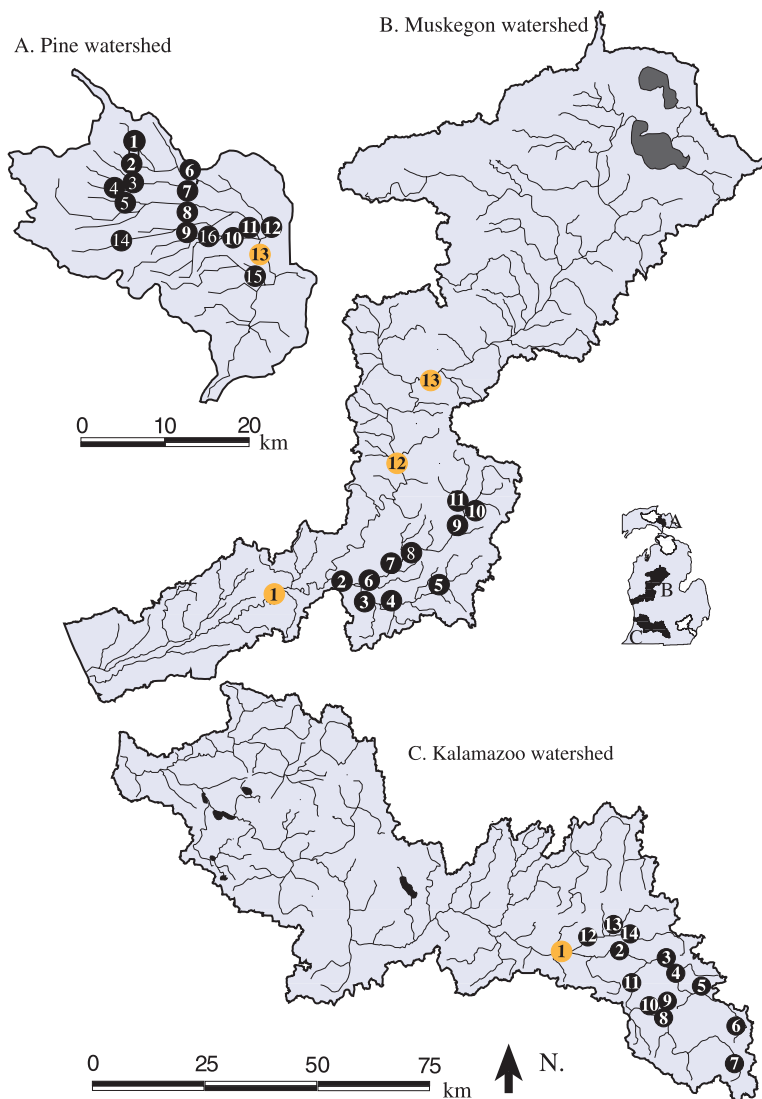
Figure 3. Drainage and samples location maps for (a) The Pine River, (b) Muskegon River, and (c) Kalamazoo River. Sample locations are indicated with a black dot and a sample number. The sample number + the watershed initials (e.g., 13P) can be found in Table 1. Locations located at an USGS/EIONET gauge are indicated with orange dots. The small Michigan map shows the relative locations of each watershed. (d) Slovenia with the subcatchments (Sava Dolinka, Sava Bohinjka, Sora, Ljubljanica, and Krka) of the Sava.

zone of a temperate watershed, the relative solubility creates the conditions for calcite to become supersaturated as dolomite continues to dissolve to equilibrium [*Palmer and Cherry*, 1984; *Szramek and Walter*, 2004; *Williams et al.*, 2007].

[7] The high carbonate weathering intensity in the Northern Hemisphere (NH) offers an opportunity to examine the controls on calcite and dolomite weathering in temperate carbonate-rich landscapes with close hydrogeochemical connections between streams and shallow groundwaters. This paper examines the geochemistry of headwater streams (Michigan and Slovenia) in two major humid-temperate drainage basins with large variations in discharge, the St. Lawrence (North America) and the Danube (Europe). Previous work on soil waters in the thick soil horizons encountered in Michigan watersheds indicates that solutes are gained rapidly once waters contact carbonate minerals in the CO_2-rich soil zones [*Jin*, 2007]. These waters migrate into unconfined aquifer systems, yielding shallow groundwaters that are typically near equilibrium with respect to dolomite and twice supersaturated for calcite at pCO_2 values much greater than the atmosphere [*Szramek and Walter*, 2004; *Szramek*, 2006; *Williams et al.*, 2007]. Groundwater discharge into streams leads to CO_2 degassing, pro-
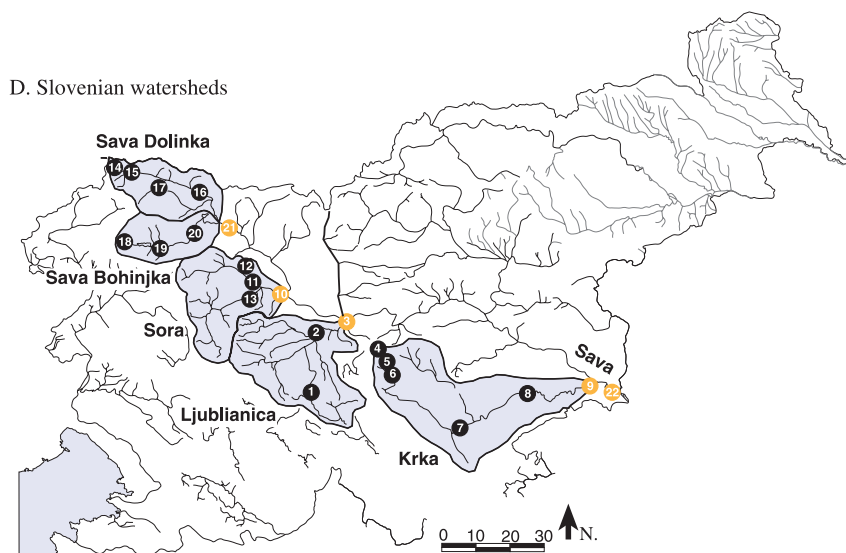
Figure 3. (continued)

ducing high degrees of calcite supersaturation, which can drive precipitation of calcium carbonate under low discharge conditions [*Szramek and Walter*, 2004; *Williams et al.*, 2007]. Our study focuses on stream geochemistry and discharge relationships in the different geologic and hydrologic settings of the Danube versus St. Lawrence drainage basins. These data are used to examine the controls on carbonate mineral saturation state, calcite versus dolomite reaction kinetics and geochemical fluxes from these different NH carbonate landscapes.

2. Study Watersheds

[8] Calcite and dolomite weathering intensities were studied in the carbonate-rich, headwater regions of the St. Lawrence and the Danube River basins. Specifically, streams draining the state of Michigan (USA) within the St. Lawrence drainage basin and upstream reaches of the Sava River watershed in Slovenia (Central Europe) were investigated in detail to better control for lithology, land use, climate, population density and pollution sources (see Figures 2a and 2b). The St. Lawrence River basin drains approximately 913,700 km^2 (at Montreal, not including waters draining to the marine influenced section) with a mean annual discharge of 8.4×10^6 L s^{-1} [*Hélie et al.*, 2002; *Rondeau et al.*, 2005]. The Danube River basin drains 800,000 km^2 with a mean annual discharge of 6.4×10^6 L s^{-1} [*Berner and Berner*, 1996]. The basins span a similar latitude range, between 35° and 48°N.

[9] Previous geochemical work on the carbonate groundwaters and surface waters from three Michigan watersheds (Tahquamenon, Cheboygan, and Huron) [*Szramek and Walter*, 2004; *Szramek et al.*, 2004; *Szramek*, 2006; *Williams et al.*, 2007] has established the close hydrogeochemical link between groundwater and surface water in these regions. This study extends the Michigan database to include discharge and chemical relations on three new watersheds. Here we integrate chemical and discharge measurements from the Michigan and Slovenian watersheds to examine the links between chemical fluxes, geology, landscapes and climate.

2.1. Physical Setting

[10] The St. Lawrence River is one of N. America's major river systems and drains the Great Lakes (Figure 2a). The state of Michigan is a peninsula located within the Great Lakes watershed a tributary to the St. Lawrence (Figures 3a, 3b, and 3c). Advance and retreat of continental ice sheets, most recently during the Pleistocene, rerouted surface water drainages in the Great Lakes region and significantly impacted the landscape. Michigan's topography is primarily controlled by the thickness of glacial deposits and elevation of glacial landforms (Figure 4b). The total topographic relief is less than 450 m; the shores of the Great Lakes are at 174 m, and the highest topographic elevation is in Michigan's Upper Peninsula (603 m).

[11] The Michigan watersheds sampled in this study are shown in Figures 3a, 3b, and 3c. The
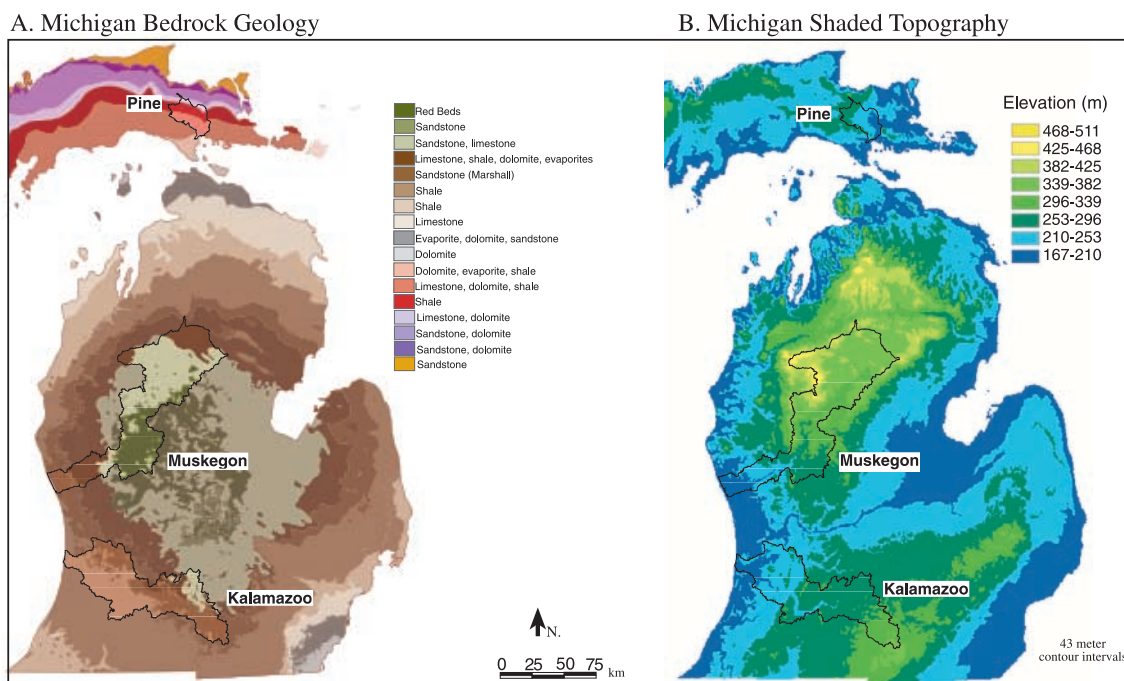
A. Michigan Bedrock Geology

B. Michigan Shaded Topography

Figure 4. (a) Bedrock geology for the eastern Upper Peninsula and the Lower Peninsula of Michigan. The ages of the units are Jurassic/Pennsylvanian (greens), Mississippian (browns), Devonian (grays), Silurian (pinks), and Ordovician (purples). The Pleistocene glacial drift which mantles the bedrock is a mixture of sediments from the underlying Michigan Basin and crystalline Canadian Shield rocks transported south with the ice sheets. (b) Topography of Michigan. Yellow shading represents the highest elevations, green represents the middle elevations, and blue represents the lowest elevations. The relief in Michigan is less than 500 meters.

