



## Inorganic carbon isotope systematics in soil profiles undergoing silicate and carbonate weathering (Southern Michigan, USA)

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### ABSTRACT

The upper Midwest USA features glacial-derived till materials enriched in carbonate minerals, but with the uppermost soil layer progressively leached of carbonates in the interval since glaciation. Groundwaters and groundwater-fed surface waters are profoundly influenced by carbonate mineral dissolution. Stable carbon isotope compositions of soil waters and groundwaters in two southern Michigan watersheds (Huron and Kalamazoo) were studied as a function of pH,  $\delta^{13}\text{C}_{\text{CO}_2}$ , types of weathering reactions (silicate vs. carbonate), and degree of isotope equilibration. This comprehensive study of carbon isotope biogeochemistry in the vadose zone, including soil gas, soil water/groundwater, and soils (organic matter/carbonate phases), elucidates relations between the chemical weathering rates and  $\text{CO}_2$  fluxes in the soil zone. Such information is important to evaluate responses of terrestrial ecosystems to global climate change.

In shallow soil zones where only silicate weathering was occurring, respiratory  $\text{CO}_2$  was the major source of soil water DIC with little addition from the atmospheric  $\text{CO}_2$ . Isotopic equilibration between  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{13}\text{C}_{\text{CO}_2}$  occurred in an open system with respect to soil  $\text{CO}_2$ . In the deeper soil horizons carbonate dissolution dominated soil water chemistry and saturation with respect to calcite and dolomite was attained rapidly. Mass balance calculation showed that large amounts of soil  $\text{CO}_2$  were consumed by carbonate dissolution, such that the deeper soil zone may not have been an open system with respect to  $\text{CO}_2$ . Constant  $\delta^{13}\text{C}_{\text{DIC}}$  values ( $\sim -11\text{‰}$ ) were observed in these deep soil waters and also in shallow groundwaters of the Huron watershed. Thus, isotopic equilibrium might not be reached between DIC and  $\text{CO}_2$ , possibly due to a rapid kinetics of carbonate dissolution and limited gas–water exchange in the soils. If so, DIC was equally contributed by carbonate minerals ( $\delta^{13}\text{C}_{\text{CaCO}_3} = 0\text{‰}$ ) in reaction with soil  $\text{CO}_2$  ( $\delta^{13}\text{C}_{\text{CO}_2} = -22\text{‰}$ ). Soils beneath an agricultural site with a wheat/corn/soybean rotation (the Kalamazoo watershed) displayed a wide range in  $\delta^{13}\text{C}_{\text{CO}_2}$  values ( $-22$  to  $-12\text{‰}$ ), and the  $\delta^{13}\text{C}_{\text{DIC}}$  of deeper soil waters in contact with carbonate minerals was controlled by seasonal variations of  $\delta^{13}\text{C}_{\text{CO}_2}$ , as well as by strong acids produced by nitrification and to a lesser degree by pyrite oxidation, both of which could react to dissolve carbonate minerals, in addition to carbonic acid dissolution.

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### 1. Introduction

Rocks transform into soils at the Earth's surface, and the reactions of mineral weathering control inorganic carbon fluxes. The soils of the vadose zone are where large carbon reservoirs interact, including those of the lithosphere (carbonate rocks), atmosphere ( $\text{CO}_2$ ), hydrosphere (dissolved and particulate organic and inorganic carbon), and biosphere (living and non-living organic matter). Interactions among these carbon reservoirs influence atmospheric  $\text{CO}_2$  and are thus

important to the energy budget of the Earth surface and in controlling the global surface temperature (Berner and Berner, 1996). The responses of the terrestrial biosphere to anticipated increases in atmospheric  $\text{CO}_2$  will be complex (Zak et al., 1993; Richter et al., 1995; Schlesinger, 1997; Houghton et al., 1998, 1999; Zak et al., 2000; Williams et al., 2003), and an important feedback entails the consumption of  $\text{CO}_2$  through chemical weathering of carbonate minerals and transport of dissolved inorganic carbon to the oceans, where most  $\text{CO}_2$  is ultimately lost from the Earth surface by carbonate re-precipitation, but after long time delays (Holland, 1978; Berner and Berner, 1996; Williams et al., 2007; Szramek et al., 2007).

