Mineral weathering rates in glacial drift soils (SW Michigan, USA): New constraints from seasonal sampling of waters and gases at soil monoliths

Lixin Jin a,⁎, Stephen K. Hamilton b, Lynn M. Walter a

a Department of Geological Sciences, University of Michigan, 2534 CC Little Building, 1100 N. University Ave., Ann Arbor, MI 48109-1005, United States
b Kellogg Biological Station and Department of Zoology, Michigan State University, 3700 E. Gull Lake Drive, Hickory Corners, MI 49060-9516, United States

Received 2 July 2007; received in revised form 4 December 2007; accepted 5 December 2007

Abstract

Soil solutions and gases were sampled along 200 cm deep soil profiles from four instrumented soil monoliths in southwest Michigan, established on coarse-grained glacial drift deposits. Seasonal sampling enabled evaluation of thermodynamic versus kinetic controls on carbonate- and silicate-mineral weathering rates, allowing better integration with past field hydrogeochemical studies of Michigan soil and surface water systems. Silicate-weathering products dominate water chemistry in the upper soil zones. Carbonate minerals, comprised of subequal amounts of calcite and dolomite, are only present at depths below 150 cm. When present, carbonate dissolution is rapid and soil water Ca2+ and Mg2+ concentrations increase dramatically as observed in other natural soil study sites in southern Michigan. Soil water saturation states are near equilibrium with respect to calcite and slightly less saturated with respect to dolomite. The divalent cations of soil waters and soil CO2 both show a seasonal trend, with concentration maxima occurring in September and minima in April, suggesting that soil water Ca2+ and Mg2+ concentrations are under equilibrium control with carbonate solubility limited by temperature-dependent pCO2 rather than by direct effects of temperatures. Importantly, monolith soil water Mg2+/Ca2+ and calcite and dolomite saturation states are lower than those of streams in the same watershed and also lower than those of soil waters in other Michigan watersheds. Because carbonate weight percentages and chemical compositions in these sites are similar, this difference likely reflects the short exposure path (thus short residence time) of soil waters to carbonate-rich horizons in the monoliths.

The dissolution reactions of primary aluminosilicate minerals are incongruent with respect to Al and Si due to kaolinite formation. However, major cations (Ca2+, Mg2+, K+ and Na+) are stoichiometrically released from silicate dissolution. Na+ (soil water Na+ after correction for atmospheric input and derived primarily from plagioclase weathering) exhibits much less seasonality than divalent cations, with only slight elevations observed in the summer months. Soil water H4SiO4− concentrations show seasonal variations similar to the divalent cations, but are determined by the balance between production (silicate-mineral dissolution) and consumption (kaolinite precipitation). Plagioclase and amphibole are below saturation, and these dissolution reactions must be kinetically controlled. Through a conservative tracer study, about 15% to 45% of applied Br passed out of the monolith profiles in 40–160 days and this long mineral–water contact time is especially important for slow reactions such as silicate dissolution.

⁎ Corresponding author. Current address: Center for Environmental Kinetics Analysis, Earth and Environmental Systems Institute, Penn State University, State College, PA 16802, United States.
E-mail address: Luj10@psu.edu (L. Jin).

Available online at www.sciencedirect.com

Chemical Geology 249 (2008) 129–154

www.elsevier.com/locate/chemgeo

⁎ Chemical Geology

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Based on water chemistry and discharge, bulk reaction rates of calcite, dolomite (Ca$_{0.5}$Mg$_{0.5}$CO$_3$), K-feldspar and plagioclase are calculated to be at 3400, 3100, 220, and 320 mol ha$^{-1}$ yr$^{-1}$, respectively. Based on mass balance of soil composition, long-term plagioclase-weathering rates (over the past 12,500 years) are calculated at about 2400 mol ha$^{-1}$ yr$^{-1}$, much higher than the current rates. This agrees with previous conclusions that weathering rates decrease with time, due to loss of reactive mineral surfaces. Furthermore, both long-term and short-term plagioclase dissolution rates in Michigan are relatively high compared to those in other watersheds with similar age, possibly due to fresh surfaces produced by glaciation, in combination with the high discharge and high plagioclase abundances.

Keywords: Carbonates; Aluminosilicates; Soil water; Reaction kinetics; Carbon dioxide; Hydrological tracers

1. Introduction

Anthropogenic CO$_2$ emissions (~8 Gt C/yr) have raised the atmospheric CO$_2$ partial pressure significantly (e.g., Schlesinger, 1997; Burgermeister, 2007). The drawdown of this additional atmospheric CO$_2$ on decadal scales depends on the response of surficial inorganic and organic carbon reservoirs, including ocean–atmosphere exchange, biotic assimilation on continents and in oceans, and short-term uptake by carbonate-mineral weathering (Sundquist, 1993; Schlesinger and Lichter, 2001). On geologic timescales, the paleo-atmospheric CO$_2$ record suggests that input and output fluxes of Earth-surface carbon have been in close balance (Berner, 1991, 1994; Berner and Caldeira, 1997). The stabilization of atmospheric CO$_2$ requires a negative feedback, and the most likely mechanism is CO$_2$ consumption during silicate weathering (Walker et al., 1981; Bickle, 1996; Edmond and Huh, 1997; Boeglin and Probst, 1998; Gaillardet et al., 1999; Quade et al., 2003; Ridgwell and Zeebe, 2005). Thus, it is geologically significant to understand how silicate- and carbonate-mineral weathering responds to changes in atmospheric CO$_2$ levels as well as global climate, especially changes in air temperature and precipitation.

Riverine chemistry has proven powerful in calculating chemical weathering rates and understanding their dependence on mineralogical and climate variables. White and Blum (1995) compiled water chemistry data for rivers draining granite/granitoid watersheds and observed only weak correlations between field-derived weathering rates and mean annual temperature and precipitation of the watersheds. Our group has studied chemical weathering in the Great Lakes region, a recently glaciated area with mixed mineralogy (carbonate and silicate minerals), providing the opportunity to investigate the correlation between climate change and chemical weathering processes in mid-continent settings (Fig. 1A; Ku, 2001; Williams et al., 2007b; Szramek et al., 2007). Ground waters and river waters were characterized in several Michigan watersheds (e.g., the Huron and Kalamazoo watersheds shown in Fig. 1A) to evaluate the weathering fluxes and carbon dioxide consumption rates (Williams et al., 2007b; Szramek et al., 2007). The Great Lakes region was shown to be a significant CO$_2$ sink due to intensive carbonate dissolution, which positively correlated with high runoff and carbonate-mineral solubility. Specifically, dolomite is more soluble than calcite in temperate-climate regions and, contrary to past estimates, contributes more than half of cations and dissolved inorganic carbon (DIC) on a global scale (Berner and Berner, 1995; Williams et al., 2007b). Contribution from silicate dissolution is difficult to evaluate from elemental relations in surface waters, as carbonate dissolution dominates the water chemistry if carbonate minerals are present. Furthermore, elemental budgets can be confounded by contaminants such as deicing salts (CaCl$_2$, NaCl), especially in the more densely populated areas of southern Michigan (Williams et al., 2007b). Soil water cation chemistry, although affected by precipitation composition, biological activity, and cation exchange processes, is predominantly controlled by the type and rate of chemical weathering reactions. In near-surface soils, carbonate minerals have been preferentially removed, permitting silicate reactions to be quantified directly. A recent study investigated soil waters in Michigan soil profiles, focusing on cation mass balance and the silicate versus carbonate weathering contributions (Jin et al., 2008). Consistent with surface water studies, dolomite dissolution contributes more than 90% of soil water Mg$^{2+}$ and more than 40% of soil water Ca$^{2+}$. Furthermore, silicate weathering was shown to be dominantly controlled by mineral abundances (surface area) while carbonate weathering was controlled by soil zone CO$_2$.

Despite the constraints these studies have placed, the actual determination of chemical weathering rates and their dependence on temperature and precipitation was hard to quantify by collection and analyses of soil waters from natural soil columns, because the frequency of sampling is limited by dry or frozen field conditions. In this study, mineral weathering reactions were investigated.
in four replicate soil monoliths at a Long-Term Ecological Research (LTER) site of Kellogg Biological Station (KBS, Michigan State University), situated in the Kalamazoo watershed of southwestern Michigan. The soil monoliths are intact soil profiles, enclosed by walls, allowing sampling and quantification of gravity infiltration exiting the bottom of the profile. The soil mineralogy at KBS was characterized and the soil solute and gas chemistry was followed over seasonal cycles. A LiBr tracer experiment was conducted to understand the hydrologic flow in the soils and to calculate the residence time of water and solutes in the soil profiles. The goals of this study were: (1) to elucidate the relative importance of thermodynamic versus kinetic controls on carbonate- and silicate-mineral weathering; (2) to investigate seasonal variation of chemical composition of soil pore waters and soil gas chemistry in relation to temperature and soil moisture; (3) to study the hydrologic controls on silicate weathering by measuring residence time of a conservative tracer in the soil profiles; (4) to calculate the infiltration fluxes of major cations and the present reaction rates of major minerals (calcite, dolomite, feldspars) in the soil profiles; (5) to calculate long-term plagioclase weathering rates by soil elemental mass balance since soil formation; and (6) to compare short-term and long-term plagioclase weathering rates.