Pine River (Figure 3a) flows into Lake Huron, while the Muskegon (Figure 3b) and the Kalamazoo (Figure 3c) Rivers flow into Lake Michigan. The Michigan watersheds were broken down into subcatchments on the basis of the overall chemical characteristics of the watersheds. The Pine watershed (Figure 3a) was sampled above the single real time U.S. Geological Survey (USGS) gauge established in this watershed (04127918). The Little Muskegon subcatchment was sampled for the Muskegon watershed (Figure 3b). USGS gauges were sampled at the mouth of the Little Muskegon River (04121944) and on the main Muskegon before (04121650) and after (04122000) the Little Muskegon joins. The North and South Branch of the Kalamazoo River were sampled in the Kalamazoo watershed (Figure 3c). Two USGS (04103010 and 04103500) gauges were sampled where these two branches of the Kalamazoo River join. Surface water geochemical and discharge data obtained from the USGS National Water Information System (NWIS, 2001; available at http://waterdata.usgs.gov/nwis/) and *Williams et al.* [2007] for the Tahquamenon and Cheboygan rivers and from NWIS (2001) and *Szramek and Walter* [2004] on the Huron River were also added for a statewide

comparison. Taken together, these six watersheds cover the range of Northern (Tahquamenon and Pine), Middle (Cheboygan and Muskegon) and Southern (Kalamazoo and Huron) Michigan drainages. The mean annual temperature (MAT) varies from a low of 5.6°C in the Tahquamenon and Pine watersheds, to about 7°C for the Cheboygan and Muskegon watersheds, to a high of about 10°C for the southernmost Kalamazoo and Huron watersheds. Michigan's mean annual precipitation (MAP) patterns are shown in Figure 6a [*Spatial Climate Analysis Service*, 2000]. Regional variations in annual precipitation values for Michigan are relatively modest (see Figure 6a) and most of Michigan receives close to 825 mm/year.

[12] The Danube River basin is the second largest drainage basin in Europe. The Danube watershed drains diverse terrain, including the Alps and the Pannonoian Basin, before discharging into the Black Sea (Figure 2b). The Sava River (Figure 3d) is one of the major tributaries of the Danube, accounting for 15% of the drainage area, but contributing 25% of the discharge. The Sava River begins in the Julian Alps, flows through alpine, alpine-dinaric karst, dinaric and hill and valley
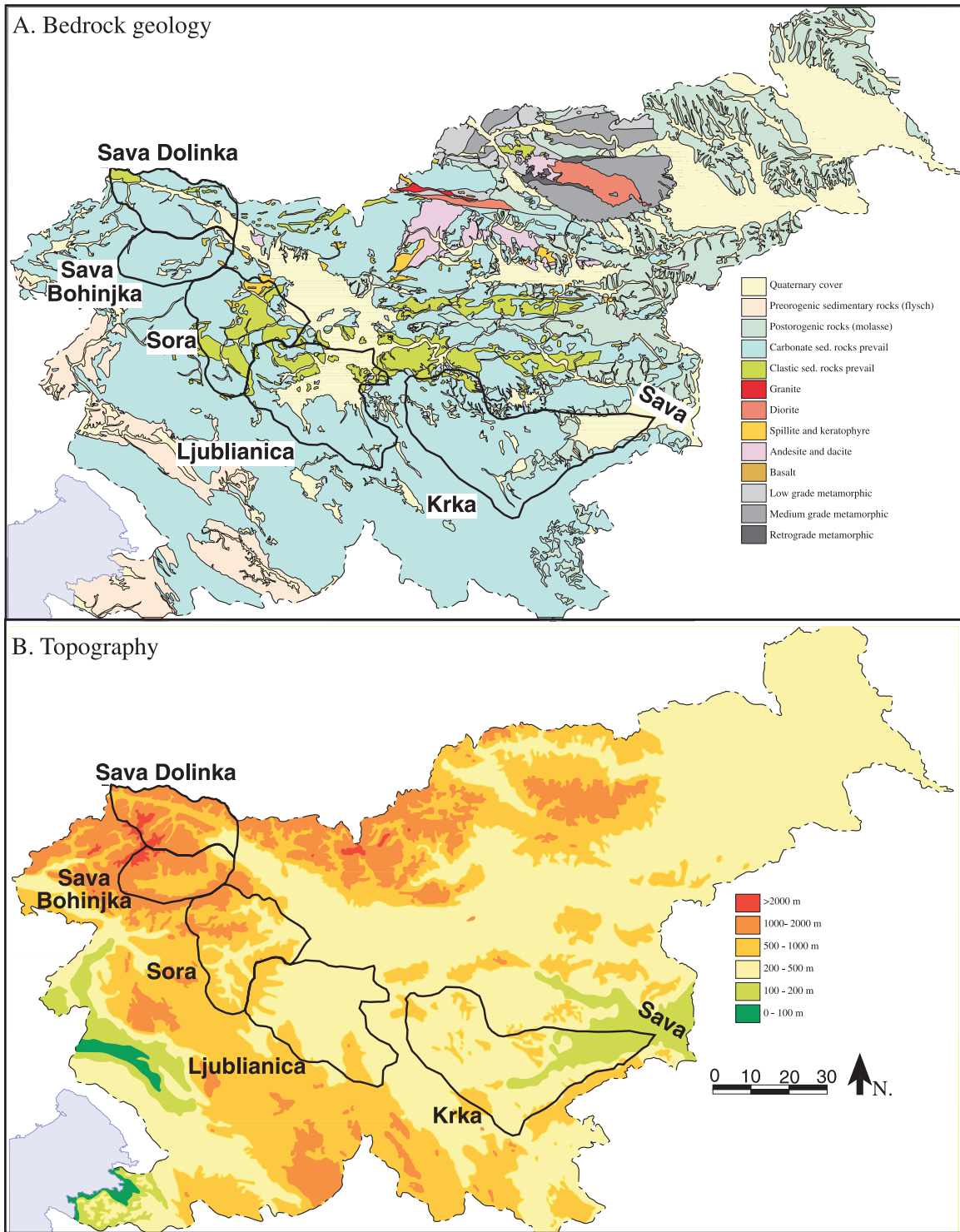
Figure 5. (a) Bedrock geology in Slovenia is dominated by carbonate (limestone and dolomite) and siliclastic lithologies. The limestones are mainly Cretaceous to Triassic, the dolomites are mainly Triassic, and the siliclastics are mainly Permian to Carboniferous in age. (b) Topography of Slovenia. The relief in Slovenia is greater than 2000 meters. The elevation ranges from the highest in red to orange to yellow to green at the lowest elevations.
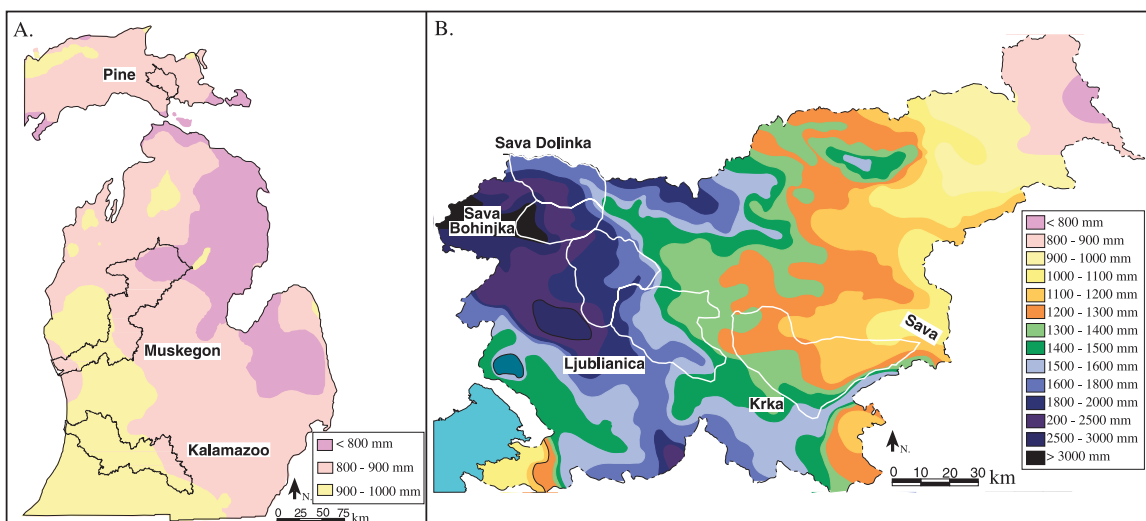
Figure 6. (a) Mean annual precipitation for Michigan [*Spatial Climate Analysis Service*, 2000]. (b) Mean annual precipitation for Slovenia (EIONET, 2003). The mean annual precipitation within the Sava watershed is higher than the any Michigan watershed.

terrain before leaving Slovenia. The dinaric region is a highly karstified region with sinking streams, sink holes, caves and springs. In this paper, regions in the southern portion of Slovenia with karst phenomenon are called dinaric karst. The topographic relief in Slovenia is 2864 m, with sea level (0 m) being the lowest elevation and Mt. Triglav (2864 m) in the Julian Alps, the highest elevation (Figure 5b). Pleistocene glaciers were restricted to the alpine regions, and today only small mountain glaciers remain.

[13] The Sava River watershed in Slovenia was separated into five subcatchments categorized by landscape type. The carbonate-bearing subcatchments are categorized into those draining alpine landscapes (Sava Bohinjka, Sava Dolinka, Sora) and those draining dinaric karst landscapes (Ljubljanica, and Krka). The mouth of the Sava River as it exits Slovenia was sampled to evaluate the relative importance of each region to the total dissolved load. Discharge gauges operated by The Environmental Agency of Slovenia are located at the mouth of each tributary before they flow into the main Sava and on the Sava at the Croatian border. Sampling locations of the Sava River and its major tributaries are shown in Figure 3d. The Sava Dolinka and Sava Bohinjka are alpine watersheds and characterized by steep topographic relief (400 to 2864 m) and thin soils (0–50 cm). The Sora River can be categorized as both alpine and dinaric karst. The majority of samples from the Sora River are dominated by runoff from alpine regions and are chemically similar to the alpine

watersheds. Only the mouth of the Sora is influenced by dinaric karst and is chemically similar to the dinaric karst rivers. For the purposes of this paper, the Sora River will be classified as alpine. The Ljubiljanica and Krka are dinaric karst watersheds characterized by low relief (<600 m), thick soils (>50 cm) and extensive underground solution of limestone/dolomite. Mean annual temperature in Slovenia is similar to Michigan, varying from about 6°C in the north to about 10.5°C in the south. Figure 6b shows Slovenia's average annual precipitation patterns (European Environment Information and Observation Network (EIONET), EIONET in Slovenia, 2003, http://eionet-en.arso.gov.si). Slovenia's maximum precipitation is 3,000 mm/year in the Julian Alps (northwest). The precipitation reaches a minimum value of less than 800 mm/year in the northeastern region of Slovenia, outside the Sava River drainage. This range in precipitation is nearly 4 times the value observed in Michigan.

2.2. Geologic Settings

[14] Michigan is centered on an underlying cratonic sag basin, the Michigan Basin, which is primarily composed of Paleozoic-age carbonates, shales, and sandstones (Figure 4a). The Pine watershed is underlain by Ordovician shales in the north and mainly Silurian carbonates in the southern portion of the watershed. The Muskegon watershed overlies Mississippian carbonates and shales and Pennsylvanian sandstones and the Little Muskegon catchment (see Figure 3b) is mainly underlain by

Jurassic Red Beds. The Kalamazoo watershed is underlain primarily by Mississippian shale and the Mississippian sulfide-rich Marshall sandstone. Advance and retreat of Pleistocene ice sheets mechanically ground up the bedrock materials and deposited glacial sediments of varying thicknesses (up to 1 km), which mantle the state of Michigan. The resulting Quaternary deposits, composed mainly of unconsolidated glacial tills and sorted outwash sands and gravels [*Dorr and Eschman*, 1970], host most of the shallow groundwater resources in Michigan [*Rheaume*, 1991].

[15] Slovenia lies at a junction between the Southern European Alps and the Adriatic-Dinaridic carbonate platform, which primarily are composed of Mesozoic carbonates (limestone and dolomite) and siliclastic sediments (e.g., conglomerates and shales), exposed near the surface, especially in areas with high topographic relief (Figure 5a). This study focuses on tributaries of the Sava River draining mainly carbonate bedrock. The Sava Dolinka watershed is mainly composed of Triassic (limestones, dolomite, and shales), Permo – Carbonian (shales, sandstones, conglomerate, and limestones) and Permian (limestones) rocks. The Sava Bohinjka watershed is mainly composed of Triassic and Jurassic limestones with some Oligocene sediment composed of sandstones, conglomerates and limestones. The Sora watershed is composed of Jurassic and Cretaceous black shales and limestones and Permo – Carbonian shales, limestones, silica sandstones and pyroclatics rocks, and Triassic dolomites. The Ljubljanica watershed is composed of Pleistocene lake and swamp carbonate sediments of Holocene age (approximately 116 m thick), Permo – Carbonian shales and sandstones. The Krka watershed is mainly composed of Triassic and Jurassic dolomite and limestone. Quaternary deposits within the Sava River basin are limited and primarily fill the river valleys.