Chemical weathering of the abundant carbonate minerals in the Northern Hemisphere represents a sink for atmospheric  $\text{CO}_2$  of global importance (e.g., Berner and Berner, 1996; Williams et al., 2007; Szramek et al., 2007). Temperate mid-continent support the most

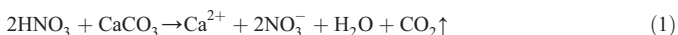
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carbonate weathering because of the combination of high water discharge, maximal carbonate mineral solubility (inversely related to mean annual temperature), and landscapes of recent glaciation containing abundant fresh mineral surfaces for reaction. Our group has investigated mineral dissolution and resultant hydrochemical fluxes in the Great Lakes drainage basin, following the chemical evolution of water in its path from precipitation to soil waters, groundwaters, and streams and rivers (Williams et al., 2007; Szramek et al., 2007; Hamilton et al., 2007; Jin et al., 2008a,b).

The relationship between chemical weathering rates and fluxes of  $\text{CO}_2$  consumed is not straightforward because there are sources of acidity other than  $\text{CO}_2$ , potentially including organic acids and sulfuric and nitric acids (Karim and Veizer, 2000; Spence and Telmer, 2005). Studies in Michigan soils have shown that dissolution of carbonate minerals could either produce or consume  $\text{CO}_2$  as shown in the following reactions (Hamilton et al., 2007):



Studies in the Mississippi River have shown an increase in the export of carbonate alkalinity over the last century, possibly due to intensification of agricultural practices and associated applications of lime and fertilizer as well as hydrological changes (e.g., Raymond and Cole, 2003). The potential for silicate mineral weathering to sequester  $\text{CO}_2$  differs from that of carbonate minerals due to mineral solubility and reactivity ( $\text{CaSiO}_3$  exemplifies silicate minerals):



Silicate weathering is normally regarded as a more permanent sink for atmospheric  $\text{CO}_2$  because carbonate mineral weathering products are subject to eventual re-precipitation and release of  $\text{CO}_2$  in approximate proportion to that which was sequestered, albeit over potentially long time scales, whereas half of the  $\text{CO}_2$  consumed in silicate mineral weathering is not subject to release upon carbonate precipitation (Ridgwell and Edwards, 2007). Thus, contributions from silicate and carbonate dissolution need to be considered separately to comprehend their roles in atmospheric  $\text{CO}_2$  regulation.

Stable C isotopic analysis has become a powerful tool for identifying carbon sources and fluxes because the carbon reservoirs have distinctively different isotope ratios (Yang et al., 1996; Telmer and Veizer, 1999; Karim and Veizer, 2000; Hélie et al., 2002; Singh et al., 2005). Marine carbonate has a relatively narrow range of C isotope ratios, with  $\delta^{13}\text{C}$  values around 0‰ by definition. The  $\delta^{13}\text{C}$  value of atmospheric  $\text{CO}_2$  is around  $-8.0\text{‰}$ , and is decreasing with the addition of more depleted  $\text{CO}_2$  from fossil fuel burning (Friedli et al., 1986; Allison et al., 2003). The C isotopic composition of soil  $\text{CO}_2$ , however, has a wide range, depending largely on the organic matter sources fueling plant and microbial respiration, which in turn reflect the biochemical pathways used for photosynthesis (Hillaire-Marcel, 1986; Ehleringer et al., 1991; Vogel, 1993). The  $\text{C}_3$  photosynthetic pathway dominates in most terrestrial ecosystems, and produces vegetation with  $\delta^{13}\text{C}$  values that range from  $-30$  to  $-24\text{‰}$  with an average value of about  $-27\text{‰}$  (Vogel, 1993).  $\text{C}_4$  plants tend to dominate in grasslands of warm climates and produce organic matter with  $\delta^{13}\text{C}$  values that range from  $-16$  and  $-10\text{‰}$ , with a mean value of about  $-12.5\text{‰}$  (Vogel, 1993).