2. Field site description and methodology

2.1. Soils and geology

Southwestern Michigan soils are developed on highly heterogeneous glacial deposits left upon retreat of the Wisconsin ice sheet (ca. 12,500 years BP) (Dorr and Eschman, 1970). The average thickness of glacial deposits in this region is about 100 m atop Mississippian age.
bedrock units as the Coldwater Shale and sulfide-rich Marshall Sandstone (Catacosinos and Daniels, 1991). The glacial drift originated from long-distance transport of erosion products from both the crystalline Canadian Shield and Paleozoic/Mesozoic sedimentary units of the Michigan Basin. The KBS field site is located on an outwash plain in the Kalamazoo watershed (Fig. 1B). Soils here are sandy loams of the Kalamazoo series (fine-loamy, mixed, mesic Typic Hapludalfs) (Rosek, 1992; Hamilton et al., 2007). These well-drained soils lie on nearly level slopes and are moderately permeable in the upper part of the profile and very permeable in the lower part. The typical sequence of horizons is Ap, E, Bt1, 2Bt2 and 2E/Bt. Textures of the Ap and E horizons are loam or sandy loam. The Bt1 is usually clay loam or sandy clay loam, whereas the 2Bt2 has a sandy loam texture. The E/Bt consists of lamellae of loamy sand (Bt) and sand (E).

2.2. Climate and precipitation chemistry

At KBS, mean annual temperature is 9.7 °C, and mean annual precipitation is 890 mm/yr over the last 30 years, with about half falling as snow. KBS maintains daily records of air temperatures, precipitation (as rain and snow), and snow depth on ground. Daily precipitation was calculated by adding the rain and snowmelt together assuming that 1-inch of snow is equivalent to 0.02-inch of rainfall. This assumption is an oversimplification since the snow/rain conversion factor varies with history and aging of the snow, but from a weekly to monthly water budget perspective, error introduced by this assumption is relatively small. Total precipitation was calculated to be 1145 mm in the calendar year of 2004, which is about 20% above the annual average. Monthly Thornthwaite potential evapotranspiration (PET) was computed based on weather data collected at KBS from 2004; this index has proven to be fairly reliable in the Midwestern USA (Thornthwaite, 1948; Palmer and Havens, 1958; Crum et al., 1990). KBS also has PET record extending over the last 30 years.

Major ion chemistry of wet atmospheric deposition was monitored weekly by the National Atmospheric Deposition Program/National Trends Network at KBS within 1 km of the study sites (NADP/NTN, 2005). The annual average composition of wet precipitation here is: $\text{NO}_3^-$ (26 $\mu$M), $\text{SO}_4^{2-}$ (18 $\mu$M), $\text{NH}_4^+$ (27 $\mu$M) and $\text{Ca}^{2+}$ (5 $\mu$M), and pH averages about 4.5.

2.3. Monoliths and tracer experiments

The four replicate soil monoliths (identified here as #2, #6, #9 and #13) are 20 m apart in an area with negligible topographic slope. Each was installed in 1989 by excavating around a 1.22 m $\times$ 2.29 m $\times$ 2 m pedon and then enclosing it within a stainless steel chamber. The area around the chamber was then backfilled, so that installation was flush with the surrounding soil surface (Fig. 1C). Gravity drainage waters are collected continuously in a receiving bucket at the base of each monolith, at a depth of 200 cm. A chamber on one side provides access to samplers. The monoliths are sealed by walls but open to natural precipitation at the top so that water discharge at the base equals to the difference between precipitation and evapotranspiration. In addition to the gravity drainage at the bottom, water was collected from 4 to 6 Prentar® tension soil-solution samplers (lysimeters) at shallow soil depths (between 20 and 100 cm). In monoliths #9 and #13, three replicate lysimeters were installed at a depth of 180 cm, just 20 cm above the monolith base. Tension (~0.5 atm) was applied to the lysimeters, and the resulting soil water was collected after 24 h. Since installation, the surfaces of the monoliths have been harvested and cultivated annually (rotations of corn/soybean/wheat) but without application of liming or fertilization.

Soil water transport through the profile was investigated by applying a tracer to snow on the soil surface. LiBr was chosen because of the low background concentrations in soils and low toxicity to plants (Jabro et al., 1991; Thies et al., 2002). The chemical behavior of $\text{Br}^-$ is conservative, as soil pH is around 5.5 to 6, which limits any significant $\text{Br}^-$ sorption to clays. To establish baseline concentrations for $\text{Li}^+$ and $\text{Br}^-$ tracers, the drainage waters were sampled before the application of the tracer. About 60 g of laboratory-grade LiBr powder was dissolved in 20 L of melted snow, and then 5 L of this tracer solution was evenly spread over each monolith with a garden sprayer. LiBr solution was applied to coincide as closely as possible with the onset of a major snowmelt event (27 Feb 2004). Gravity drainage samples were collected approximately weekly for the first 3 months after tracer injection, followed by less frequent sampling of the lysimeters at all depths and the gravity drainage at the base of the monoliths. Two types of gravity drainage waters were collected at the base (200 cm): the water that was actually dripping from the monolith drainage pan on each sampling date and the water that had accumulated over time in the receiving bucket. We will hereafter refer to the instantaneous sample as the “drip” sample and the integrated sample of drainage between sampling events as the “tub” sample. The volumes of drainage in the buckets were measured, the instantaneous dripping rates recorded, and then the buckets were emptied for the next sampling interval. Average water-flow rates were calculated from 1 Mar to 10 Jun 2004.
2.4. Collection and analyses of soil, soil gas and soil water samples

Five gas sampling tubes were installed at depths ranging from 20 to 100 cm in each monolith and samples were collected multiple times over the year to investigate seasonal variations. Soil gas was withdrawn by syringe from Teflon capillary tubing (0.5 mm ID) extending at least 50 cm into the monolith from the side wall. Partial pressures of soil gas CO₂ (pCO₂) were measured by gas chromatography (GC) with thermal conductivity detection, calibrated with 4 standards ranging from 500 to 10,000 ppmv CO₂.

Soil cores up to 200 cm deep were collected with a pneumatic coring device about 5 m away from each monolith, and the cores were sectioned every 10 cm. Soil samples were dried at 45 °C and ground to pass a sieve of mesh 200 (75 μm diameter). Mineralogy of these samples was determined by Scintag powder X-ray diffraction (XRD) in the Electron Microbeam Analysis Lab (EMAL) at the University of Michigan. Thin sections of parent sediments were examined by scanning electron microscope (SEM) at EMAL to identify the trace minerals and to characterize the features of mineral surfaces. Sediments less than 2 μM in diameter (clay fraction) were separated using sedimentation method and analyzed for mineralogy by XRD. Representative bulk soils were leached by aqua regia (3HCl:1HNO₃) at room temperature for 3 h to selectively dissolve carbonates and Al/Fe oxyhydroxides (Sparks, 1996). The acid leachate provides the best estimate of the carbonate content (dolomite and calcite) as it has been found to remove negligible amounts of cations from silicate minerals in these soils (Jin, 2007). Another soil core was collected in a mature deciduous forest near the monolith site. Elemental composition of representative bulk soils from this profile was measured by X-ray fluorescence (XRF, Rigaku SMAX) at the Michigan State University, following the method of Hannah et al. (2002). Water temperature was measured in the field with a temperature meter. The pH values of the soil waters were measured in the field immediately after sample collection with a Corning 315 pH meter with an Orion Ross glass combined electrode. The electrode was calibrated with two low-ionic-strength standard buffer solutions (pH 4.10 and 6.97), and the pH measurement precision is 0.05 pH units. Water for chemical analyses was filtered through 0.45-μm Whatman glass-fiber filters and stored in HDPE bottles at 4 °C. For cation samples, about 30-mL filtered solution was collected and acidified to pH 4 with ultrapure concentrated HNO₃. Major cations and anions were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES) and ion chromatography (IC), respectively, in the Environmental and Analytical Geochemical Lab (EAGL) at the University of Michigan. The precision of IC and ICP analyses was better than 3% for major elements and 10% for minor elements. Total alkalinity was determined by weak acid titration within a day of sampling over a pH range of 2 to 3 using the Gran method (Edmond, 1970; Gieskes and Rogers, 1973; Stumm and Morgan, 1996). The uncertainty for alkalinity titrations is less than 2% for most of our samples, except for those with very low alkalinity values where uncertainty is 0.05 meq/L.

Mineral saturation state calculations were performed for soil water samples where complete geochemical analyses were available (pH, temperature, alkalinity and major ion concentrations) using the USGS program SolminEQ.88 (Kharaka et al., 1988). Saturation indexes (SI) of the solution with respect to calcite are defined as SI = Log ([Ca²⁺][CO₃⁻²]/K(calcite)), where [Ca²⁺] and [CO₃⁻²] are activities of Ca²⁺ and CO₃⁻², and K(calcite) is the solubility constant of calcite. The normalized saturation state is used to compare the ionic activity product (IAP) of dolomite Ca₀.₅Mg₀.₅(CO₃) on the same molar basis as that of calcite (CaCO₃). This was accomplished by taking the square root of IAP(dolomite) from SolminEQ.88 and the thermodynamic data for dolomite stability from Hyeong and Capuano (2001) were used to evaluate the saturation index of intermediate-order dolomite. Given the uncertainties in pH measurement, the degree of saturation is accurate within 0.3 SI units.