3. Methods

3.1. Sampling Protocols

[16] River sampling locations in both Michigan and Slovenia were selected on the basis of relationships to established gauging sites, tributary streams, fluvial-lake systems, with respect to sampling ease and upstream of large roads and developments to limit potential contamination from local runoff. Streams from the three Michigan watersheds were sampled between 2002–2004 with efforts made to cover the range of seasonal vari-

ability in discharge regime. The Pine watershed was sampled eight times, the Muskegon watershed was sampled six times, and the Kalamazoo watershed was sampled five times between June 2002 and July 2004. In Slovenia, sampling trips for the Sava watershed were conducted five times; during August 2003, September/October 2003, April/May 2004, September 2004, and January 2005, the range of discharge regimes established for this drainage basin by the [*Hrvatin*, 1998]. Sampling locations are shown in Figure 3.

3.2. Field Measurements

[17] Stream discharge was one of the primary parameters characterized at the sample sites. USGS and The Environmental Agency of Slovenia databases were used to determine discharge at time of sampling. In Michigan, where relatively fewer gauging sites were available detailed discharge measurements were taken using an A Price flowmeter and an AutoCalc 6000 following the USGS method of 0.6 depth [*Carter and Davidian*, 1968].

[18] Temperature, dissolved oxygen (DO) and pH of each sample were determined in the field. Dissolved oxygen and temperature was measured directly in the stream, using an YSI model 58 meter and an YSI 5239 DO probe with high sensitivity membranes. Dissolved oxygen measurements were precise to $\pm 5\%$ O_2 saturation. DO is not reported because it used in the field to provide a rapid geochemical reference point.

[19] A Corning 315 high sensitivity pH meter with an Orion Ross combination pH electrode, calibrated with low ionic strength buffer solutions of 4.1 and 6.97 (corrected for temperature), were used to measure pH in the field as close to the water temperature as possible. The pH of a sample can rapidly change due to degassing and warming; therefore the samples were placed in a large volume airtight container and measured at least twice to ascertain electrode stability. The reproducibility of field pH determinations is ± 0.02 pH units.

[20] Sample aliquots for later chemical analysis in the laboratory were filtered in the field through a 0.45 μm nylon filter into their respective bottles and kept cold until analyzed. Acid washed HDPE bottles were used to collect cation aliquots and were preserved in the field with HNO_3. Double deionized (DD) water rinsed HDPE bottles were used to collect alkalinity and anion samples. HCl washed glass serum bottles capped by Teflon liners were used to store samples for dissolved inorganic

carbon (DIC) analysis. These were poisoned with $CuCl_2$ in the field to inhibit biological activity and were filled to the top with no headspace before capping.

3.3. Laboratory Analysis

[21] Total bicarbonate (HCO_3^-) alkalinity was measured by electrometric endpoint titration using a Radiometer TitraLab automated titration system with a TIM900 titration manager and ABU91 or ABU93 autoburette. Due to the given measurement precision (±0.01 meq/kg), the pH range of the samples, and the ionic composition of the solutions, HCO_3^- concentrations (mmol L^{-1}) are essentially equivalent to total alkalinity (meq L^{-1}). Samples gathered for DIC were analyzed on a UIC Coulometrics CO_2 coulometer with a precision of ±2%. The measured DIC and titration alkalinity measurements of the samples agreed to within the precision of the two measurements, thereby supporting this assumption.

[22] Major element chemistry was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) for cations and ion chromatography (IC) for anions. Analysis of cations (Ca, Mg, Na, K, Sr, Fe, and Si) was conducted by ICP-OES on three different instruments. Samples collected prior to 2002 were analyzed on a Leeman Labs, Inc. Plasma-Spec ICP-OES 2.5 with a precision of ±2% for major and ±5% for minor elements. Samples collected during 2002 were analyzed on a Perkin Elmer Optima 3300 DV with an analytical precision of ±2%. Samples analyzed from 2003 and beyond were processed on a Jobin Yvon Horiba Ultima 2C with an analytical precision of ±2%. Anions (Cl^-, SO_4^{2-}, and NO_3^-) were analyzed on a Dionex 4000I series ion chromatograph (IC) with an AS14 column with a precision of ±3% prior to 2002. Anions were analyzed on a Dionex ICS-2500 IC after 2003 with an analytical precision of ±2%.

[23] Charge balance calculations were performed on water chemistry data to check for internal analytical consistency, using the relationship

$$C.B. = \frac{\sum c_{cations} - \sum c_{anions}}{\sum c_{cations} + \sum c_{anions}} \times 100$$

where c is concentration (charge equivalents L^{-1}). The majority of the data were within ±5%, except for dilute samples with total dissolved solids under 1 mmol L^{-1}.

3.4. Thermodynamic Modeling and Aqueous Speciation

[24] Aqueous speciation and mineral saturation state modeling was conducted on water chemistry data using the USGS program Solminequation 88 [*Kharaka et al.*, 1988]. Major elements (Ca^{2+}, Mg^{2+}, Na^+, K^+, Sr^{2+}, Si, Cl^-, SO_4^{2-}, and NO_3^-), alkalinity (HCO_3^-), pH and temperature were input into the program for calculation. Calculated values for pCO$_2$ and IAP/K$_{calcite}$ (Ωc) were obtained from the Solminequation 88 output. The log K$_{sp}$ for calcite at 25°C from Solminequation 88 is −8.48.

[25] The uncertainty in the pCO$_2$ values provided by Solminequation 88 is related to the precision of the pH and alkalinity. Given a precision of ±0.02 pH units and the uncertainty in the titration alkalinity, the uncertainty in the pCO$_2$ is about 10%. The error in the IAP/K$_{calcite}$ is within 25% and is determined by the precision in the measuring of carbonate parameters (alkalinity, DIC, pH, temperature), K$_{sp}$, and the errors in cation measurements.

4. Results

[26] Geochemical data for the Michigan (Pine, Muskegon and Kalamazoo) and Slovenia (Sava Dolinka, Sava Bohinjka, Sora Ljubiljanica and Krka) surface waters, collected by the experimental and analytical geochemistry lab (EAGL) at the University of Michigan, are presented in Table 1. Discharge data represented as specific runoff for the Michigan and Slovenian watersheds are also shown in Table 1. Historical geochemical and discharge data published online by the USGS (NWIS, 2001) on the Tahquamenon, Cheboygan, Muskegon, Kalamazoo, and Huron watersheds are presented as auxiliary material[1] in Table S1. Geochemical and discharge data published by The Environmental Agency of Slovenia on the EIONET server (EIONET, 2003, http://eionet-en.arso.gov.si) for alpine (Sava at Otoce), dinaric karst (Krka and Ljubiljanica), and the Sava River at the Slovenia Croatia boarder are presented as auxiliary material in Table S2.

4.1. Carbonate Weathering Contributions to Stream Chemistry

[27] The geochemistry of surface waters in Michigan and Slovenia are dominated by carbonate mineral dissolution, with the majority of samples

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Table 1 (Representative Sample). Michigan and Slovenia Geochemistry and Discharge (EAGL) [The full Table 1 is available in the HTML version of this article at http://www.g-cubed.org]

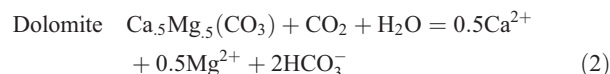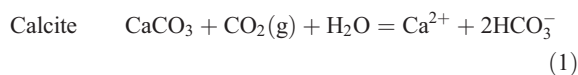| Sample ID	Sample Name	Date	Lat., deg N	Long., deg W	Drainage Area, km²	T, °C	pH	Alk$_t$ HCO$_3^-$, meq/l	DIC, meq/l	Log pCO$_2$, bars	Calcite Log, IAP/K
			Michigan Watersheds								
Pine River watershed											
P-1	Sullivan C @3132	6/21/02	46.3298	84.8202		8.3	7.91	0.389	0.33	−3.12	−1.84
P-1	Sullivan C @3132	8/8/02	46.3298	84.8202		8.3	7.48	0.398	0.40	−3.19	0.13
P-1	Sullivan C @3132	10/19/02	46.3298	84.8202		7	7.55	0.404	0.45	−3.67	−1.32
P-1	Sullivan C @3132	4/26/03	46.3298	84.8202		6.3	8.06	0.430	0.45		
P-1	Sullivan C @3132	7/16/03	46.3298	84.8202		8.4	7.70	0.409	0.57		
P-1	Sullivan C @3132	9/13/03	46.3298	84.8202		7.9	7.68	0.427	0.43	−3.29	−1.65
P-1	Sullivan C @3132	11/9/03	46.3298	84.8202		6	7.67	0.420	0.48	−3.29	−1.71
P-1	Sullivan C @3132	7/1/04	46.3298	84.8202		7.5	7.90	0.413			
P-2	S. Sullivan @3132	6/21/02	46.303	84.84		18.4	6.06	0.258	0.37		
P-2	S. Sullivan @3132	8/8/02	46.303	84.84		17.2	5.84	0.117	0.42		
P-2	S. Sullivan @3132	4/26/03	46.303	84.84		8.2	6.12	0.045	0.22		
P-3	Sweiger C @3132	6/21/02	46.2899	84.8515		12.1	7.43	0.399	0.37	−3.07	−1.82
P-3	Sweiger C @3132	8/8/02	46.2899	84.8515		10.1	7.09	0.406	0.49	−2.72	−2.22
P-3	Sweiger C @3132	10/19/02	46.2899	84.8515		6.2	7.28	0.404	0.52	−2.92	−2.06
P-3	Sweiger C @3132	4/26/03	46.2899	84.8515		5.6	7.02	0.268	0.38	−2.83	−2.68
P-3	Sweiger C @3132	7/16/03	46.2899	84.8515		14.3	7.31	0.361	0.36		
P-3	Sweiger C @3132	9/13/03	46.2899	84.8515		11.4	7.54	0.565	0.60	−3.03	−1.52
P-3	Sweiger C @3132	11/9/03	46.2899	84.8515		0.5	7.35	0.511	0.60	−2.88	−1.94
P-3	Sweiger C @3132	7/1/04	46.2899	84.8515		10.8	7.35	0.376			
P-4	Black C @3132	6/21/02	46.2783	84.8735		13.1	7.08	0.319	0.43		
P-4	Black C @3132	8/8/02	46.2783	84.8735		11.7	6.92	0.351	0.43		
P-4	Black C @3132	10/19/02	46.2783	84.8735		5.9	6.80	0.247	0.32	−2.65	−2.75
P-4	Black C @3132	4/26/03	46.2783	84.8735		5	6.62	0.155	0.26		
P-4	Black C @3132	7/16/03	46.2783	84.8735		14.1	6.91	0.297	0.32		
P-4	Black C @3132	9/13/03	46.2783	84.8735		10.4	7.47	0.669	0.79	−2.89	−1.48
P-4	Black C @3132	11/9/03	46.2783	84.8735		1.5	7.08	0.459	0.50	−2.66	−2.29
P-4	Black C @3132	7/1/04	46.2783	84.8735		12.7	6.91	0.307			
P-5	Pine R @3139	6/21/02	46.2322	84.8962		14.2	7.67	1.010	0.97	−2.91	−0.86
P-5	Pine R @3139	8/8/02	46.2322	84.8962		11.9	7.64	1.123	1.14	−2.84	−0.82
P-5	Pine R @3139	10/19/02	46.2322	84.8962		6	7.48	0.974	1.06	−2.74	−1.18
P-5	Pine R @3139	4/26/03	46.2322	84.8962		7.5	6.42	0.365	0.45		
P-5	Pine R @3139	7/16/03	46.2322	84.8962		14.4	7.70	1.219	1.28		
P-5	Pine R @3139	9/13/03	46.2322	84.8962		13.1	7.68	1.316	1.37		
P-5	Pine R @3139	11/9/03	46.2322	84.8962		0.2	7.61	1.141	1.14	−2.81	−0.71
P-5	Pine R @3139	7/1/04	46.2322	84.8962		13.2	7.52	1.086			
P-6	N. Pine R @3131	6/21/02	46.2757	84.7177	81.0	17.1	7.42	0.329	0.68		
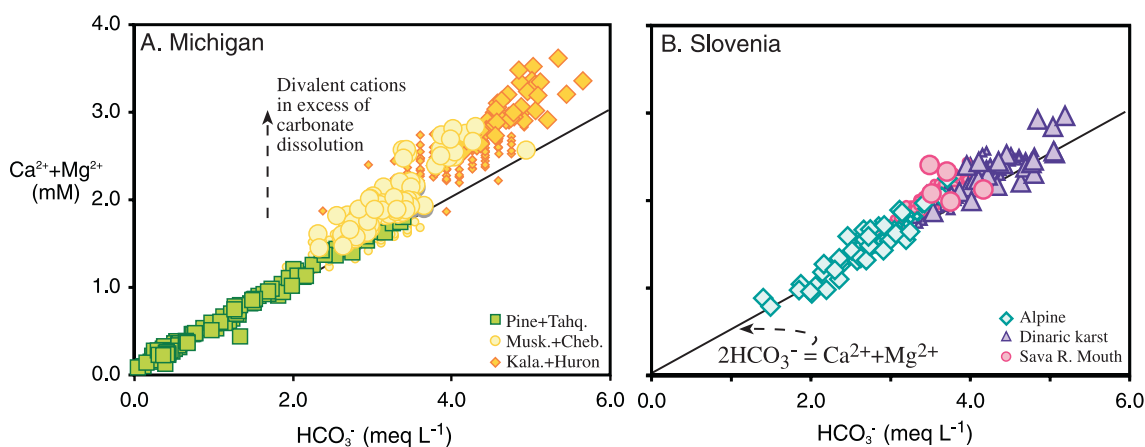
Figure 7. The dissolution of carbonate minerals (calcite and dolomite) contributes 2 moles of HCO_3^- for every 1 mole of $Ca^{2+} + Mg^{2+}$. River waters in (a) Michigan and (b) Slovenia plot along the 2:1 line of $HCO_3^- : Ca^{2+} + Mg^{2+}$, indicating that the major element chemistry is controlled by the dissolution of carbonate minerals. The symbols are in two sizes; the larger symbols represent data gathered in this study, and the smaller symbols represent USGS (NWIS, 2001) and EIONET (2003) data.