Previous carbon isotope studies have mainly focused on riverine waters, with little information available for waters in soil profiles, even though this is a critical zone of carbon transformation. Here we present a study of carbon dynamics in southern Michigan soils developed on glacial drift deposits since the last glacial retreat. Soil evolution over the last 15,000 years has led to an accumulation of organic carbon at greatly accelerated rates relative to non-glaciated

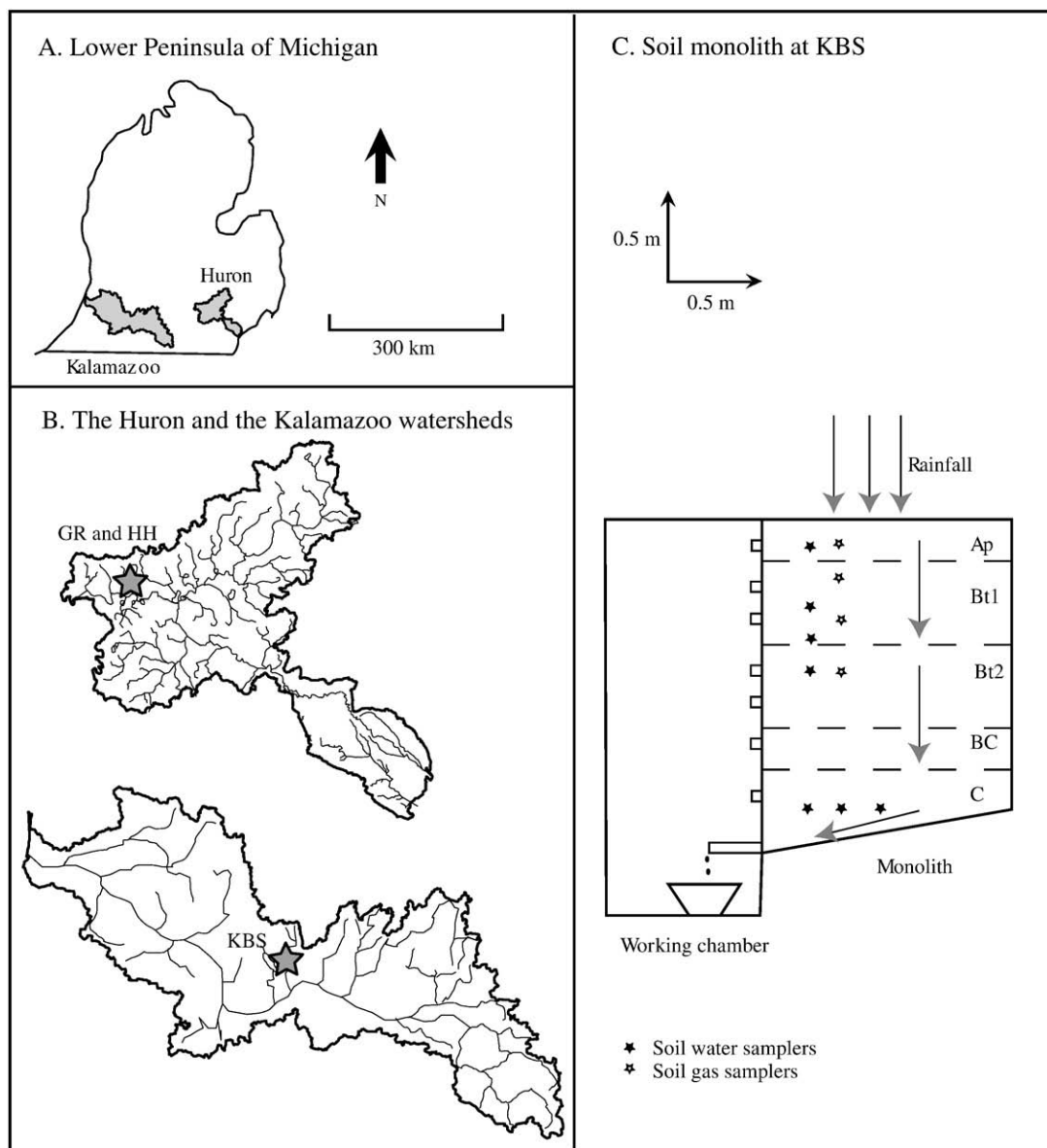
landscapes (Futyma, 1981; Harden et al., 1992). In southern Michigan, soil parent materials contain up to 30 wt.% of carbonate minerals, often including both dolomite and calcite (Schaeztl, 1992; Jin et al., 2008a). With carbonate minerals leached from the shallow horizons, a transition from silicate weathering to carbonate weathering occurs with depth in the soil profile, which offers the opportunity to separate mineral weathering carbon contributions from those of soil organic carbon respiration or gas exchange with the atmosphere. These features make Michigan soils a natural laboratory to study carbon transformation processes among soil, soil gas and soil water phases. In this study we analyze stable carbon isotope ratios to: 1) identify sources of DIC in soil water and groundwater; 2) study the controls on DIC acquisition as water passes through the vadose zone; and 3) evaluate the mass balance between soil  $\text{CO}_2$  production and losses to the overlying air and to infiltrating waters.