3. Results

3.1. Soil mineralogy

The major minerals identified by XRD in parent materials of monoliths were quartz, K-feldspar, calcite, dolomite, plagioclase, and amphibole in the order of decreasing abundance, with trace amounts of mica, magnetite, ilmenite, and pyrite. Clay fractions of parent sediments were dominated by quartz, with little illite and kaolinite. Plagioclase composition of the glacial deposits had been previously reported as Na₀.₈Ca₀.₂Al₁.₀Si₂.₈Oi₈ throughout Michigan watersheds (Ab of 0.80±0.10; Williams et al., 2007a). Elemental compositions of the acid leachable fractions and bulk soils are reported in Table 1. Completely leached from the shallow soils, calcite and dolomite co-occurred in the soil zones of monoliths and deciduous forest beginning at around 150 cm depth. Precipitation of secondary Al/Fe oxyhydroxides produced a visible red-brown layer in the B-horizon, generally just above the top of the carbonate-bearing layer. The carbonate fraction ranges from 5 to
30 wt.% in the soils, averaging at 20 wt.% (Table 1). Dolomite and calcite occur in approximately equal mass in the carbonate soil zones, similar to previously studied soil profiles in Michigan (Jin, 2007). Also, soil textures were similar between the soil monolith and deciduous forest sites, being loamy in the shallow soils, sandy below ~100 cm depth, and much coarser in the C-horizon (below 150 cm). Weight percentages of MgO and Na2O in the bulk soils are linearly correlated with the abundances of amphibole and plagioclase where carbonate is absent. The KBS site has similar soil mineralogy to the soils in the Huron watershed, but with different soil textures (Jin et al., 2008). The organic matter content decreased with depth in each monolith but reached up to 2 wt.% of dry weight at the uppermost horizons of the soil (Jin, 2007).

### 3.2. Water budget

Data on mean air temperature, total precipitation, Thornthwaite PET, long-term mean PET at KBS (30 years), and water infiltration (difference between

### Table 2
Basic climate information at KBS in the year of 2004

<table>
<thead>
<tr>
<th>Unit</th>
<th>Jan</th>
<th>Feb</th>
<th>Mar</th>
<th>Apr</th>
<th>May</th>
<th>Jun</th>
<th>Jul</th>
<th>Aug</th>
<th>Sep</th>
<th>Oct</th>
<th>Nov</th>
<th>Dec</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitation (P) mm</td>
<td>62</td>
<td>38</td>
<td>118</td>
<td>11</td>
<td>252</td>
<td>100</td>
<td>80</td>
<td>169</td>
<td>44</td>
<td>85</td>
<td>112</td>
<td>74</td>
<td>1145</td>
</tr>
<tr>
<td>Mean monthly temperature °C</td>
<td>−6</td>
<td>−2</td>
<td>6</td>
<td>12</td>
<td>17</td>
<td>20</td>
<td>23</td>
<td>21</td>
<td>19</td>
<td>12</td>
<td>6</td>
<td>−1</td>
<td></td>
</tr>
<tr>
<td>PET1 mm</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>41</td>
<td>83</td>
<td>140</td>
<td>180</td>
<td>142</td>
<td>80</td>
<td>40</td>
<td>10</td>
<td>0</td>
<td>721</td>
</tr>
<tr>
<td>PET2 mm</td>
<td>0</td>
<td>0</td>
<td>19</td>
<td>55</td>
<td>95</td>
<td>119</td>
<td>140</td>
<td>114</td>
<td>95</td>
<td>45</td>
<td>16</td>
<td>0</td>
<td>698</td>
</tr>
<tr>
<td>Discharge (P-PET1) mm</td>
<td>62</td>
<td>38</td>
<td>113</td>
<td>−30</td>
<td>169</td>
<td>−40</td>
<td>−100</td>
<td>27</td>
<td>−36</td>
<td>45</td>
<td>102</td>
<td>74</td>
<td>424</td>
</tr>
</tbody>
</table>

PET1 is potential evapotranspiration averaged from 30-year record.
PET2 is potential evapotranspiration calculated from Thornthwaite equation (Thornthwaite, 1948).
Monthly precipitation and temperature data are from a National Weather Service station at KBS.
precipitation and PET) are reported in Table 2. Monthly PET values show a seasonal cycle typical of temperate regions (Fig. 2), with PET exceeding precipitation throughout the warmer months while precipitation exceeds PET during the cooler months. Thus, recharge would normally be significant only in early spring and late fall, although it could also occur during a mid-winter thaw or after a particularly heavy rainfall in the summer. Negative infiltration values in Table 2 indicate a net loss of soil water to evapotranspiration, assuming that the plant canopy was fully developed so that evapotranspiration would reach its potential maximum. The bulk density of the Kalamazoo soils is around 1.7 g/cm³ (LTER site at KBS, unpublished data), which would require an approximate porosity of 30% given the mineral assemblages. Thus, the monolith is a large water reservoir (around 1600 L of water if saturated) and has a buffering capacity for the water budget. After a low moisture period, inputs by precipitation would have to re-wet the soils before any significant infiltration would commence. In 2004, an estimated 424 mm out of 1145 mm of precipitation (~37%) infiltrated the soils, and reached the water table to recharge the aquifer, ultimately discharging to streams. Water budget studies on a nearby sub-catchment within the Kalamazoo watershed showed that 580 mm of the annual precipitation (890 mm) was evapotranspired back to the atmosphere, with the rest (~35%) discharged by streams (Allen et al., 1972; Rheaume, 1990). Calculations of upland soil water balance from these two perspectives thus yield consistent annual evapotranspiration to precipitation ratios of ~65%.

Fig. 2. Variation of the mean monthly precipitation (P), air temperature (T) and potential evapotranspiration (PET) at KBS in year 2004. PET1 is monthly PET averaged from 30-year record at KBS, while PET2 stands for monthly PET calculated following Thornthwaite (1948).

Fig. 3. Br⁻ concentrations of soil solutions collected from soils less than 200 cm as a function of time after tracer application (A: monolith #2, B: monolith #6, C: monolith #9, and D: monolith #13). Breakthrough peaks arrived soon after the application of Br⁻ in the surface soils and arrived later in deeper soils as shown in monolith 6. Three replicate tension samplers at 180 cm deep at monoliths # 9 and #13 have different patterns of Br release, suggesting that flow paths through the soils are heterogeneous.
3.3. Conservative solute tracer experiment

The downward transport of bromide through the four monoliths was followed for several months after its application. Li⁺ was not detectable in any of these soil pore waters, in contrast to Br⁻. Both clay minerals and solid organic materials in the soils have negative surface charges, which permit the Li⁺ adsorption, while anions such as Br⁻ would not be affected. Compared to the concentrations resulting from the applied tracer solution, the baseline Br⁻ concentrations can be considered negligible. Patterns of Br⁻ concentrations over time for each monolith are shown in shallow soils (less than 200 cm; Fig. 3) and in drainage at the bottom (at 200 cm; Fig. 4). Even though the number of shallow soil water samples was limited by dry conditions, a general trend could be discerned. The tracer moved through the shallow soil layers (~25 cm–30 cm) very quickly, as evidenced by early sharp peaks in Br⁻ concentrations (Fig. 3), consistent with the very permeable nature of the sandy shallow soils. In monolith #6, Br⁻ concentration breakthrough peaks were observed from 4 depths in sequential order from shallow to deep (Fig. 3B).

The patterns of transport of Br⁻ into deeper soil horizons (below 100 cm) differed markedly among the monoliths. Even within a given monolith, soil waters sampled at the same depth (A, B and C at 180 cm) showed different patterns of Br transport over time (Fig. 3D). These differences were likely driven by heterogeneous soil flow paths. Arrival of Br⁻ peaks at the depth of 200 cm in the four monoliths exhibits complex temporal and spatial variation (see Fig. 4). The most rapid Br⁻ transport was observed in monolith #2. Concentrations of Br⁻ in monolith #13 showed an early peak immediately following tracer addition, and then decreased sharply. Following that, Br⁻ concentrations slowly increased again and showed another peak around 100 days after tracer application. In contrast, Br⁻ concentrations increased slowly in monoliths #6 and #9 and did not show peaks until 100 and 150 days, respectively, after the addition of the tracer. Daily precipitation data are presented in the insets of Fig. 4. Except for monolith #2, Br⁻ concentrations increased.
in the monoliths were sensitive to precipitation intensity. For example, between day 30 and day 60, there was no rain and \(\text{Br}^-\) concentrations remained unchanged. After day 60, heavy rain fell at KBS, and thereafter soil water \(\text{Br}^-\) concentrations increased in the drainage water (see insets of Fig. 4).