having a 2:1 mole ratio of HCO_3^- to $Ca^{2+} + Mg^{2+}$ (Figure 7) following the reactions

Calcite
$$CaCO_3 + CO_2(g) + H_2O = Ca^{2+} + 2HCO_3^- \quad (1)$$

Dolomite
$$Ca_{.5}Mg_{.5}(CO_3) + CO_2 + H_2O = 0.5Ca^{2+} + 0.5Mg^{2+} + 2HCO_3^- \quad (2)$$

The half reaction for dolomite is used in order to put dolomite and calcite on an equal stoichiometric basis for the HCO_3^- produced during dissolution.

[28] In Michigan, mineral weathering in the soil zones and shallow aquifers in the upper glacial drift deposits contributes Ca^{2+}, Mg^{2+}, and HCO_3^- to surface waters (Figure 7a) due to the close connections between groundwaters and streams. The Pine River waters are the most dilute of the Michigan watersheds; the HCO_3^- values for the Pine range from less than 0.2 to 3.5 meq L^{-1}, and $Ca^{2+} + Mg^{2+}$ values range from 0.1 to 1.3 mM. The majority of the Muskegon and Kalamazoo watershed samples have HCO_3^- values between 3.5 to 5.0 meq L^{-1} and 3.8 to 5.7 meq L^{-1}, respectively. However, some of the samples within these two watersheds have $Ca^{2+} + Mg^{2+}$ concentrations greater than the ideal stoichiometry. The divalent cation excess (between 0.2 to 0.5 mM for the Muskegon and 0.2 to 1.0 mM for the Kalamazoo) is mainly charge balanced by chloride and sulfate. The geochemical relationships within the study watersheds follow very closely the previously studied Michi-

gan watersheds, which are proximate in location. The northern Tahquamenon waters are similar to the adjacent Pine River, the Cheboygan waters are similar to those of the Muskegon, and the southernmost Huron River waters are very similar to those of the Kalamazoo, both in terms of carbonate geochemistry and of anthropogenic salt inputs [*Szramek and Walter*, 2004; *Williams et al.*, 2007; NWIS, 2001].

[29] In Slovenia, the chemistry of the Sava River waters falls into two distinct groups that are close to the ideal stoichiometry of carbonate dissolution (Figure 7b). The watersheds draining predominately alpine areas (S. Dolinka, S. Bohinjka, and Sora) have compositions between 1.2 and 3.2 meq L^{-1} for HCO_3^-, and 0.6 and 1.6 mM for $Ca^{2+} + Mg^{2+}$. The two dinaric karst watersheds (Krka and Ljubljanica), the mouth of the Sora and the Sava River at the Slovenia/Croatia border all have higher ionic loads, with HCO_3^- concentrations ranging from 3.5 to 5.5 meq L^{-1} and $Ca^{2+} + Mg^{2+}$ concentrations between 2.0 and 2.8 mM, both about twice the concentration observed in alpine drainages.

[30] Differences in the HCO_3^- concentrations in carbonate-bearing watersheds are related to mean annual temperature (MAT), the depth of the weathering zone (i.e., soil thickness), the surface area of carbonate minerals available to weather, and residence time of water within the system. Weathering rates are known to decrease in thinner soils due to the shorter residence time of shallow groundwaters in contact with minerals, and decreased mineral surface area in the thinner soils [e.g., *Drever and*
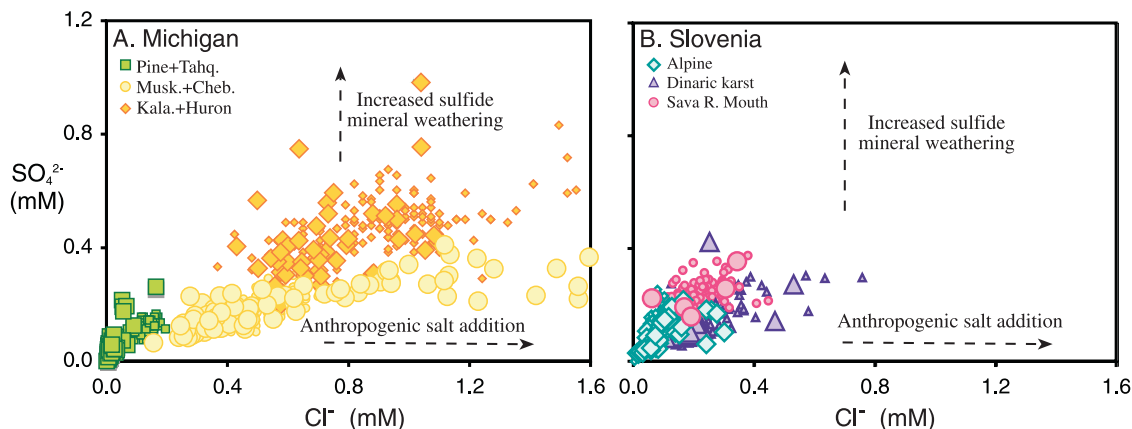
Figure 8. A plot of Cl^- versus SO_4^{2-} for (a) Michigan and (b) Slovenia rivers helps to determine anion input from anthropogenic pollution and natural sources (e.g., sulfide mineral weathering). The Pine and the Slovenian watersheds have minimal anthropogenic input, while the other Michigan watersheds indicate varying degrees of anthropogenic input. For explanation of symbols, see Figure 7.

Zobrist, 1992]. MAT influences growing season, organic carbon turnover, organic-inorganic transformation rates and the CO_2 concentration of the soil zone [*Reardon et al.*, 1979]. Root respiration and microbial activity elevate soil CO_2, relative to the atmosphere [*Brady and Weil*, 1996]. The increase in soil CO_2 is directly linked to an increase in carbonate mineral solubility [e.g., *Freeze and Cherry*, 1979]. In Michigan, streams in the Pine watershed are dilute primarily due to a colder MAT, thinner soil, and a lower percentage of carbonate minerals in the drift than in the more carbonate rich Muskegon and Kalamazoo watersheds. Similarly, in Slovenia, there are large differences in the weathering environments for streams draining the alpine versus dinaric karst terrain. The alpine regions have very high relief (Figure 5b), which creates unstable surfaces for soil development, with the depth to bedrock less than 40 cm (European Soil Database-Soil Map Internet Server, 2005, http://eusoils.jrc.it). The lower MAT in the higher elevations reduces the growing season and the thinner soils reduce the vegetative cover relative to the lower relief dinaric karst regions which also have higher MAT and denser forest vegetation.

4.2. Atmospheric and Anthropogenic Contributions to Stream Geochemistry

[31] Atmospheric input in Michigan, corrected for the amount of evapoconcentration provides approximately 100 μeq L^{-1} of ionic charge (Ca^{2+}, Mg^{2+}, Na^+, Cl^-, SO_4^{2-}) [*National Atmospheric Deposition Program*, 2005]. Atmospheric input

of major ions to stream waters is relatively insignificant for the carbonate-rich watersheds, contributing less than 2% of the overall ionic charge. Precipitation input is significant only for the dilute streams of the northernmost watersheds, contributing up to 15% of the total ionic charge. Similarly, Slovenian streams have ion contribution from atmospheric input accounting for less than 5% of the ionic charge.

[32] Dissolution of anthropogenic salts (NaCl, $CaCl_2$, KCl), however, accounts for an appreciable amount of dissolved ions in the Michigan streams, especially as population densely increases to the south. Typically these salts are added to the roadways as deicers and to control dust [*Szramek and Walter*, 2004]. The Muskegon and Kalamazoo drainages have Cl^- concentrations up to 1.6 mM and Na^+ up to1.2 mM. The Pine watershed is more dilute, with Cl^- and Na^+ values less than 0.2 mM. The Pine watershed has few inhabitants, since the majority of the watershed is in the protected US Hiawatha National Forest. Cl^- is in excess of Na^+ for the majority of samples in the Muskegon and Kalamazoo watersheds, indicating that NaCl and $CaCl_2$ are being added to the watersheds (see Table 1). In the Huron watershed the Ca^{2+} from $CaCl_2$ was found to mask the natural process of carbonate precipitation occurring within the watershed [*Szramek and Walter*, 2004]. Likewise, *Williams et al.* [2007] noted that the elevated Na^+ from this kind of salt pollution overwhelmed the Na^+ signal from silicate weathering within watersheds draining glacial sediments.

[33] In contrast, the Slovenian watersheds are relatively dilute in terms of Cl^- and Na^+ and are not strongly influenced by anthropogenic salt pollution. Na^+ and Cl^- concentrations are below 0.6 mM for all Slovenian watersheds. Precipitation contributes roughly 50 μM of Na^+ and Cl^-, in the more dilute samples, those less than 0.18 mM, resulting in at least a 30% contribution to the total Na^+ and Cl^- of the sample. The amount not accounted from precipitation input is likely from human waste or albite mineral weathering.

[34] Sulfate (SO_4^{2-}) is derived from natural mineral weathering of gypsum or sulfide minerals, such as pyrite. Anthropogenic sulfate is also typically added to watersheds by application of sulfate fertilizers and coal burning power plants. The SO_4^{2-} concentrations in Michigan and Slovenia waters are similar for all watersheds, except the Kalamazoo (Table 1). The Kalamazoo watershed has 2 to 3 times higher SO_4^{2-} values than all the watersheds studied. In a plot of SO_4^{2-} versus Cl^- (Figure 8a), the Muskegon and Kalamazoo watersheds have variable SO_4^{2-} concentrations, from 0.05 to 0.4 mM for the Muskegon and from 0.3 to 1.0 mM for the Kalamazoo. Despite the difference in SO_4^{2-}, Cl^- values remain constant indicating that SO_4^{2-} has different sources than Cl^-. The Pine watershed is dilute in terms of both SO_4^{2-} and Cl^-, with the majority of samples having concentrations below 0.2 mM for both anions. The Kalamazoo watershed has elevated SO_4^{2-} values likely from weathering sulfides contained in the Marshall Formation, a Mississippian age marginal marine sandstone that subcrops very near the surface.