## 2. Study areas

The study sites are soil profiles in the Huron and Kalamazoo river watersheds, located in southern Michigan (Fig. 1A). The mean annual temperature is similar between these two watersheds (Huron:  $10.0\text{ °C}$  and Kalamazoo:  $9.7\text{ °C}$ ), as is the mean annual precipitation (Huron 840 mm/year and Kalamazoo: 890 mm/year) (NOAA, 1992). Topography of the watersheds is determined by glacial drift deposits from multiple Pleistocene glacial advances and retreats (Farrand and Eschman, 1974). The last glacial retreat from this region occurred about 15,000 years ago, and soils have been developing since then (Futyma, 1981). Glacial sediments are derived from the northern Canadian Shield and from Paleozoic/Mesozoic sedimentary rocks within the Michigan basin. The soils in these watersheds are developed on glacial moraine and outwash deposits and generally are very permeable, producing a close hydrogeochemical linkage between soil water, shallow groundwaters and streams.

There are two primary forest-soil study locations in the Huron watershed, the George Reserve (GR) and Hell Fen (HH) (Fig. 1B). The study area in the Kalamazoo watershed includes four monolith sites in a Long Term Ecological Research (LTER) site at the Kellogg Biological Station (KBS) of Michigan State University (Fig. 1B). Characteristics of these sites have been presented in detail elsewhere, focusing on rates and controls of chemical weathering reactions (Jin et al., 2008a,b) and so are only briefly described here. The two locations in the Huron watershed are composed of  $\text{C}_3$  vegetation, mainly mixed coniferous and deciduous forests. There are multiple sites in each location, spanning variable topography (GR1, GR2, GR3 and GR4; HH1 and HH2), each equipped with soil water and soil gas samplers. The KBS LTER is a long-term agricultural research site with a corn/soybean/wheat rotation, where we were able to sample fluids directly from established soil monoliths. The monoliths are intact 2-m soil profiles, enclosed by stainless steel on the sides and at the bottom but open to natural precipitation at the top and cultivated for row crops (Fig. 1C). The four replicate monoliths are 20 m apart (denoted as ML2, ML6, ML9 and ML13) and located in a relatively flat outwash plain.

The bulk mineralogy of soil parent materials at these sites is predominantly composed of quartz, K-feldspar, plagioclase, calcite, dolomite and lesser amounts of amphibole. Weathering rates and controls on chemical dissolution reactions in the soil profiles were previously evaluated by Jin et al. (2008a,b). Briefly, the depths to which carbonate minerals have been leached out typically extend to  $\sim 100$ – $150$  cm below ground surface. Thus, there is a sharp transition; silicate weathering dominates in shallow zones while carbonate dissolution controls water chemistry in the deeper horizons. Weathering rates of silicate minerals such as plagioclase are fast in the surface layers, where dissolved organic carbon concentrations are high and pH values are relatively low. Silicate weathering rates were primarily controlled by surface areas, and therefore, mineral abundances. Where carbonate minerals are present (i.e., beneath the upper



**Fig. 1.** Location map of the study area (A). The Huron and the Kalamazoo river watersheds (B): GR and HH sites are in the Huron watershed, and monoliths of the KBS site are in the Kalamazoo watershed. Schematic map of the soil monoliths at the KBS site (C) with arrows indicating water flow directions (modified from Jin et al., 2008a,b).

carbonate-leached zone), carbonate dissolution is rapid, and soil water/groundwater DIC is only limited by mineral solubility and soil zone  $pCO_2$ .