### 3.4. Soil water chemistry and soil zone pCO2

Chemical composition of soil waters from each monolith is reported in Suppl. Table 1, together with Na* concentrations and saturation indices with respect to calcite. The soil water data can be evaluated by ionic stoichiometry because soil water samples dominantly influenced by carbonate dissolution should lie on 2:1 relationship.
between concentrations of major divalent cation (Ca\(^{2+}\) + Mg\(^{2+}\)) and alkalinity in equivalents (Fig. 5A). The soil waters and ground waters from the neighboring Huron watershed in southeast Michigan (Jin et al., 2008) are also plotted in Fig. 5A for comparison. Inter-laboratory data quality comparison was made of analyses of replicate samples at the EAGL lab at the University of Michigan and Dr. S. Hamilton’s lab at KBS; over 90% of the major element concentrations agreed within 3%. The shallow soil waters (< 100 cm) were very dilute and alkalinity was less than 200 μeq/L. The dominant cations of these soil waters are Mg\(^{2+}\), Ca\(^{2+}\), K\(^+\), and Na\(^+\) with soil water Ca\(^{2+}\) concentrations were less than 600 μM and Mg\(^{2+}\) less than 300 μM (Fig. 5B). The pH values of soil solutions were generally lower than 7 in the shallow layers and increased to 7–8 below 150 cm depth. Soil waters at 180 cm collected by Prenart lysimeters and drip and tub samples at 200 cm were Mg\(^{2+}\)–Ca\(^{2+}\)–HCO\(_3^-\) dominated water (Fig. 5B; up to 700 μM Mg\(^{2+}\) and 2500 μM Ca\(^{2+}\)). The Ca\(^{2+}\) concentrations in drainage water from each of the monoliths show a similar seasonal trend, with maxima in September and minima in April (Fig. 6). Drip and tub samples collected on the same day had very similar Ca\(^{2+}\) concentrations during most of the year, except in the summer months when the soil moisture was low and water discharge was minimal. The Mg\(^{2+}\) concentrations in deep soil solutions showed the same trend as Ca\(^{2+}\) (Fig. 7B). In early spring, soil water Mg\(^{2+}\) and Ca\(^{2+}\) concentrations were about 300 μM and 1000 μM, respectively, while in summer and early fall months, Mg\(^{2+}\) and Ca\(^{2+}\) concentrations almost doubled. In contrast, Mg\(^{2+}\)/Ca\(^{2+}\) ratios were invariant throughout the year at around 0.3 (Fig. 7C).

**Fig. 7.** The soil gas pCO\(_2\) (A), soil water (drip water, 200 cm) Mg\(^{2+}\) (B), Mg\(^{2+}\)/Ca\(^{2+}\) molar ratios (C), H\(_4\)SiO\(_4\)^0 (D), Na\(^+\) (E), and Cl\(^-\) (F) as a function of time for each monolith.
these soils, the dominant sources of Mg$^{2+}$ and Ca$^{2+}$ were chemical weathering of carbonate minerals; Mg$^{2+}$/Ca$^{2+}$ ratios in the soil solutions reflected the relative contribution of calcite and dolomite dissolution to these two divalent cations. Mg$^{2+}$/Ca$^{2+}$ ratios of 0.3 would require roughly equal bulk molar contributions of calcite and dolomite dissolution.

$Na^*$ is defined as $Na^+$ concentrations in soil solutions after correcting for the atmospheric inputs according to the following equation:

$$Na^* = Na^+ - [Cl^- \times (Na^+/Cl^-)_{\text{precipitation}}]$$

(1)

In contrast to divalent cations, the shallow versus deeper soil waters do not significantly differ in $Na^*$ and silica ($H_4SiO_4^0$) concentrations (Fig. 5C) with $Na^*/$silica mole ratios less than 3. Seasonal variations of $H_4SiO_4^0$, $Na^*$, and Cl$^-$ concentrations in drainage soil solutions are plotted in Fig. 7D, E and F. Silica exhibits a pattern similar to divalent cations (Fig. 7D), with concentrations ranging from 60 to 140 $\mu$M. The Cl$^-$ concentrations were elevated somewhat in February and March. After that, Cl$^-$ concentrations decreased markedly and remained constant at around 20 $\mu$M for the rest of the year (Fig. 7F). Focusing on sodium data obtained after Cl$^-$ concentrations had stabilized, $Na^*$ concentrations increase gradually from April and reach a peak value of 140 $\mu$M in July, and decline to around 60 $\mu$M (Fig. 7E).

In addition to carbonate alkalinity, NO$_3^-$ and SO$_4^{2-}$ can also contribute significantly to the anion budget in soil solutions, with NO$_3^-$ concentrations ranging from 50 to 500 $\mu$M and SO$_4^{2-}$ from 100 to 200 $\mu$M. The NO$_3^-$ and SO$_4^{2-}$ concentrations in drip and tub samples are plotted with calendar year (Fig. 8A and B) because of the association of these anions with annual agricultural rotation at the sites. The NO$_3^-$ and SO$_4^{2-}$ concentrations show different temporal trends; with SO$_4^{2-}$ concentrations remaining almost constant over the year while NO$_3^-$ concentrations steadily decrease with time over the duration of this study.

Soil pCO$_2$ at KBS was higher than the atmospheric CO$_2$ partial pressure at all depths and on all collection dates (Table 3). Soil pCO$_2$ ranged from 1000 to 18,000 ppmv and fluctuated by about an order of magnitude over time at any particular sampling point. The soil pCO$_2$ generally increased with depth then remained constant at each soil profile, clearly indicating the effect of gaseous diffusion to atmosphere (Reardon et al., 1979; Bacon and Keller, 1998). Soil pCO$_2$ values at about 100 cm depth (the deepest gas samples available) are plotted in Fig. 7A, showing a strong correlation of pCO$_2$ with season. In the deeper soil layers of KBS, pCO$_2$ was about 50 times as high as atmospheric CO$_2$ in the summer. Even in the winter, soil pCO$_2$ was still 5 times higher than atmospheric CO$_2$ partial pressures, indicating that frozen ground and snow cover may impede gas exchange and maintain high pCO$_2$ values even in the absence of active respiration.

4. Discussion

4.1. Seasonal variation in solute concentrations

The complex nature of temperature and soil moisture controls on mineral weathering has been increasingly recognized (Velbel, 1993; Richards and Kump, 2003; Anderson, 2005). Temperature regulates dissolution rates according to the Arrhenius equation (a kinetic factor), but also modifies the solubility constants of minerals (a thermodynamic equilibrium factor). Temperature also exerts indirect controls on chemical weathering by modifying the biological activity, therefore the soil zone pCO$_2$ and biological sources of mineral acidity (e.g., respiration, nitrification). Precipitation dilutes the soil solutes and flushes water out of soil zones, thereby controlling dissolution rates through chemical affinity (saturation state) effects. Closer inspection of seasonal variations in soil
Table 3
Soil gas CO$_2$ concentrations at four monoliths of KBS

<table>
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<th>Monolith #6</th>
<th>Monolith #9</th>
<th>Monolith #13</th>
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water and gas chemistry allows identification of key reaction controlling factors.

To quantify the ion fluxes under different environmental conditions, one must consider whether natural waters have reached equilibrium with the primary or secondary minerals. If chemical equilibrium is attained, the water composition would depend on the phases and thermodynamic properties of secondary minerals, and weathering fluxes should be a simple function of water discharge and elemental solubility. If, on the other hand, the system is far from chemical equilibrium, the evolution of water composition will be rate-limited and vary with kinetic-related factors such as time, mineral surface area, mineral reactivity, pH regime, and chemical affinity. The responses of solute concentrations to varying soil moisture conditions provide an indication of kinetic versus equilibrium control on weathering rates.

Some studies of stream water chemistry report power law relationships between ion concentrations (such as Ca\(^{2+}\) and Mg\(^{2+}\)) and discharge, showing variations over time as streams carry variable mixtures of precipitation, surface runoff, and shallow and deep ground water (e.g., Hooper et al., 1990; Kirchner, 2003). Others have observed that concentrations of divalent cations vary little with discharge for carbonate mineral-dominated watersheds (Williams et al., 2007b; Szramek et al., 2007). On a larger scale, differences in stream water chemistry could also reflect changes in relative contributions from different areas with different lithology (e.g., Tipper et al., 2006). Solution chemistry in a soil depth profile, in contrast, depends only on the direction and rate of chemical reactions along a defined flow path influenced by a relatively stable mineralogical assemblage (Wolt, 1994). With frequent sampling of soil waters and discharge measurement from the soil monoliths, we aimed to understand the chemical weathering mechanisms and to calculate reaction rates.

About 37% of the 1145 mm of precipitation infiltrated the soil monoliths and was thus available for ground water recharge (see Fig. 2 and Table 2). Given the dimensions of the monoliths, this would equal a discharge of 1185 L for the year 2004. Field water-flow rates are listed for all four monoliths for the first 3 months of the tracer experiments (Table 4). Discharge peaks followed rainfall intensity closely, with a lag time of less than 15 days. As expected, instantaneous and average flow rates can differ significantly, indicating variable discharge on even a weekly timescale. Drip and tub soil water samples had very similar Ca\(^{2+}\) and Mg\(^{2+}\) concentrations, except for the summer months (Figs. 6 and 7B and Suppl. Table 1). The Ca\(^{2+}\) and Mg\(^{2+}\) concentrations did not change with drainage discharge, suggesting that carbonate-mineral weathering was not controlled by soil moisture or infiltration rates but by mineral solubility, consistent with results from riverine flux studies in carbonate-bearing watersheds (e.g., Szramek et al., 2007). Concentrations of silica and other silicate-weathering derived cations (such as Na\(^{+}\)) (Fig. 7D and E) decreased moderately during the major snowmelt event in the middle February of 2004 but generally varied little with discharge. This suggests that instead of the power law relationship reported for riverine silicate-weathering fluxes, chemical weathering in these soil profiles appears to be the first-order control on water chemistry, consistent with results from Clow and Drever (1996).