[35] SO_4^{2-} concentrations in the Slovenian watersheds are much lower than Michigan, with over 90% of the samples under 0.4 mM (Table S1). Figure 8b shows the SO_4^{2-} and Cl^- relationship for the Slovenian watersheds. The alpine regions have SO_4^{2-} and Cl^- both less than 0.3 mM. The dinaric karst and Sava mouth have SO_4^{2-} and Cl^- values typically less than 0.5 mM. The downstream samples show evidence of being influenced by anthropogenic pollution, but to a smaller degree than seen in the Michigan watersheds.

4.3. Dolomite Versus Calcite Dissolution and Mass Transport in Streams

[36] Riverine mass transport of dissolved inorganic carbon is influenced by saturation state of carbonate minerals and riverine discharge. The solubility of dolomite increases relative to that of calcite at temperatures below 25°C [*Drever*, 1997; *Langmuir*,

1997]. Due to the common ion effect, the dissolution of both dolomite and calcite contribute HCO_3^- and Ca^{2+} needed to increase the saturation state of calcite (log IAP/K_{cal}). Groundwaters within three Michigan watersheds at temperatures between 6 to 10°C are observed to be at saturation with dolomite and as a result calcite is approximately 2 times saturated due to the common ion effect and enhanced solubility of dolomite [*Szramek and Walter*, 2004; *Williams et al.*, 2007]. Groundwaters degas after they discharge increasing pH, as CO_2 is lost, thereby increasing the saturation state of carbonate minerals [e.g., *Herman and Lorah*, 1987; *Szramek and Walter*, 2004; *Williams et al.*, 2007].

[37] pCO_2 versus calcite saturation state for Michigan and Slovenian streams are presented in Figures 9a and 9b. Calcite saturation ranges from below saturation to 30 times saturation and pCO_2 ranges from $10^{-1.6}$ to about $10^{-3.5}$. All rivers display increasing calcite saturation as pCO_2 decreases toward atmospheric pCO_2 at $10^{-3.5}$. The Pine watershed is consistently undersaturated with respect to calcite, with the North Pine branch significantly more undersaturated than the Pine branch. The North Pine has a shallower circulation system as a result of thick impermeable shale layers, which underlie the thin sandy glacial deposits. The Pine River subwatershed has thicker soil horizons and carbonate rich glacial deposits derived from the subjacent Silurian carbonate bedrock. All other Michigan and Slovenia streams are at or supersaturated for calcite. Increase in calcite saturation resulting from degassing can lead to possible Ca-carbonate back precipitation in surface waters. Ca-carbonate precipitation typically occurs in streams that are 5–10 times saturated for calcite [*Herman and Lorah*, 1987; *Suarez*, 1983] and occurs at low flow stages of the river during the warmer months of the year [*Roy et al.*, 1999; *Szramek and Walter*, 2004]. Michigan's Huron watershed has experienced calcium carbonate back precipitation [*Szramek and Walter*, 2004]. Many factors affect carbonate growth kinetics including availability of nucleation sites [*Suarez*, 1983], inhibition by Mg^{2+} and PO_4^{3-} [*Suarez*, 1983; *Zhang and Dawe*, 2000], and dissolved organic carbon (DOC) concentrations in excess of 0.05 mM [*Lebron and Suarez*, 1996, 1998]. In supersaturated water, these kinetic inhibitors are a major reason supersaturation with respect to calcite can be maintained.

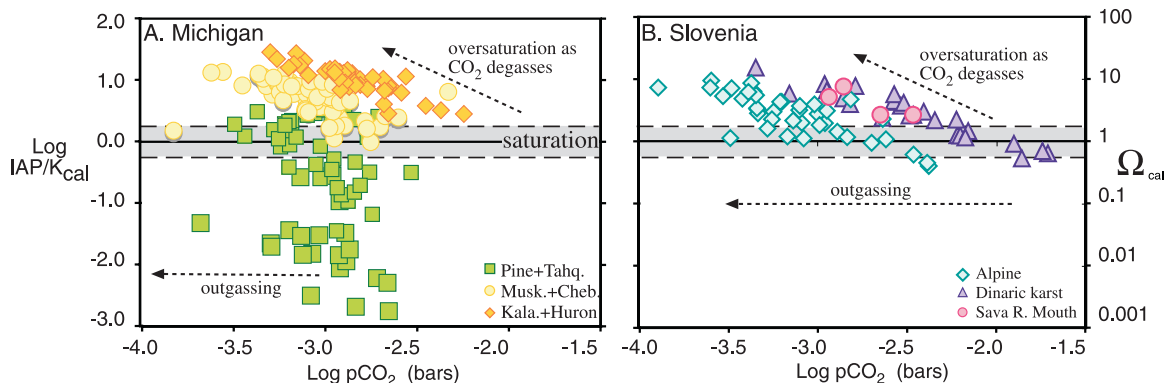[38] Dolomite dissolution produces waters with a molar Mg^{2+}/Ca^{2+} ratio of 1. Dissolution of equal

Figure 9. Saturation with respect to calcite ($IAP/K_{calcite}$) is shown versus pCO_2 for (a) Michigan and (b) Slovenia rivers. Saturation for calcite is defined as Log $IAP/K_{calcite} = 0$ or $\Omega_{calcite} = 1.0$. The gray band on the plot is the uncertainty of saturation for the samples based on errors associated with pH, alkalinity, and ion measurement errors. Atmospheric pCO_2 is -3.5. The majority ($\sim$90%) of the samples have pCO_2 values greater than the atmosphere. The loss of CO_2 from the study rivers drives the increase calcite saturation for the samples.

moles of dolomite and calcite contributes 0.5 mole of Mg^{2+} and 1.5 moles of Ca^{2+}, producing waters with an Mg^{2+}/Ca^{2+} ratio of 0.33. The Mg^{2+}/Ca^2 ratio is less than 0.11 when greater than 75% of the carbonate mineral weathering is calcite. Michigan glacial drift has roughly equal proportions of calcite and dolomite by mole [*Jin*, 2007]. Michigan surface waters have Mg^{2+}/Ca^{2+} ratios of 0.5 ± 0.1, over the wide range of HCO_3^- values (Figure 10a). This ratio indicates that dolomite weathering contributes over 65% of the total stream dissolved loads of HCO_3^- and Ca^{2+}. The Kalamazoo and Muskegon watershed have a few samples with higher Mg^{2+}/Ca^{2+} ratios, between 0.6 and 0.8. These higher Mg^{2+}/Ca^{2+} ratios are accompanied by lower Ca^{2+} values in those watersheds, with a similar range in Mg^{2+} (see Table 1). This relative loss of Ca^{2+} to Mg^{2+} is likely a result of calcium carbonate precipitation within the watershed, which has been observed in the Huron watershed in southern Michigan [*Szramek and Walter*, 2004].

[39] In Slovenia, bedrock geology is either primarily calcite or dolomite. The variations in bedrock lithology within subcatchments of the Sava River produce waters with much more variable Mg^{2+}/Ca^{2+} ratios (Figure 10b) than the relatively constant values observed in Michigan streams (Figure 10a). When averaged at the mouth of the tributaries the Mg^{2+}/Ca^{2+} ratios for Slovenia rivers (alpine region, 0.42 ± 0.2; dinaric karst region 0.49 ± 0.3) are similar to the value at the mouth of the Sava (0.43 ± 0.2) (Figure 10b). The major differences in the Mg^{2+}/Ca^{2+} ratios are seen in a comparison of the smaller tributaries feeding these regions. The dinaric karst region has streams with Mg^{2+}/Ca^{2+} ratios

approaching 1 indicating dominantly dolomite weathering, while the Mg^{2+}/Ca^{2+} ratios in other streams are less than 0.2, indicating less than 30% dolomite contribution to weathering. These data suggest that dolomite weathering on average contributes about 60% of the HCO_3^- in the Sava River. Although the Mg^{2+}/Ca^{2+} ratios for streams in Michigan and Slovenia differ in their range of variation, it appears that, on average, dolomite weathering in these two different carbonate terrains is as, or more important, than calcite weathering to the HCO_3^- flux from the watersheds.

4.4. Relations Between Stream Discharge and Carbonate System Geochemistry

[40] The relationship of stream discharge to the concentration of dissolved species is important for modeling the mechanisms controlling mineral dissolution on a watershed scale. The hydrological characteristics of the watershed combined with dissolved load patterns can help constrain the mineral dissolution kinetics and suggest the depth where mineral reactions are occurring [e.g., *Freeze and Cherry*, 1979]. An invariant concentration of a dissolved ion with increasing discharge indicates a rapid weathering reaction able to maintain saturation or piston flow pumping of evolved water to the surface. Within a single watershed, different dissolved constituents may behave quite differently; for example, an ion from kinetically slower silicate weathering may be greatly diluted as discharge increases [*Probst et al.*, 1992], whereas an ion from more rapid carbonate mineral weathering may maintain its concentration over a large range of discharge.
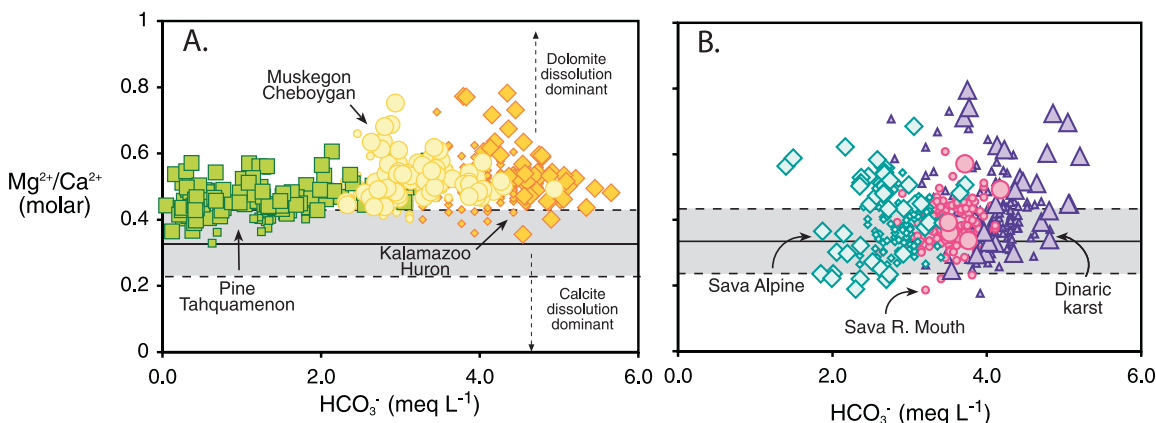
Figure 10. The riverine Mg^{2+}/Ca^{2+} ratio for (a) Michigan and (b) Slovenian rivers. The Mg^{2+}/Ca^{2+} ratio can help to discriminate the relative proportion of calcite and dolomite dissolution within the weathering zone of the watershed. A ratio of 0.33 indicates the equal molar dissolution of calcite and dolomite. The band of gray indicates the range of uncertainty in equal molar dissolution, stemming from variable Mg^{2+} concentrations in the calcite and additions from other lithologies. For explanation of symbols, see Figure 7.

[41] To better compare patterns of discharge from watersheds with different areas, the discharge is normalized to the drainage area and termed "specific runoff". The two main carbonate weathering parameters we examined with discharge are HCO_3^- and Mg^{2+}/Ca^{2+} ratio. Extreme discharge events, representing less than 2% of the data are excluded from these plots. Michigan watersheds display two discharge-concentration relationships (Figure 11a). The dilute Pine and Tahquamenon, display decreasing HCO_3^- concentrations as the specific runoff increases. The other Michigan watersheds show slight decreases in HCO_3^- concentration with discharge; however, the change tends to be less than 0.5 meq L^{-1}. Combining the Slovenian EIONET (2003) data with the results of our own sampling study has allowed discharge comparisons to be made for the Slovenian streams (Figure 11b). The alpine streams have the highest specific runoff values, ranging from $5-150$ L $km^{-2}s^{-1}$. The alpine watersheds have the smallest drainage areas and the highest MAP, compared to the other watersheds in this study. Importantly the HCO_3^- concentration remains constant over the range of discharge values, with a change in HCO_3^- of 1.34 meq L^{-1} from 1.85 to 3.19 meq L^{-1}. The watersheds draining dinaric karst terrains have specific runoff values 2 times less than the maximum alpine value. The dinaric karst watersheds display less variability in specific runoff than the alpine regions. One major reason for the difference is the complex nature of the subsurface hydrology of the dinaric karst region. Streams draining the dinaric karst have HCO_3^- values, which are rela-

tively constant over a range of discharge. The mouth of the Sava River represents mixing of streams draining the dinaric karst and alpine regions. At low specific runoff values (<50 L km^{-2} s^{-1}), the Sava mouth has HCO_3^- values similar to the dinaric karst region (3.5 meq L^{-1} ± 0.5). At times of high specific runoff, the HCO_3^- values decrease to a value of 3 meq L^{-1}, close to that of the alpine catchments, which dominate the water and solute fluxes.