### 3. Methods

#### 3.1. Sample collection

At both the GR and HH sites of the Huron watershed, a 1.5 m-deep pit was dug, and soils were sampled at 10 cm intervals. Below 150 cm, soils were collected by hand auger until the parent drift material (i.e. the C-horizon) was reached. Soil horizons were described in the field by soil color and texture; the presence of carbonate was tested with a dilute HCl solution. At the KBS site of the Kalamazoo watershed, only one sample was collected from each horizon. A deep core (~200 cm) was collected near the monoliths using a Geoprobe, and sectioned every 10 cm for analyses.

In the Huron watershed, soil gas tubes were installed only at the HH sites (HH1 and HH2), at depths ranging from 20 to 200 cm. The tubes consisted of 1/8-inch ID Teflon tubing with a perforated stain-

less steel tip (Williams, 2005). At the KBS site in the Kalamazoo watershed, Teflon soil gas tubes (0.5 mm ID) had been installed when the monoliths were set up 20 years ago (Fig. 1C). Generally 4–6 soil gas tubes were placed into each monolith, sampling soil depths from 10 to 100 cm. The soil gas samples in these two watersheds were collected in the field using either 10 or 20-ml gas-tight plastic syringes after purging multiple times to clear the sampler tube. Gas samples were immediately transferred to pre-evacuated 4-ml glass serum vials. Soil gas  $CO_2$  samples were collected about 10 times over the study period, covering most months of a year. Soil gas samples for  $\delta^{13}C$  analysis were collected in the same way as  $CO_2$  concentration samples but only three times a year including within and outside the growing season.

Lysimeters (tension soil water samplers) were installed in both watersheds (details in Jin et al., 2008a). In the Huron watershed sites, typical sampling depths within a given nest were 15–25, 50, 75, 100, 150, 250, and 400 cm. At the KBS site, monoliths were equipped with lysimeters at depths of 30, 60, 90 and 180 cm. One day prior to sampling, a vacuum of  $-0.5$  bar was applied to draw water into the lysimeter cups. The actual depth range in the soil column sampled by

**Table 1**

Organic C and inorganic C contents and their C isotope compositions in representative soils.

Depth (cm)	OC (wt.% C)	IC (wt.% C)	Depth (cm) or horizon	$\delta^{13}\text{C}_{\text{SOM}}$ (‰)	$\delta^{13}\text{C}_{\text{carbonate}}$ (‰)
<i>A. GR1 site, Huron</i>					
10	2.2	BDL	2	-27.0	NA
20	1.2	BDL	7	-25.6	NA
30	0.5	BDL	11	-24.7	NA
40	0.3	BDL	200	-29.4	0.3
50	0.3	BDL	284	-27.4	0.7
60	0.4	BDL	304	-26.6	0.1
90	BDL	0.5			
100	BDL	5.4			
110	BDL	3.4			
120	BDL	2.7			
<i>B. ML6 site, Kalamazoo</i>					
10	1.1	BDL	ML13: Ap	-22.6	NA
30	0.8	BDL	ML9: Ap	-22.3	NA
50	0.5	BDL	ML6: Ap	-22.4	NA
70	0.4	BDL	ML2: AP	-22.3	NA
145 <sup>a</sup>	BDL	3.3	145 <sup>a</sup>	NA	0.0
155	BDL	3.2	175	NA	-0.1
165	BDL	2.9	183	NA	-0.2
175	BDL	3.0	184	NA	-0.4
183	BDL	2.1			
190	BDL	1.8			

BDL = below detection limit; NA = not applicable.