4.1.1. Na\(^{+}\) and Cl\(^{−}\) variation: atmospheric contributions and evapoconcentration

Because Cl\(^{−}\) is not a product of chemical weathering of native soil minerals nor is it influenced by biological activity, it can serve as a conservative tracer for hydrological processes (e.g., Quade et al., 2003; West et al., 2005). After the initial snowmelt input, concentrations of Cl\(^{−}\) in the four monoliths showed little seasonal variability, demonstrating that evapotranspiration is not responsible for the increases in concentrations of major
cations and silica observed during the warmer months (Fig. 7F). Similar conclusions were also reached by White et al. (2005b) in silicate-rich Merced soils of Central California. Thus, the fluctuations in major solute chemistry of the soil solutions may be attributed directly to seasonal variation in chemical weathering processes.

The elevated soil water Cl$^-$ and Na$^+$ concentrations observed in February and March likely result from elution of snowpack solutes, presumably deposited via wet or dry atmospheric deposition. NADP data also show that Na$^+$ and Cl$^-$ concentrations in wet precipitation tend to be highest in the winter/spring and lowest in the summer. Comparison of the rainfall chemistry among different stations in Michigan along a N–S gradient (the Tahquamenon watershed in Upper Peninsula, the Muskegon watershed at northern Lower Peninsula and the Kalamazoo watershed of this study in southern Lower Peninsula) showed that Na$^+$ and Cl$^-$ concentrations decreased in the watersheds from the north to south in the winter/spring, but they were very similar in the summer (Suppl. Table 2). Thus, the different Na$^+$ and Cl$^-$ concentrations observed in the rainfall during winter/spring among these watersheds are probably explained by atmospheric inputs of deicing salts from local sources. In the Upper Peninsula of Michigan, population density is low and deicing salts are not applied as frequently and over as large an area compared to the Lower Peninsula. But in the summer, the atmospheric source of dissolved solutes is similar for all of Michigan; therefore, there is no difference in rainwater Na$^+$ and Cl$^-$ concentrations among these three watersheds.

### 4.1.2. Soil water Ca$^{2+}$ and Mg$^{2+}$, carbonate-mineral dissolution, and soil zone pCO$_2$

When present in soils, carbonate minerals are the dominant contributors of Ca$^{2+}$ and Mg$^{2+}$ (Caroll, 1970; Horton et al., 1999; Jacobson et al., 2002, 2003; White et al., 2005a; Jin et al., 2008). Saturation indices of soil solutions with respect to calcite and dolomite are plotted in Fig. 9. All the soil solutions collected by Prenart lysimeters from the 180 cm depth were near equilibrium with respect to calcite (SI=0.0±0.5) and undersaturated with respect to dolomite (SI=−1.0±0.5), and neither SI varied much with season (Fig. 9A and B). In contrast, the saturation indices of drip soil solutions from 200 cm depth showed seasonal variation, tending to be oversaturated with respect to calcite in the summer and fall months (Fig. 9C and D). This difference between Prenart and drip samples may be attributed to more rapid degassing of the CO$_2$ from the drip samples thereby increasing calcite saturation state. Oversaturation reached maximum values in the summer months, when soil CO$_2$ greatly exceeded atmospheric CO$_2$. In contrast, Prenart samplers are isolated from the atmosphere before sampling and most likely provide the best measure of in-situ saturation indices for soil waters. The tub samples had even longer exposure time to air before collection, which could lead to higher oversaturation and calcite precipitation, consistent
with the lower Mg$^{2+}$ and Ca$^{2+}$ concentrations observed in the tub relative to drip samples in the summer months. The constant saturation indices of carbonate minerals throughout the year also suggest that soil waters became saturated with respect to carbonate minerals rapidly tracking large seasonal variations in pCO$_2$.

Considering that all of the Prenart soil water samples had similar saturation indexes, the changes in Ca$^{2+}$ and Mg$^{2+}$ concentrations reflect the seasonal variation of calcite and dolomite solubility, which decreases with increasing temperature and increases with increasing pCO$_2$. Thus, higher Ca$^{2+}$ and Mg$^{2+}$ concentrations of the drainage water in the summer must be related to the seasonal increase in soil pCO$_2$, which in turn is related to seasonal variation in soil temperature (Fig. 7A). Microbial and root respiration are the major processes that regulate the daily and long-term soil CO$_2$ and they are temperature-dependent and, in the case of roots, linked to the seasonal growth cycle of the plants.

Equations have been proposed by previous studies to predict soil pCO$_2$ levels based on air temperature (e.g., Brook et al., 1983; Drake, 1983; Wood et al., 1993; Andrews and Schlesinger, 2001; Hui and Luo, 2004). Anderson et al. (2003) studied stream waters in Alaska and found a positive correlation between calculated pCO$_2$ and the amount of calcite dissolved per liter even though pyrite dissolution contributed more than 10% of protons. The most common and consequential effects on soil-solution pH arose from the aqueous phase distribution of inorganic carbon species and the gas-phase/liquid-phase partitioning of CO$_2$. The pH values of the Prenart soil solutions ranged from 7.5 to 8.2 and showed an opposite seasonal trend compared to the soil pCO$_2$. This agreed with the general trend of modeled pH values assuming soil solutions are saturated with measured soil pCO$_2$ and calcite, where a ten-fold increase in pCO$_2$ results in a full unit decrease in soil-solution pH. The solubility of carbonate minerals decreases with increasing temperature, and this direct effect of temperature is therefore secondary to the temperature-dependent pCO$_2$ in affecting carbonate dissolution and soil-solution pH.

4.1.3. Sources and reactivity of NO$_3^-$ and SO$_4^{2-}$

The NO$_3^-$ concentrations decreased in drainage water over the course of this study (Fig. 8A). The decrease in NO$_3^-$ since 2003 corresponds to the corn (2002)–soybean (2003)–wheat (2004) crop rotation cycle, because soybeans tend to increase soil nitrogen contents by biological N$_2$ fixation. Nitrification produces soil nitrate and denitrification removes it. Thus, NO$_3^-$ leaching depends on the balance of plant demands and these two microbially mediated processes. In previously studied forested sites of
the Huron watershed, soil-solution NO₃⁻ concentrations were much lower than in the four monoliths (shaded area in Fig. 8A; data from Jin, 2007). The high SO₄²⁻ concentrations were relatively constant throughout the year (Fig. 8B). One study in this area showed that dry and wet deposition together only contributed about 18% of the SO₄²⁻ in the streams (Rheaume, 1990). Pyrite dissolution must be a significant SO₄²⁻ source, as Marshall Sandstone is enriched in sulfide minerals such as pyrite. The streams in the Kalamazoo watershed had been shown to have much higher SO₄²⁻ concentrations than those in other Michigan watersheds, because of the existence of shallow subcropping of the Marshall sandstone beneath glacial drift (Szramek et al., 2007).

In soil monoliths, nitric and sulfuric acids can become a major driver of chemical weathering reactions and an important component in anion charge balance (Fig. 5A). These strong acids could react with carbonate minerals to produce either CO₂ or HCO₃⁻, which is an important process for atmospheric CO₂ cycling (Spence and Telmer, 2005; Hamilton et al., 2007).

4.2. Controls on chemical weathering of carbonates and silicates

4.2.1. Soil exchangeable cation pool and its equilibrium with soil solutions

Seasonal variation in concentrations of major solutes (Ca²⁺, Mg²⁺ and silica) was observed at the study sites, while Mg²⁺/Ca²⁺ molar ratios remained constant throughout the year (Figs. 6 and 7). Similar seasonal trends in concentrations but with constant ratios between divalent cations and between univalent cations have been observed in other soil water and stream water studies (Berner et al., 1998; Grasby et al., 1999; White et al., 2005b). At the Hubbard Brook Experimental Forest (New Hampshire, USA), positive correlations were found between soil water Ca²⁺ and Mg²⁺ concentrations as well as between Na⁺ and K⁺ concentrations, and this was interpreted as control by equilibria between the very dilute soil solutions and an exchangeable pool associated with clay and organic matter (Berner et al., 1998). A clear sinusoidal trend was apparent for silica, Ca²⁺ and K⁺ over an annual cycle, which was interpreted as being related to the acid production in the soil as a function of temperature. Another possible explanation, the effect of varying temperature on the rate of release of cations and silica from primary mineral dissolution, was refuted because no similar seasonal variation of HCO₃⁻ was observed. White et al. (2005b) also emphasized cation exchange capacity in the control of soil-solution Mg²⁺/Ca²⁺ ratios, although that study examined relatively clay-rich soils in central California.

At our study sites, no linear correlation was observed between K⁺ and Na⁺, or between Na⁺ and Ca²⁺ in our more concentrated soil solutions. Furthermore, the clay fraction was dominated by quartz and only significant in the first 90 cm, with soils becoming sandy below this depth. Another component of the soil cation exchange complex, organic matter, was only abundant at the top 30 cm of these soils. The sharp increase in divalent cation concentrations occurred right below the carbonate layer (150 cm), below the zone of potential control by the cation exchange pool. Taken together, these indicate a very minor role for soil cation exchange processes in the soil water solute budgets for the soil monolith at KBS.