[42] The relationship of variations in the Mg^{2+}/Ca^{2+} ratio to specific runoff also provides important constraints. An increase in the Mg^{2+}/Ca^{2+} ratio at low flow conditions may indicate carbonate precipitation or a shift in the contributions from subcatchments (i.e., dolomite/calcite streams). This relationship between specific runoff and Mg^{2+}/Ca^{2+} is represented in Figures 11c and 11d. The typical Mg^{2+}/Ca^{2+} ratio of Michigan streams is 0.5 ± 0.1 (Figure 11c). At lower specific runoff values, less than 8 L $km^{-2}s^{-1}$, the Mg^{2+}/Ca^{2+} ratio appears to increase slightly relative to the average flow values. For example, some water samples from the Kalamazoo and Muskegon rivers exceed Mg^{2+}/Ca^{2+} ratios of 0.6. This deviation from the "normal" value indicates that either Ca^{2+} is being lost from the system via carbonate precipitation or that relatively more dolomite is being weathered. *Szramek and Walter* [2004] observed that Mg^{2+} behaved conservatively between groundwaters and streams, and the small relative losses of Ca^{2+} in streams are driven by the precipitation of low-Mg calcite within the lakes and wetlands of the Huron watershed. Ignoring the slight depletions driven by
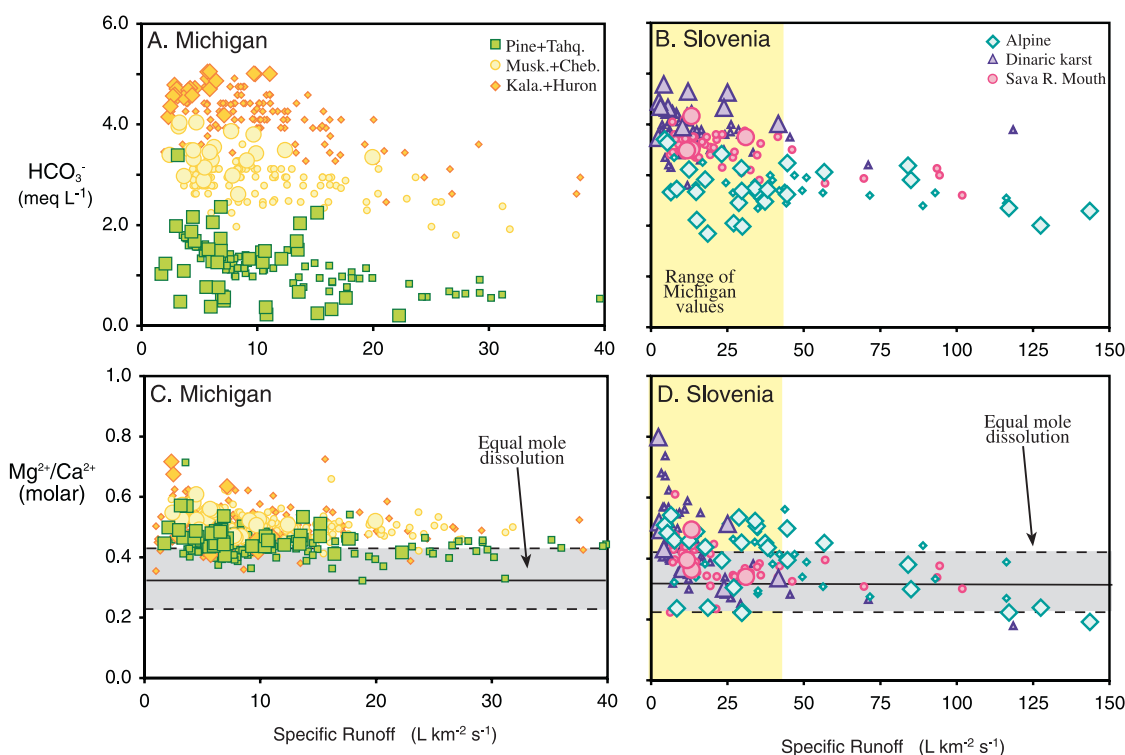
Figure 11. Concentration relationships for HCO_3^- and Mg^{2+}/Ca^{2+} variation with normalized stream discharge (e.g., specific runoff) are shown for all (a and c) Michigan and (b and d) Slovenian watersheds. The yellow vertical band on the Slovenian data represents the range of specific runoff for the Michigan samples. The horizontal gray bands in Figures 11c and 11d represent the uncertainly in equal molar dissolution of calcite and dolomite (see Figure 10). For explanation of symbols, see Figure 7.

calcite precipitation, the nearly constant Mg^{2+}/Ca^{2+} ratio of the streams in Michigan supports the mixed calcite and dolomite mineralogy of the glacial drift.

[43] The Mg^{2+}/Ca^{2+} ratios in the Slovenian dinaric karst catchments vary with stream discharges, from a high Mg^{2+}/Ca^{2+} of 0.8 to a low of 0.2 (Figure 11d). The high Mg^{2+}/Ca^{2+} values at low specific runoff values may be a result of Ca-carbonate precipitation within these dinaric karst drainage areas. In Figure 11d, the alpine watersheds appear to have a wide variation in Mg^{2+}/Ca^{2+} ratios. This is a result of grouping the watersheds together by type, because when the subcatchments are viewed individually the variability is low. The two main alpine watersheds, the S. Dolinka and the S. Bohinjka maintain a consistent Mg^{2+}/Ca^{2+} ratio over the range of discharges with the S. Dolinka at 0.53 ± 0.01 and the S. Bohinjka at 0.25 ± 0.1. In the alpine watersheds, the HCO_3^- and Mg^{2+}/Ca^{2+} ratios (Figures 11b and 11d) show that the incorporation and source of carbonate (calcite and dolomite) is constant. The hydrogeology of these alpine regions is relatively simple, especially compared to the

complex flow systems in the southern dinaric karst watersheds where solution channel flow can be pervasive.

5. Discussion

5.1. Comparison of Carbonate Weathering Intensities in Michigan and Slovenia Streams

[44] The major control on carbonate weathering intensity is runoff, with weathering being scaled with runoff [e.g., *Holland*, 1978; *Amiotte Suchet and Probst*, 1993]. Carbonate weathering intensity quantifies HCO_3^- produced from mineral weathering with CO_2 normalized to drainage area. The pH, temperature, and pCO_2 of a watershed determine the carbonate speciation, controlling the HCO_3^- carrying capacity. Figures 12a and 12b compare carbonate weathering intensities as a function of specific runoff for Michigan and Slovenia drainages, combining new data from this study with published government data (NWIS, 2001; EIO-
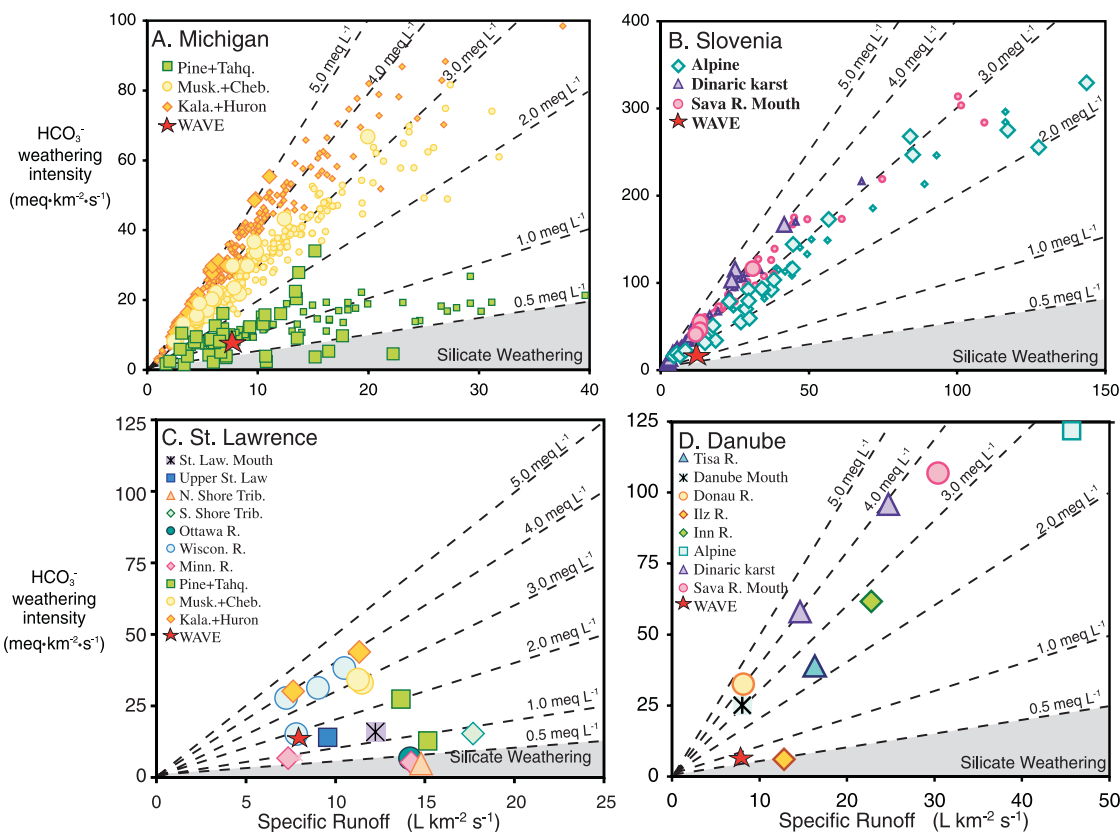
Figure 12. Carbonate weathering intensity (HCO_3^- meq km^{-2} L^{-1}) and specific runoff for individual samples for (a) Michigan and (b) Slovenian watersheds. The world average value (WAVE) is plotted for reference. Dashed lines indicate the bicarbonate alkalinity concentration. Note that each watershed has a limited range of alkalinity values over the range of specific runoff. Carbonate weathering intensity and specific runoff for rivers in (c) the St. Lawrence River and (d) the Danube River drainage basins. St. Lawrence drainage basin includes rivers from this study (Muskegon, Cheboygan, Huron, Kalamazoo, Tahquamenon and Pine), USGS NWISweb (Minnesota and Wisconsin), *Hélie et al.* [2003] (Ottawa River), and *Berner and Berner* [1996] (St. Lawrence and WAVE). Danube drainage basin includes rivers from this study (Karst, Sava Mouth, Sava Alpine), *Lyons et al.* [1992] (Tisa), *Pawellek et al.* [2003] and *Pawellek* [1995] (Donau, Ilz, and Inn), and *Berner and Berner* [1996] (Danube and WAVE).

NET, 2003) (see Tables 1, S1, and S2). Because the waters have a relatively constant HCO_3^- concentration, carbonate weathering intensity is a linear function of specific runoff. Soil and river pCO_2 is influenced by vegetation, land use, aquifer, and soil type. Carbonate rich watersheds with high weathering zone pCO_2 have the greatest ability to dissolve carbonates and maintain higher HCO_3^- concentrations. Global theoretical models of CO_2 consumption in carbonate watersheds show an alkalinity value near 3 meq L^{-1} determined from a best-fit line [*Amiotte Suchet and Probst*, 1993]. Although this value appears reasonable as an average for all the Michigan and Slovenian drainages, many drainages have waters with significantly higher HCO_3^- concentrations (see Figures 12a and 12b).