<sup>a</sup> Samples deeper than 140 cm are collected from a core near ML6.

the suction lysimeters was at least 6 cm above and below the mean depth of the porous cup due to both the cup length and the zone of influence of the capillary force. Soil waters were also collected in drainage from the bottom of the monoliths, representing the gravity driven drainage water and thus acting as a zero-tension lysimeter. Two types of gravity drainage waters were collected at the base (200 cm): the water that was actually dripping from the monolith drainage pipe on each sampling date and the water that had accumulated over time in the receiving bucket. Hereafter, the instantaneous sample will be referred to as the “drip” sample, and the integrated sample of drainage between sampling events will be referred to as the “tub” sample. Collection buckets were generally emptied one day prior to the sampling event. Groundwater samples in the Huron watershed were collected in May 2006 from domestic wells near the soil water sampling sites. These wells are all situated in glacial drift aquifers and closely related to the soil waters hydrologically and geochemically.

Soil water and groundwater samples were filtered through 0.45  $\mu\text{m}$  Whatman polypropylene filters into pre-cleaned HDPE bottles. One aliquot of each sample was acidified with high-purity nitric acid for cation analyses. Another filtered aliquot was left untreated for alkalinity titrations and anion analyses. Samples for concentrations and stable isotope analyses of DIC were filtered and stored in glass bottles. These samples were poisoned with two drops of dilute  $\text{CuCl}_2$  solution to inhibit biological and microbial activity that could alter DIC concentration and its C isotopic composition during storage. The glass bottles were capped with a stopper leaving no headspace and subsequently crimped to avoid any exchange with atmosphere. All samples were maintained on ice until return to the laboratory, where samples were stored in a dark cold room at a temperature of about 4 °C until analysis.

### 3.2. Analyses of soils and soil gases

Soils were dried in the oven at 45 °C for two days, then ground to pass a sieve (mesh 200 or 75  $\mu\text{m}$ ). Solid organic carbon contents of all soil samples were determined at the Environmental and Analytical Geochemistry Lab (EAGL) at the University of Michigan, after acid-

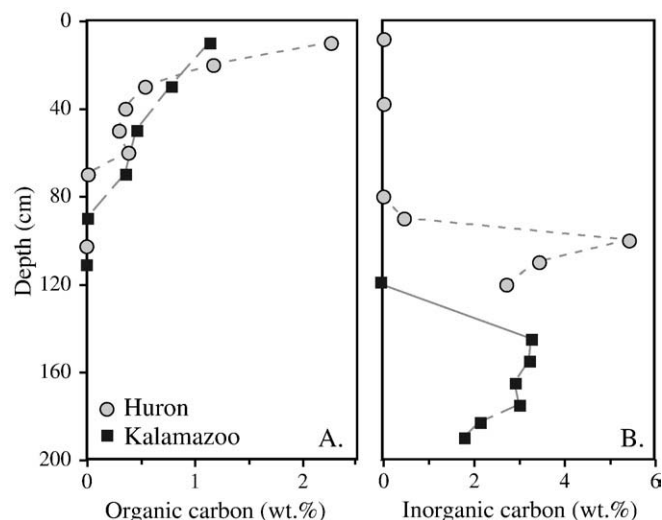
fuming to remove inorganic carbonate, by platinum-catalyzed combustion at 900 °C with a Shimadzu TOC 5000-A total carbon analyzer equipped with a solid sample module. Soil samples for organic C isotope analyses were pre-treated with 1 M HCl to remove carbonate minerals. The sample residues were washed with distilled water and dried in the oven at 60 °C. Approximately 8 mg sample was weighed into a tin capsule for carbon analysis. The isotopic composition of carbon was determined after combustion of the capsules by a Europa Scientific 20–20 continuous flow isotope ratio mass spectrometer (IRMS) with ANCA-SL preparation module for solid and liquid samples. NBS22 (oil), and IAEA-CH7 were used as reference materials.

Representative soils were leached by aqua regia (3 HCl:1  $\text{HNO}_3$ ) at room temperature for 3 h to selectively dissolve carbonates and oxyhydroxides (Sparks, 1996). The acid leachates provide an estimate of inorganic carbon (carbonate mineral) content (Jin et al., 2008a). To measure C isotope composition of the carbonate minerals, about 8 mg of the soil sample was placed into ampoules, capped, flushed with helium and then reacted with  $\text{H}_3\text{PO}_4$  for one day at 25 °C. The released  $\text{CO}_2$  was then measured with a Europa Scientific 20–20 continuous flow IRMS ANCA-TG preparation module for trace gas samples. For these measurements NBS18 and NBS19 were used as reference materials.