4.2.2. Dolomite versus calcite dissolution

The Mg²⁺/Ca²⁺ molar ratios of soil waters at KBS are about 0.3, lower than those of soil waters and ground waters in the Huron watershed and also lower than those of streams in the Kalamazoo watershed (Fig. 10; Szramek et al., 2007; Hamilton et al., 2007; Jin et al., 2008). This cannot be explained by cation exchange processes as previously discussed, nor by lower Mg²⁺ contribution from silicate dissolution, as amphibole contents and soil water Mg²⁺ concentrations in shallow carbonate-free soil zones were similar between KBS and the Huron watershed (Table 1; Jin et al., 2008). Thus, lower Mg²⁺/Ca²⁺ ratios reflect a proportionately smaller contribution from dolomite dissolution relative to calcite, even though similar amounts of dolomite and calcite are present in all southern Michigan soils. This is consistent with the fact that Prenart soil water samples were still

![Fig. 10. Evolution paths of soil water chemistry (Ca²⁺ and Mg²⁺) by carbonate dissolution. Ranges of the soil waters and the ground waters from the Huron watershed and stream waters from the Kalamazoo watershed are shown for comparison (data from Jin et al., 2008; Szramek et al., 2007). See text for discussion of the two-stage evolution of carbonate weathering reactions.](image_url)
undersaturated with respect to dolomite but at equilibrium with calcite.

Theoretical models have been presented previously to reconstruct evolution paths of soil water chemistry under the influence of carbonate dissolution and to evaluate dolomite versus calcite dissolution kinetics in systems open to CO$_2$ (Jin et al., 2008). As shown in Fig. 10, these models include two stages: first, calcite and dolomite dissolve at a certain rate and soil water reaches equilibrium with calcite but remains undersaturated with dolomite; second, dolomite continues to dissolve to equilibrium, driving calcite to supersaturation. Model results indicated Mg$^{2+}$/Ca$^{2+}$ ratios of the soil waters depend dominantly on the relative dissolution rates of calcite and dolomite and the progress of hydrogeochemical evolution of the system. Soil waters in the Huron watershed have reached the second stage in their evolution, and similar dolomite and calcite dissolution rates were required (Jin et al., 2008). Soil waters at KBS are at equilibrium with calcite, suggesting that carbonate dissolution at KBS has only evolved to the first stage, and Mg$^{2+}$/Ca$^{2+}$ ratios of ~0.3 require similar dolomite and calcite dissolution rates, as in the Huron watershed. Model results at the end of stage one would produce a saturation index of dolomite around ~0.4, consistent with those calculated for KBS soil waters (Fig. 9D).

Therefore, both theoretical models and water chemistry suggest that at KBS dolomite dissolution has not reached equilibrium within the soil zones and will continue to evolve chemically in deeper soil zones and/or below the water table. This is consistent with the higher Mg$^{2+}$/Ca$^{2+}$ ratios observed in surface waters of the Kalamazoo watershed (Fig. 10; Szramek et al., 2007). We attribute different carbonate dissolution scenarios between KBS and the Huron watershed to the shorter contact time of dolomite and soil waters at KBS, due to both the coarser soil textures and the shorter carbonate-bearing soil column path length exposed to dolomite dissolution before water exits the monoliths.

4.2.3. Residence time of water in the soil column

Solute transport in soil media can be conceptualized as consisting of variable proportions of preferential flow and piston flow. In a preferential flow-dominated profile, well-connected macropores form flow channels. Solutes in flow channels are rapidly transported downward preferentially while those in the surrounding matrix (micropores) are transported only after encountering a flow channel (Harrington and Bales, 1998; Feng et al., 2001). Profiles of Br$^-$ in monolith #2 clearly exhibit preferential flow (see Figs. 3 and 4) where Br$^-$ peaks in drainage water arrive immediately after tracer application and thereafter, Br$^-$ concentrations decreased regardless of infiltration rate. The CO$_2$ profile is governed by production rates, diffusion upward to atmosphere and advective transport downward by fluids. Soil CO$_2$ and soil water are more easily moved in a well-connected channel than in the isolated matrix, and this may be the reason that pCO$_2$ concentrations and soil water Ca$^{2+}$ concentrations are the lowest in monolith #2. In piston flow, water progressively migrates through the medium, carrying solutes down the hydraulic head gradient (Hibberd, 1984) with channel and lateral flow relatively insignificant. This pattern of transport is well illustrated by monoliths #6 and #9 (see Fig. 4) where increases in Br$^-$ concentrations in drainage waters coincide with rain events.

The Br$^-$ recovery after 1 year was calculated based on the following equation:

$$\text{Recovery} = \frac{\sum ([Br]_t \times V_{H_2O})}{[Br]_{total}}$$

(2)

While $[Br]_t$ is the concentration of Br$^-$ in the tub at time $t$, $V_{H_2O}$ is the volume of the water recorded from $t - 1$ to $t$, $t$ is the number of days since tracer injection, and $[Br]_{total}$ is the total amount of Br$^-$ applied. The buckets overflowed during high rainfall events and the volume of the bucket was used for the calculation, which should underestimate the recovery rate. Approximately 40% of Br$^-$ was recovered from monoliths #2, #9 and #13 and only 16% of Br$^-$ was recovered from monolith #6. Using the amount of Br$^-$ recovered, and Br$^-$ concentration/time data, the residence time of Br$^-$ was calculated based on the following equation:

$$\text{Residence time} = \frac{\sum ([Br]_t \times V_{H_2O} \times t)}{\sum ([Br]_t \times V_{H_2O})}$$

(3)

The residence time of recovered Br$^-$ in these monoliths ranged from 43 to 160 days (Table 5). Because more than half of the Br$^-$ was retained in the soil profile after 1 year, it is reasonable to assume that residence time for all the Br is two or more years. Soil texture affects waterflow patterns as well as residence time of solutes in a soil

<table>
<thead>
<tr>
<th>Monolith</th>
<th>Recovery (%)</th>
<th>Residence time (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#2</td>
<td>45.0</td>
<td>43.4</td>
</tr>
<tr>
<td>#6</td>
<td>15.8</td>
<td>162.7</td>
</tr>
<tr>
<td>#9</td>
<td>44.3</td>
<td>156.8</td>
</tr>
<tr>
<td>#13</td>
<td>40.9</td>
<td>109.3</td>
</tr>
</tbody>
</table>

* Residence time of Br is calculated only for recovered Br. The actual residence time of Br should be much longer than this.
profile. Residence time affects the proportion of soil water that is lost to evapotranspiration versus infiltrated downward into the ground water reservoir.

Residence time is also a very important determinant of water/rock interaction, controlling whether mineral equilibrium can be attained in the soil zone. This is particularly important for the silicate minerals that react much more slowly than do carbonate minerals (Gilbert, 1877; Carson and Kirkby, 1972; Heimath et al., 2001; Gabet et al., 2006). Previous studies have shown that soil waters in micropores and macropores have very different major solute compositions (Richards and Kump, 2003). However, the residence time is defined as the average time the bromide tracer stayed over the whole 200 cm soil profile. KBS soils tend to be heterogeneous; soils from O-, A- and C-horizons are sandy loams and loams, while B-horizons have a much higher clay content. Thus, it is reasonable to assume that water resides in the first 150 cm for most of the time, flowing rapidly out of the more permeable deeper C-horizon. This textural difference could explain why dolomite which occurs only in the C-horizon can remain undersaturated despite the long average water residence time.

4.2.4. Silica, Na* and silicate weathering

The Na* value is a proxy for plagioclase dissolution because plagioclase is the only significant mineral source of Na in these soils. Amphibole can contain small amounts of Na (less than 1 wt. %), averaged from semi-quantitative EDX-SEM analysis. Given that amphibole is less abundant but has similar reactivity to plagioclase (Blum and Stillings, 1995), the contribution of Na from amphibole dissolution is relatively minor. In calculation of soil water Na*, Na*/Cl− ratios of the wet precipitation were averaged over 1 year, and this seasonal variation is the major source of error according to Eq. (1) (about 17 μM). As the study area is more than 300 m away from the road, the direct efflux of road salt is minimum, and the elevated Cl− is due to wet/dry precipitation as discussed in previous Section 4.1.1. Silica in the soil solutions must have been produced mainly by the dissolution of the silicate minerals plagioclase, mica and amphibole because quartz and K-feldspar react much more slowly. The molar ratio of soil-solution silica to Na* concentration is less than 3, requiring stoichiometric loss of silica (Fig. 5C). Silicates dissolve incongruently, with gibbsite stable at low silica concentrations (<20 μM) and kaolinite and smectite at progressively higher silica concentrations (Bricker and Garrels, 1965; Helgeson et al., 1969; Colman and Dethier, 1986; White and Blum, 1995; Berner and Berner, 1996). At KBS, silica concentrations range from 60 to 140 μM, placing soil waters within the stability field of kaolinite, similar to previously studied Michigan watersheds (Jin et al., 2008). Soil waters at KBS were generally undersaturated with respect to plagioclase and amphibole, but oversaturated with kaolinite. Thus, the seasonal variation of silica observed in the KBS soil waters is not solely controlled by silicate dissolution but also by precipitation of secondary minerals. Mineral saturation state results show that kaolinite was less oversaturated in the summer months even though silica concentrations were higher and kaolinite solubility was lower at this time. This is probably due to the lower pH caused by higher pCO2 values in the summer. Since the kinetics of kaolinite precipitation are complicated and poorly studied in soils, the variation of silica concentrations with season cannot be ascribed to a single reaction mechanism.