[45] The Michigan watersheds (Figure 12a) span a large range of alkalinity concentrations. Over 95% of surface waters in the Pine and Tahquamenon watersheds have alkalinity values below 2 meq L^{-1}. Samples from the Pine watershed fall along the 1 meq L^{-1} line and the 0.5 meq L^{-1} line for specific runoff values between 8 and 32 (L km^{-2} s^{-1}). As discussed, this results from the different hydrogeochemical setting for the two catchments of the Pine watershed, the North Pine and the Pine. The Muskegon, Cheboygan, Kalamazoo and Huron watersheds have on average slightly higher specific runoff values than the northern watersheds as a result of higher MAP (~100 mm/year). The Muskegon and Cheboygan watersheds fall along the 3 meq L^{-1} line; however, the Kalamazoo and Huron watersheds have alkalinity values ranging

from 3.5 to 5 meq L^{-1}. The southern Michigan watersheds have a longer growing season (longer time to have elevated pCO_2 in the soils) and less permeable drift (CO_2 diffusion decreased) than the northern watersheds [*Albert*, 1995]. The higher pCO_2 and availability of carbonate minerals in the southern Michigan watersheds produces greater carbonate weathering intensity values.

[46] Large differences for carbonate weathering intensity and specific runoff values are also observed in Slovenia between alpine and dinaric karst watersheds of the Sava River (see Figure 12b and Table S2). The dinaric karst watersheds have alkalinity values near 4 meq L^{-1}, with specific runoff reaching maximum values of 50 L $km^{-2}s^{-1}$ and the carbonate weathering intensity reaching maximum values of 175 meq HCO_3^- $km^{-2}s^{-1}$. Relative to the dinaric karst drainages, the alpine watersheds have slightly lower alkalinity values (between 2–3 meq L^{-1}) with 2.5 times the specific runoff ($\sim$150 L km^{-2} s^{-1}) and 2 times the carbonate weathering intensity ($\sim$325 meq HCO_3^- km^{-2} s^{-1}) of the dinaric karst watersheds. The waters discharging at the mouth of the Sava River represent a mixture of the two watershed types (alpine and dinaric karst), with alkalinity and specific runoff values intermediate between the two.

[47] The gradient of climate (MAT and MAP) in the Slovenian watersheds is an important influence on the carbonate weathering intensity and specific runoff. *Roy et al.* [1999] noted that linked factors such as lithology, residence time of water, mechanical erosion, etc. have more influence together than they do separately. Topographic relief is another important control on Slovenian watershed chemistry. Most studies on weathering in alpine regions conclude that enhanced mechanical weathering in these environments also increases chemical weathering [*Fairchild et al.*, 1999; *Anderson et al.*, 2000; *Jacobson and Blum*, 2003]. Stress on the mineral and the increased mineral surface area create conditions where minerals are more easily dissolved. Due to the nature of dinaric topography with karst phenomenon, the dinaric karst region also has high mineral surface area resulting from the numerous underground flow paths.

5.2. Significance of Headwater Streams to River Basin-Wide Carbonate Intensities and Fluxes

[48] Michigan and Slovenian watersheds typically have higher carbonate weathering intensities than

the world average value of 7 meq HCO_3^- km^{-2} s^{-1} (see Figures 12a and 12b). Carbonate weathering intensities and specific runoff for other tributaries within the St. Lawrence and Danube River basins, along with data on the mouth of each system are presented in Figures 12c and 12d. The carbonate weathering intensity results show that both carbonate and silicate-dominated tributaries drain into the St. Lawrence watershed (Figure 12c). Rivers from Michigan and Wisconsin draining into the Great Lakes subbasin are dominated by carbonate mineral weathering. Silicate weathering and atmospheric inputs dominate streams entering into the Great Lakes subbasin from Minnesota, where they are drain volcanic rocks along the north shore of Lake Superior. The St. Lawrence subbasin has silicate-dominated tributaries entering the river from the north that drain the Canadian Shield. The Ottawa River is an example of one of the silicate-dominated tributaries with only 8% carbonate rocks within the drainage basin [*Telmer and Veizer*, 1999] that contributes $\sim$15% of the St. Lawrence discharge [*Hélie et al.*, 2002]. The HCO_3^- concentration of the St. Lawrence River decreases by 0.2 meq L^{-1} near the confluence with the Ottawa River. In spite of the decrease in HCO_3^-, the Ottawa River contributes 11% of the dissolved inorganic carbon (DIC) flux from the St. Lawrence [*Telmer and Veizer*, 1999].

[49] The Danube River drainage basin has fewer available data on tributary chemistry and discharge value; however, the limited data indicate that both silicate and carbonate weathering dominated tributaries originate in the alpine headwater regions. The trend of mixing silicate and carbonate-dominated streams begins in the headwater regions of the Danube River with the Inn and Ilz rivers (see Figure 2) [*Pawellek*, 1995; *Pawellek et al.*, 2002] and the Sava River tributaries. The carbonate weathering intensity of the Inn river is 61 meq HCO_3^- km^{-2} s^{-1}, clearly dominated by carbonate weathering and the Ilz watershed has an intensity of 6 meq HCO_3^- km^{-2} s^{-1}, and drains mainly silicate rocks. The upstream Danube River location (Donau) [*Pawellek*, 1995; *Pawellek et al.*, 2002] is after both the Inn and Ilz join the main river and thus its chemistry is remarkably similar to the mouth, with a carbonate weathering intensity of 32 meq HCO_3^- km^{-2} s^{-1}. The mouth of the Danube has a carbonate weathering intensity of 25 meq HCO_3^- km^{-2} s^{-1}. The Tisa (also known as Tizsa) River, which drains the sediments of the Pannonian Basin, has an intensity of 37 meq HCO_3^- km^{-2} s^{-1} [*Lyons et al.*, 1992]. Similar to

the northern headwater regions, the headwater streams in Slovenia are between 2 to 4 times higher in carbonate weathering intensity than the mouth of the Danube River.

[50] Taken together, the data show that mineral weathering in headwater catchments of the Danube and St. Lawrence drainage basins is not accurately accessed by solute fluxes determined at the river mouth. Headwater catchments play a major role in regulating downstream river chemistry. The Danube annually discharges 6.32×10^{14} meq of HCO_3^- with 5% of this flux coming from Slovenia, which is only 1.2% of the total Danube drainage area. The St. Lawrence watershed discharges 5.49×10^{14} meq of HCO_3^- annually with 2.7% of this flux coming from the Michigan watersheds in this study. Using the flux at a river mouth to calculate chemical denudation rates of landscapes averages the flux over the entire river basin, underestimating the chemical erosion of carbonate regions and overestimating the chemical erosion of silicate regions.

[51] Global climate models indicate that global precipitation patterns will likely be altered and decrease/increase precipitation in different locations around the globe [Intergovernmental Panel on Climate Change (IPCC), 2001]. While a drainage basin may receive the same total annual precipitation, the distribution of that precipitation may change. Increasing the amount of precipitation to a carbonate-bearing watershed for example, may increase the HCO_3^- flux from those watersheds since carbonate mineral weathering is primarily controlled by solubility. Regions already saturated for $CaCO_3$ could maintain saturation as stream discharge increases, increasing the area normalized flux of carbonate dissolution. This is contrary to many early studies of river carbonate saturation states, where rivers were generally considered to be undersaturated with respect to calcite [Holland, 1978].

5.3. Relative Contribution of Dolomite to Carbonate Weathering Intensity

[52] Few pure dolomite watersheds are reported in the literature [e.g., Han and Liu, 2004]. Coupled with the lack of modern dolomite mineral precipitation and poorly understood kinetic inhibitors [McKenzie, 1991], there is limited understanding of dolomite weathering and its contribution to the solute flux of world rivers. The Mg^{2+}/Ca^{2+} ratios for the Michigan and Slovenian rivers are shown in Figures 13a and 13b. As seen previously, the Michigan rivers maintain a relatively constant

Mg^{2+}/Ca^{2+} mole ratio (0.5 ± 0.1) (Figure 13a). The local groundwaters, which discharge into the streams, also have Mg^{2+}/Ca^{2+} mole ratios near this value [Szramek and Walter, 2004; Williams et al., 2007]. Slovenian streams have a wider range of Mg^{2+}/Ca^{2+} ratios indicating variations in relative contribution of calcite and dolomite in the different tributaries, the ratio ranges from 0.2 to nearly 0.8 (Figure 13b). The alpine watersheds tend to have a higher density of samples with lower Mg^{2+} concentrations than the dinaric karst watersheds. The mouth of the Sava River sums the catchments with an average Mg^{2+}/Ca^{2+} mole ratio of 0.47 with a total variability of 0.2, indicating dolomite weathering is greater than calcite over the entire Sava River watershed.

[53] The Mg^{2+}/Ca^{2+} ratios and solute concentrations for tributaries of the St. Lawrence and Danube River watersheds illustrate the importance of dolomite weathering contributions at the large scale. In Figure 13c, tributaries (Minnesota rivers) into the St. Lawrence previously indicated to be draining silicate rocks have Mg^{2+}/Ca^{2+} ratios indicating dolomite dissolution; however, the concentration is too low to be sourced from abundant carbonate rocks. In this instance, Mg^{2+} is sourced from silicate rocks, but only at very low concentrations. This is consistent with results from Jin [2007] about the relative contributions of silicate versus carbonate weathering contributions to the divalent cation flux. In Figure 13d the Danube watershed Mg^{2+}/Ca^{2+} ratio indicates equal calcite and dolomite weathering, except for the Ilz and Tisa rivers. The Ilz River drains silicate rocks and has overall solute concentrations too low for carbonate weathering [Pawellek, 1995; Pawellek et al., 2002]. The Tisa River drains the Tertiary age sedimentary basin fill of the Pannonian basin [Lyons et al., 1992]. Dolomite rocks are limited in the Tertiary and the Mg^{2+} in the Tisa again is low in concentration, reflecting the lack of dolomite weathering within the basin.

[54] The Mg^{2+} weathering intensity of a carbonate mineral-bearing watershed indicates the relative contribution of dolomite weathering among drainages. The world Mg^{2+} weathering intensity is 1.2 mmol km^{-2} s^{-1} (see Figure 1c). Figures 14a and 14b show Mg^{2+} weathering intensity versus specific runoff for Michigan and Slovenian watersheds. Michigan watersheds have average intensity values from 2.3 (mmol km^{-2} s^{-1}) for the Pine and Tahquamenon to 11 (mmol km^{-2} s^{-1}) for the Kalamazoo watershed. Slovenian (Figure 14b)
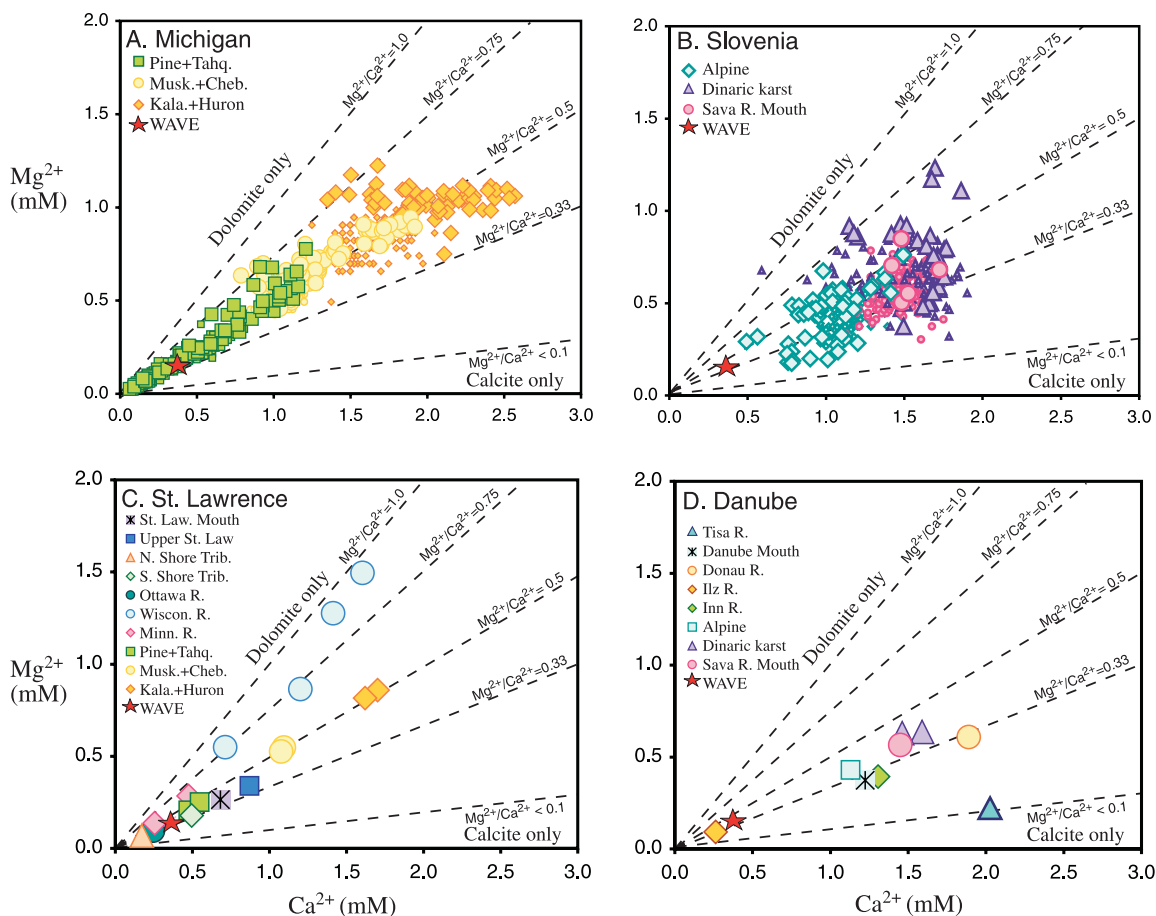
Figure 13. Mg^{2+} versus Ca^{2+} is shown for (a) Michigan and (b) Slovenian watersheds and for rivers draining (c) the St. Lawrence River and (d) the Danube River drainage basins. See Figure 12 for data sources.