Soil gas  $\text{pCO}_2$  was measured within a week of sampling by a Perkin Elmer packed-column gas chromatograph (GC) at EAGL lab, calibrated with four  $\text{CO}_2$  standards ranging from 350 to 10,000 ppmv. The isotopic composition of soil  $\text{CO}_2$  was determined using a Europa 20–20 continuous flow IRMS with an ANCA-TG preparation module for trace gas samples. Gas samples were flushed with a continuous flow of helium across two chemical traps that removed water and then trapped the  $\text{CO}_2$ .

### 3.3. Analyses of water samples

Water pH was measured in the field using a Corning 315 portable pH meter and a Ross glass-body combination pH electrode calibrated on the NBS scale using two low-ionic-strength buffer solutions. Great care was taken during the pH measurement by using a sealed chamber to avoid the degassing of  $\text{CO}_2$  to the atmosphere. However, with the vacuum applied to the lysimeters during the sampling period, degassing could not be totally avoided (Sigfusson et al., 2006), and the estimated uncertainty in pH measurements is  $\pm 0.05$  pH units. Temperature was measured in the field with a temperature meter with uncertainty of  $\pm 0.1$  °C. Concentrations of major cations and anions were measured with inductively coupled plasma optical



**Fig. 2.** The organic carbon (A) and inorganic carbon (B) contents in representative soil profiles of the Huron and the Kalamazoo watersheds.

emission spectrometry (ICP-OES) and ion chromatography (IC), respectively, at the EAGL lab. The precision of IC and ICP analyses was better than  $\pm 3\%$  for major elements and  $\pm 10\%$  for minor elements. Total alkalinity was determined on refrigerated soil water samples by weak acid titration within a day of sampling in the lab over a pH range of 2 to 3 using the Gran method (Edmond, 1970; Gieskes and Roders, 1973; Stumm and Morgan, 1996). The uncertainty for alkalinity titrations is less than  $\pm 2\%$  for most samples, except for those with very low alkalinity values where uncertainty was estimated to be  $\pm 0.05$  meq/l.

DIC concentrations were analyzed on a UIC C coulometer with a precision of  $\pm 2\%$ . The stable isotope composition of dissolved inorganic carbon ( $\delta^{13}\text{C}_{\text{DIC}}$ ) was determined with a Europa Scientific 20–20 continuous flow IRMS ANCA-TG preparation module for trace gas samples modified after Miyajima et al. (1995) and Spötl (2005). Phosphoric acid (100%) was added (100–200  $\mu\text{l}$ ) to a septum tube and purged with pure He. The water sample (6 ml) was then injected into the septum tube and  $\text{CO}_2$  was directly measured from the headspace after extraction. In order to determine the optimal extraction procedure for surface water samples, a standard solution of  $\text{Na}_2\text{CO}_3$  (Carlo Erba) was prepared with a concentration of 4.8 meq/l (for samples with an alkalinity above 2 meq/l) and another of 2.4 meq/l

(for samples with alkalinity concentrations below 2 meq/l) with a known  $\delta^{13}\text{C}_{\text{DIC}}$  value of  $-10.8 \pm 0.2\%$ .

All stable carbon isotope results are expressed in the convention delta ( $\delta$ ) notation, defined as per mil (‰) deviation from reference standard VPDB. Overall analytical error was  $\pm 0.2\%$  for  $\delta^{13}\text{C}_{\text{DIC}}$ ,  $\delta^{13}\text{C}_{\text{CaCO}_3}$ ,  $\delta^{13}\text{C}_{\text{SOM}}$  and  $\delta^{13}\text{C}_{\text{CO}_2}$ , respectively.