Silica concentrations and fluxes have been used as proxies of silicate-weathering intensity in riverine systems (Bluth and Kump, 1994; White and Blum, 1995; White et al., 1999). However, silica fluxes are complicated by potential silica consumption (e.g., in-river processes such as uptake by diatoms and kaolinite precipitation) (Meybeck, 1987; Velbel, 1989; Berner et al., 1998; Huh et al., 1998; Miretzky et al., 2001; Pawellek et al., 2002). Also, silica is involved in biogenic cycles of terrestrial environments, which is a sizable pool of Si (Conley, 2002). Dissolved silica also forms complexes with dissolved organic molecules, increasing its solubility (Gérard et al., 2003). Taken together, stream water and soil water silica concentrations in Michigan can only provide a minimum estimate for silicate-mineral weathering rates.

Concentrations of Na* decreased only slightly in response to the increasing mean seasonal drainage rate (Fig. 7E), indicating that geochemical processes in the soil tend to mitigate the dilution effect attributable to precipitation inputs. The higher Na* concentrations observed in the summer months could result from elevated plagioclase dissolution rates associated with high pCO2 and/or high temperature. Decreases in soil pH caused by increased pCO2 may not in themselves influence silicate dissolution rates because experiments have shown that reaction rates are invariant between pH 5 and 8 (e.g., Oelkers et al., 1994; Oelkers and Gislason, 2001). The effect of pCO2 on silicate weathering, therefore, may be indirect, from the CO2 fertilization of organic activity and chelating of Al by carbonic ions (Brady and Carroll, 1994; Berg and Banwart, 2000).

As previously stated, residence time of solutions in the soils might be sufficient for solute concentrations to build up enough to decrease the dissolution rates via a
chemical affinity effect (Clow and Drever, 1996). Soil water Na⁺ at KBS ranged from 40 to 120 μM, slightly lower than those in the Huron watershed (50–150 μM; Jin et al., 2008). Plagioclase in the KBS soils is also slightly less abundant than in soils of the Huron watershed, based on Na₂O wt.% in bulk soil. This agrees with our previous observation that silicate weathering is primarily controlled by mineral contents, and specifically by weathering surface areas.

4.3. Mineral weathering rates from solute fluxes and from soil mass balance

4.3.1. Short-term weathering rates from solute fluxes

Szramek and Walter (2004) showed that most streams draining glaciated watersheds in southern Michigan are too contaminated by road deicing salts to evaluate silicate-weathering contributions to the overall cation fluxes. A similar study was made of riverine Na⁺ fluxes in two northern Michigan watersheds, where pollution was at minimal values due to extremely low population densities (Williams, 2005). Here, silicate-weathering fluxes were in the upper range of those reported by White and Blum (1995) in the streams draining granitoid watersheds, even though mean annual temperatures were relatively low in northern Michigan (Williams, 2005). The results presented here from the soil monolith studies permit evaluation of silicate-weathering fluxes from the Kalamazoo watershed, typical of southern Michigan landscapes, because of the availability of soil water budgets. To compare the Kalamazoo watershed silicate-weathering rates with prior studies, elemental fluxes via chemical mass balance: 1300 mol ha⁻¹ yr⁻¹ from Na⁺ fluxes.

Glacial drift deposits typically host unconfined aquifers with close hydrogeochemical links between soil waters and ground water/surface water systems (e.g., Szramek and Walter, 2004; Williams et al., 2007b) and soil zone processes can exert strong controls on surface water chemistry. Previous studies have shown that soil Na⁺ concentrations in several Michigan watersheds increase sharply in shallow soil horizons and then remain relatively constant with depth, suggesting that silicate weathering occurs early in the soil water column with carbonate weathering proceeding at greater depths (Williams et al., 2007a; Jin et al., 2008). High DOC concentrations and low pH values of the shallow soil waters also favor silicate hydrolysis reactions (e.g., Oelkers et al., 1994; Williams et al., 2007a; Jin, 2007). The Br tracer results presented earlier estimate solute residence time in the monoliths to be long, allowing slow kinetic silicate dissolution reactions to proceed towards equilibrium. Once the carbonate-mineral dissolution starts in the deeper soil profile, soil water pH increases and DOC decreases rapidly, both preventing further silicate-mineral dissolutions. Thus, short-term weathering rates derived from the soil monoliths studies are good estimates of silicate-weathering fluxes and they are especially valuable in watersheds like the Kalamazoo where stream water chemistry cannot be used to compare directly to riverine watershed-scale cation flux data (e.g., White and Blum, 1995).

The Na⁺ fluxes in this study are plotted versus annual runoff in Fig. 11A, as well as data from granitoid watersheds in eastern North America compiled by White and Blum (1995) and from two northern Michigan watersheds by Williams (2005). The contribution of runoff (x axis) and the volume-weighted Na⁺ concentrations (slopes) to the overall cation fluxes can be evaluated from these relations. Regardless of glacial history, plagioclase-weathering rates are much lower in the watersheds with extremely low mean annual temperature (e.g., Rawson Lake, Exp. Lake, and Loch Vale watersheds) and higher in the warmer watersheds (e.g., Coweeta and Panola watersheds). Mineral surface areas from modern glacial environments are shown to be enhanced by glacial abrasion, but relative silicate-weathering rates still are low due to the extremely low temperature in the vicinity of the glaciers (Anderson, 2005).

Williams et al. (2007a) compared soil-solution chemistry in natural and experimental soils profiles developed on Pleistocene glacial drift in the same Michigan

<table>
<thead>
<tr>
<th>Table 6A</th>
<th>Cation fluxes and short-term mineral weathering rates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Species of interest</td>
<td>Fluxes (mol ha⁻¹ yr⁻¹)</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>5500</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>1700</td>
</tr>
<tr>
<td>K⁺</td>
<td>210</td>
</tr>
<tr>
<td>Na⁺</td>
<td>250</td>
</tr>
<tr>
<td>H₂SiO₄</td>
<td>340</td>
</tr>
</tbody>
</table>

Water discharge = 1185 L yr⁻¹.

<table>
<thead>
<tr>
<th>Table 6B</th>
<th>Long-term plagioclase-weathering rates (soil age = 12.5 ka)</th>
</tr>
</thead>
<tbody>
<tr>
<td>By Zr mass balance:</td>
<td>2400 mol ha⁻¹ yr⁻¹</td>
</tr>
<tr>
<td>By Ti mass balance:</td>
<td>1300 mol ha⁻¹ yr⁻¹</td>
</tr>
</tbody>
</table>

Long-term weathering rates are calculated based on data in Table 1; see text for details.
watershed. Here, plagioclase dissolution rates were accelerated in disturbed experimental soils. It was further suggested that the disturbed soils allowed more reactive mineral surface to be exposed, analogous to soils in glaciated regions (Williams et al., 2007a). Jin et al. (2008) compared soil water Na concentration in three Michigan watersheds along climate and lithology gradients, and showed that plagioclase weathering is most intensive in the Huron watershed which also has the highest abundance of plagioclase in the soils. In the soil monoliths of the Kalamazoo watershed, glacially derived mixed mineralogy sediments are weathered at relatively high mean annual temperature, both of which favor rapid silicate weathering. Thus, as shown in Fig. 11A, the high weathering rates combined with high mean annual precipitation make the Na+ fluxes from the mid-continent region among the largest short-term fluxes in the eastern USA region.

Although up to 10% of the soil water Ca2+ and Mg2+ can be provided from silicate dissolution in glacial drift soil profiles in Michigan (Jin et al., 2008), silicate weathering introduces little uncertainty in calculating carbonate dissolution rates from divalent cation fluxes. Following these estimates, 90% of Ca2+ and Mg2+ fluxes are used herein to calculate calcite and dolomite weathering rates (calcite: 3400 mol ha\(^{-1}\) yr\(^{-1}\); dolomite: 3100 mol ha\(^{-1}\) yr\(^{-1}\)). Carbonate weathering rates are primarily controlled by pCO2-dependent solubility and annual discharge in soil monoliths, in agreement with surface water fluxes calculated in Michigan streams (Szramek and Walter, 2004; Williams et al., 2007b; Szramek et al., 2007).

The monoliths studied are manipulated agricultural sites, and surface soils have been cultivated since 1987. Compared to the natural forests, soil solutions here are high in nitrate concentrations, which lower the soil water pH and potentially accelerate the leaching of major cations. Thus, the short-term weathering rates calculated from Na-fluxes may have been slightly overestimated relative to those in natural environments.