watersheds draining the alpine regions have Mg^{2+} intensities from 5 to 40 (mmol km^{-2} s^{-1}) and the dinaric karst watersheds have Mg^{2+} intensity values from approximately 5 to 20 (mmol km^{-2} s^{-1}). Typically the Mg^{2+} concentration for the Slovenian watersheds is around 0.5 ± 0.2 (mmol L^{-1}). Because the Mg^{2+} concentrations are similar for the alpine and dinaric karst drainages, the observed differences in Mg^{2+} intensity values result from the large difference in specific runoff between the regions.

[55] Mg^{2+} weathering intensity values for the St. Lawrence and Danube watersheds (Figures 14c and 14d) cover the same range, up to 18 mmol km^{-2} s^{-1}, despite having very different values of overall carbonate weathering intensity (see Figures 12c and 12d). The mouths of the St. Lawrence and Danube Rivers have very similar Mg^{2+} weathering intensities at 3.2 and 3.0 mmol km^{-2} s^{-1}, respectively. The Ottawa River in the St. Lawrence basin has an Mg^{2+} intensity of 1.3 mmol km^{-2} s^{-1} typical of silicate-dominated

drainages. The carbonate dominated rivers range between 4 to 18 mmol km^{-2} s^{-1}. This range reflects both the amount of silicate versus carbonate weathering and the degree of dolomite weathering. The Mg^{2+} weathering intensity along with the Mg^{2+} concentrations further highlights the higher degree of dolomite weathering. The carbonate watersheds in the St. Lawrence basin have higher Mg^{2+} concentrations than the carbonate basins in the Danube. The low concentrations and high specific runoff of the Danube and the high concentrations and low specific runoff of the St. Lawrence create similar Mg^{2+} weathering intensities within the headwater catchments. These relationships point toward a higher degree of dolomite relative to calcite weathering in the St Lawrence basin that is not evident at the mouth due to the comparable specific runoff values.

6. Conclusions

[56] The major element geochemistry of the Michigan and Slovenian watersheds is dominated by the
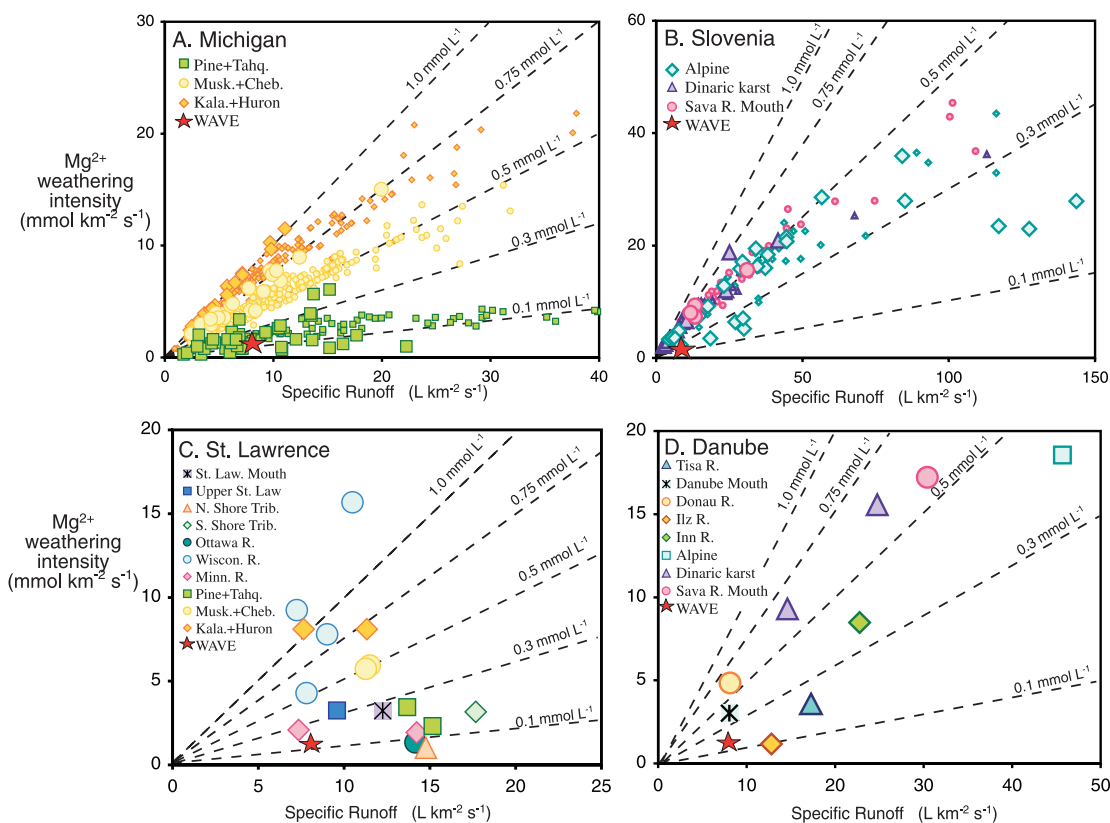
Figure 14. Mg^{2+} weathering intensity plotted versus specific runoff for individual samples from both (a) Michigan and (b) Slovenian watersheds. Dashed lines indicate the Mg^{2+} concentration in mmol L^{-1}. The Mg^{2+} weathering intensities for all the watersheds mimic the HCO_3^- weathering intensities in Figures 14c and 14d. Mg^{2+} weathering intensity is plotted versus specific runoff for rivers in (c) the St. Lawrence River and (d) the Danube River drainage basins. Note that the Mg^{2+} weathering intensity values cover the same range within the two drainage basins. See Figure 12 for data sources.

dissolution of carbonate minerals. The thick soil weathering zones in Michigan (100 to 300 cm) allow for higher solute concentrations of carbonate mineral weathering products (Ca^{2+}, Mg^{2+}, HCO_3^-), than the thin soil weathering zone (0 to 70 cm) in Slovenian watersheds. Calcite supersaturation of river waters is typical for temperate carbonate-bearing watersheds draining silicate + carbonate lithologies [*Barth et al.*, 2003; *Szramek and Walter*, 2004; *Williams et al.*, 2007]. This is a result of the temperature-dependent relative solubility of dolomite and calcite with dolomite increasingly more soluble than calcite at temperatures below 25°C. As demonstrated in the Michigan watersheds, increased dolomite solubility in groundwaters at temperatures between 6 and 10°C enables calcite to be supersaturated [*Szramek and Walter*, 2004; *Williams et al.*, 2007]. The majority of Michigan and Slovenian rivers are at saturation or supersaturated (up to 20 times) for calcite. The northern carbonate poor watersheds in Michigan (Pine and

Tahquamenon) are the exception, being nearly 100 times undersaturated for calcite and having chemistries dominated by silicate dissolution and atmospheric contributions.

[57] In a carbonate-bearing watershed, the Mg^{2+}/Ca^{2+} ratio can be used to determine the degree of dolomite versus calcite mineral weathering. The Mg^{2+}/Ca^{2+} ratios (from 0.4 to 0.6) of the Michigan rivers draining the glacial drift indicate that dolomite is between 55 to 70% of the carbonate mineral weathering. These ratios are supported by the proportions of original sedimentary carbonate in the glacial drift, which contain approximately 50/50 dolomite and calcite by mole. The variable distribution of limestone and dolomite bedrock in the Slovenian watersheds is manifested in the wide range of Mg^{2+}/Ca^{2+} ratios. These range between 0.1 to ~0.75, reflecting weathering mass ratios of 20 to 85% dolomite, with an average around 60%. At the mouth of the Sava River, the average Mg^{2+}/Ca^{2+} ratios is 0.43, indicating that nearly equal

proportions of dolomite and calcite are contributing to the overall weathering.

[58] The carbonate weathering intensity on catchment and watershed scales indicate important processes controlling the weathering of carbonate minerals. Rivers in Michigan and Slovenia maintain relatively unchanged concentrations of carbonate mineral weathering products with increased discharge. As a result of the steady concentrations the extremely high flux from Slovenia is largely determined by the high discharge values, while the high flux from the Michigan watersheds is controlled by the depth and pCO_2 of the weathering zone. This demonstrates the importance of temperate landscapes contributions to the global integrated riverine fluxes of Ca^{2+}, Mg^{2+} and HCO_3^-. Changes in precipitation, runoff, and organic-inorganic carbon transformations influence both the soil development rate and the pCO_2 of the weathering zone. As such, global climate change will likely increase the continental weathering fluxes from carbonates to the surface oceans.

[59] At the larger scale, the carbonate weathering intensity for the St. Lawrence and Danube River basins is inversely related to the catchment area. The Michigan and Slovenian headwater carbonate watersheds have the highest weathering intensities within each basin. Michigan streams have carbonate weathering intensities 2 to 6 times higher than the world average and the Mg^{2+} weathering intensities 2 to 8 times the world average. Carbonate and Mg^{2+} weathering intensities for Slovenian rivers are 7 to 18 times and 6 to 15 times higher than the world average, respectively. As the watershed scale is increased the weathering intensities decrease. As seen in Figure 12c, the St. Lawrence River system has a carbonate weathering intensity of 13 (meq HCO_3^- km^{-2} s^{-1}) at its mouth, compared to 8.5 for the entire North American continent. The Danube River (Figure 12d) has a carbonate weathering intensity of 25 (meq HCO_3^- km^{-2} s^{-1}) at its mouth, compared to 11.5 for all of Europe. Clearly, the headwater regions of two river systems play a major role in regulating the overall weathering intensities from the larger drainages and allow them to maintain intensity values greater than the "average" continental values.

[60] The Mg^{2+} weathering intensities along with the Mg^{2+}/Ca^{2+} ratio for these watersheds indicate that dolomite mineral weathering contributes typically between 50 to 70% of the HCO_3^- flux. Therefore dolomite dissolution is a major contributor to the HCO_3^- flux from these carbonate rich temperate landscapes. Global climate models predict that global precipitation patterns will likely be altered [IPCC, 2001]. Increasing the amount of precipitation into temperate and cold regions such as those occupied by the St. Lawrence and Danube River basins may increase both the HCO_3^- flux and the dolomite sourced riverine Mg^{2+} flux to the ocean from these areas. Taken together, the enhanced solubility of dolomite relative to calcite at these relatively low mean annual temperatures ($<15°C$) and the relatively constant HCO_3^- concentrations with increasing discharge suggest that these weathering environments may contribute disproportionately to Mg^{2+} and HCO_3^- fluxes from rivers.

Acknowledgments

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