4.3.2. Long-term plagioclase-weathering rates from soil elemental mass balances

Elemental inventories in soil profiles reflect loss of cations over the thousands of years required for soil development and thus can estimate long-term weathering rates by both physical and/or chemical erosion (e.g., Taylor and Blum, 1995; White et al., 1996; Bain et al., 2001; White, 2002; Nezat et al., 2004; Price et al., 2005). This method assumes the following mass balance relationships (Brimhall and Dietrich, 1987; Chadwick et al., 1990):

\[
m_W C_{j,W} = m_P C_{j,P} + m_{j,\text{flux}}
\]

where \(m\) is the mass of soil, \(C_j\) is the concentration of element \(j\) in the soil, and subscripts \(P\) and \(W\) indicate parent material and weathered soil. Because there is little topographic relief in the vicinity of the soil monoliths it is reasonable to assume that elements leave the profile only
through chemical weathering. In Eq. (4), \( m_{j,\text{flux}} \) is the amount of element \( j \) that is lost (or gained) in soil profiles and is defined as zero for immobile elements such as Ti and Zr. Thus, Eq. (4) can be simplified and the variation of soil mass be evaluated (Zr as an example):

\[
m_p = m_w C_{Zr,w} / C_{Zr,p}
\]

(5)

If \( m_p \) in Eq. (4) is replaced by Eq. (5), the amount of element that is lost from soils can be calculated as:

\[
m_{j,\text{flux}} = m_w (C_{j,w} - m_p C_{j,p}) = m_w (C_{j,w} - C_{j,p} C_{Zr,w}/C_{Zr,p})
\]

(6)

where mass of the soils can be calculated by \( Z_w \) and \( \rho_w \), thickness and density of the soils:

\[
m_w = Z_w \rho_w
\]

(7)

Some soil development has been shown to be isovolumetric and thus the thickness does not change during conversion from parent materials to soil profiles (\( Z_p = Z_w \); White et al., 2005b). Because up to 30 wt.% of carbonate minerals originally present in soils have been removed by dissolution (Table 2), iso-volumetric development of the soil profile could not be assumed in Michigan. For example, soils developed in karst regions of south China have been shown to collapse by almost 100% (Ji et al., 2004). The amount of volume loss relative to the parent material can be evaluated by the following equation:

\[
Z_p \rho_p C_{Zr,p} = Z_w \rho_w C_{Zr,w}
\]

(8)

Rearranging gives:

\[
Z_w / Z_p = \rho_p C_{Zr,p} / \rho_w C_{Zr,w}
\]

(9)

The volume change factor (\( Z_w/Z_p \)) is much less than 1 in the KBS soil profiles (Table 1), indicating that significant volume loss must be considered to arrive at valid long-term weathering fluxes from these carbonate-rich soils.

Because \( C_{j,w} \) varies with soil depth, the weathered soil zone is divided into discrete layers and the total elemental loss is integrated over the entire soil column. Ti and Zr are commonly used as examples of immobile elements and they mainly occur in soils as stable accessory minerals ilmenite and zircon. Using the calibrated \( Z_p \) values from Eq. (9) yields long-term plagioclase-weathering rates based on Ti and Zr mass balances of 1300 and 2400 mol ha\(^{-1}\) yr\(^{-1}\) respectively (see Table 6B). Zr/Ti (as TiO\(_2\)) ratios are constant at the two deepest soil samples (including the parent material at 190 cm), but are much higher in the shallow weathered soils, indicating that Ti has been preferentially removed via chemical weathering relative to Zr (Table 1). Because ilmenite is less stable in surface environments, plagioclase-weathering rates derived by Zr concentrations may be more accurate, than those derived from Ti mass balance.

The long-term plagioclase-weathering rates calculated from soil mass balance are about 8 times the present weathering rates calculated from solute chemistry and fluxes (24000 vs. 320 mol ha\(^{-1}\) yr\(^{-1}\)). This is in agreement with the general trend that weathering rates decrease as a soil profile develops (Taylor and Blum, 1995). Silicate-weathering rates diminish over time due to the loss of reactive minerals and fresh mineral surfaces, partly due to development of Al- or Si-rich leached layers or further deposition of secondary Al and Fe oxyhydroxides at the mineral surfaces (e.g., Bain et al., 1993; Taylor and Blum, 1995; White and Brantley, 2003).

In Fig. 11B, long-term Na loss (proportional to plagioclase-weathering rates according to the An content of the plagioclase) is plotted versus soil ages. Also presented are data from Wind River Mountain (Wyoming), Panther Lake (New York), Plastic Lake (Ontario) and Hubbard Brook (New Hampshire) (April et al., 1986; Kirkwood and Nesbitt, 1991; Bain et al., 1993; Taylor and Blum, 1995; Nezat et al., 2004). A power law relation between plagioclase-weathering rates and soil age is observed for these sites collectively (Nezat et al., 2004). The plagioclase dissolution rate in Kalamazoo soil is significantly higher than those in other watersheds of the same age.

There are differences among the watersheds in terms of climate and parent materials. Relative to the localities shown in Fig. 11B, the Kalamazoo watershed is in the upper range of mean annual temperatures, and is mid-range in terms of precipitation. The sedimentary rock sources for Michigan glacial drift soils likely increase the weathering rates due both to particle surface areas and high plagioclase abundances. This would be consistent with the observations from current silicate-weathering rates as well. Additional study of silicate-weathering rates in mixed mineralogy, sedimentary sourced profiles would be required to quantify how important each of these variables is in controlling short- and long-term rates.

5. Conclusions

Soils, soil waters and gases were characterized in soil monoliths at the KBS LTER agricultural site (SW Michigan) to study chemical weathering processes during the initial contact of infiltrating waters with soils and underlying glacial drift materials. Soil solutions attained a strong signature of carbonate-mineral
weathering by a depth of 200 cm, and Ca\(^{2+}\) and Mg\(^{2+}\) concentrations reflected roughly equal contributions from calcite and dolomite dissolution with little addition by silicate-mineral weathering. Frequent sampling has illuminated temporal variations of soil gas pCO\(_2\) and soil water Ca\(^{2+}\) and Mg\(^{2+}\), with concentration maxima in the summer and minima in the winter. Carbonate weathering reactions are sufficiently rapid that soil waters have equilibrated with calcite but remained slightly undersaturated with respect to dolomite by 50 cm below the upper extent of carbonates.

The saturation states of calcite and dolomite changed little throughout the year and did not vary with precipitation intensity, implying first-order control of Ca\(^{2+}\) and Mg\(^{2+}\) concentrations by carbonate-mineral solubility. Thus, higher carbonate solubility and resultant higher Ca\(^{2+}\) and Mg\(^{2+}\) concentrations in the soil solutions during the warm season were related to temperature-dependent soil pCO\(_2\). Soil water Mg\(^{2+}\)/Ca\(^{2+}\) molar ratios at KBS are slightly lower than those in the Huron watershed as a result of less contribution from dolomite dissolution. This is consistent with the fact that soil waters at KBS were still undersaturated with respect to dolomite. Previously developed theoretical models reproduced the field-observed chemistry data and suggested that the extent of dolomite dissolution was reduced due to shorter contact time with soil waters.

Silicate-weathering studies based on analysis of Na concentrations in surface waters of Michigan have proven problematic due to contamination by deicing salts and fertilizers. Soil water studies, on the other hand, can have better controls on sources of cations and mineral compositions. At KBS, Na\(^+\), an indicator of plagioclase dissolution, ranged from 40 to 160 \(\mu\)M with slightly higher concentrations during warmer months. In contrast to carbonate-mineral weathering, the soil solution was always undersaturated with respect to plagioclase, suggesting the plagioclase dissolution rates were subject to kinetic regulation by factors such as temperature and availability of reactive surfaces. Therefore, the higher Na\(^+\) during warmer months could be due to higher reaction rates as influenced by higher soil temperature and higher pCO\(_2\), and longer residence time of infiltrating water in the soil profiles. The LiBr tracer experiments suggest that water residence times in 200 cm deep soil profiles varied among the monoliths, but were likely on the order of a couple of years. Silica concentrations were elevated in the summer, similar to the divalent cations, but not likely controlled solely by silicate dissolution rates as soil waters fall into the kaolinite field in stability diagrams and silicate weathering is thus incongruent.

Seasonal variability of stream water chemistry has been attributed to mixing of waters from different parts of a watershed with different lithology or mixing of dilute surface runoff with relatively solute-rich ground waters (Douglas, 2006; Tipper et al., 2006). This study suggests that at least in glacial drift watersheds, seasonal variation in stream water composition could also be due to the residence time of water in subsurface flow paths (silicate weathering) and temperature- and pCO\(_2\)-controlled solubility (carbonate weathering). Infiltration for year 2004 was estimated by the difference between precipitation and evapotranspiration and cation fluxes were calculated. Cations were assigned to minerals and short-term weathering rates of calcite, dolomite and plagioclase dissolution rates were calculated at 3400, 3100 and 320 mol ha\(^{-1}\) yr\(^{-1}\), respectively based on soil water solute budgets. Plagioclase dissolution rates at KBS are high, because of fresh mineral surfaces and high water infiltration rates at this glaciated mid-continent region. Furthermore, soil profile mass balances suggest that the long-term plagioclase-weathering rates are about 2400 mol ha\(^{-1}\) yr\(^{-1}\), much higher than the short-term average, and this is consistent with the general trend that chemical weathering rates of silicate minerals decrease with age due to loss of fresh mineral surfaces. It is also notable that the long-term plagioclase-weathering rates observed in KBS soils are much higher than those from studies of soil sequences of similar age, as a result of high mineral surface areas by glacial abrasion, high mean annual temperature and plagioclase abundances.

Acknowledgements

Special thanks to David Weed and Corey Lambert for their assistance in the field and lab. The tracer experiment was partially funded by a Scott Turner Award from the Department of Geological Sciences at the University of Michigan and a student grant from Geological Society of America to L. Jin. The KBS LTER site including the monoliths were supported by grants 9810220 and 0423627 from the US National Science Foundation. Support from US National Science Foundation grants EAR-0208182 and -0518965 to LMW is also acknowledged. We thank editor Jeremy Fein for handling the manuscript and Steve Dworkin and another anonymous reviewer for their comments, which greatly improved this paper.

Appendix A. Supplementary data

References