## 4. Results

### 4.1. Soil carbon content and isotopic composition

Soil organic and inorganic carbon contents at representative soil profiles are reported in Table 1. Organic carbon concentrations at both GR1 sites (Huron) and the ML6 site (Kalamazoo) were highest (1–2.5 wt.%) at the soil surface, and decreased with depth (Fig. 2A). The depth at which carbonate minerals first occur in the soils varied significantly in the Huron watershed, most often being encountered at about 80 cm but occurring at more than 400 cm in GR4 (not shown). Carbonate materials were not detected in the soils of KBS sites until below 150 cm. The carbonate mineral contents were up to 40 wt.% (equivalent to 5 wt.% inorganic C) in some soil samples (Fig. 2B).

**Table 2**  
Seasonal variations of  $\text{pCO}_2$  and C isotopic compositions of  $\text{CO}_2$  in soil profiles of the two watersheds.

Sample	Depth (cm)	$\text{pCO}_2$ (ppm)	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰)	Sample	Depth (cm)	$\text{pCO}_2$ (ppm)	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰)	Sample	Depth (cm)	$\text{pCO}_2$ (ppm)	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰)
<b>A. Huron</b>											
<i>2/22/06</i>											
HH2	20	725	-20.8	6/9/06	0	391		7/14/05	20	1717	
HH2	45	1735	-21.7	HH2	20	1719		HH2	45	4060	
HH2	75	1766	-22.6	HH2	45	4669		HH2	75	5301	
HH2	110	3693	-23.3	HH2	75	5512		HH2	110	8546	
HH2	150	4113	-22.5	HH2	110	8123		HH2	150	7654	
HH2	200	4749	-22.3	HH2	150	7101		HH2	200	7435	
				HH2	200	6844		HH1	0	1004	
				HH1	20	2357		HH1	20	2274	
								HH1	75	6384	
<i>8/31/05</i>											
HH2	20	1293		9/26/05	20	2454	-20.5	10/31/05	0	404	-11.1
HH2	45	3227		HH2	45	6389	-20.9	HH2	20	830	-17.8
HH2	75	4531		HH2	75	6061	-21.1	HH2	45	1931	-20.9
HH2	110	7895		HH2	110	7853	-20.7	HH2	75	2647	-21.3
HH2	150	7762		HH2	150	7368	-20.3	HH2	110	5173	-21.2
HH2	200	8248		HH2	200	2598	-19.6	HH2	150	5409	-21.6
HH1	20	1691		HH1	20	3145	-21.2	HH2	200	5870	-21.0
HH1	75	4351		HH1	75	6777	-20.7	HH1	20	1057	-20.9
								HH1	75	2870	-21.4
<b>B. Kalamazoo</b>											
<i>4/24/06</i>											
ML2-1	25	1754	-15.9	9/7/06	25	10,019	-20.5	12/22/04	25	2070	-18.1
ML2-2	51	3440	-16.3	ML2-1	51	14,606	-19.1	ML2-1	51	2591	-17.3
ML2-3	63	3203	-16.9	ML2-2	63	14,918	-19.7	ML2-2	63	2868	-17.4
ML2-4	76	3373	-16.4	ML2-3	76	15,580	-19.7	ML2-3	76	2830	-17.6
ML2-5	82	3093	-17.7	ML2-4	82	13,705	-20.1	ML2-4	82	1992	-17.5
ML6-1	25	2728	-14.1	ML2-5	25	9136	-21.9	ML6-1	25	1651	-16.9
ML6-2	40	1985	-14.0	ML6-1	40	5872	-21.4	ML6-2	40	2296	-17.2
ML6-3	55	3006	-14.8	ML6-2	55	13,640	-20.8	ML6-3	55	1988	-18.2
ML6-4	66	2992	-14.7	ML6-3	66	12,969	-20.8	ML6-4	66	1929	-17.9
ML6-5	74	2748	-15.6	ML6-4	74	13,736	-20.9	ML6-5	74	1569	-18.2
ML6-7	95	2443	-17.1	ML6-5	95	13,978	-21.2	ML6-7	95	1464	-20.0
ML9-1	25	2472	-15.3	ML6-7	25	4802	-21.5	ML9-1	25	1667	-16.3
ML9-2	40			ML9-1	40	10,143	-22.0	ML9-2	40	637	-13.2
ML9-3	53	2186	-13.9	ML9-2	53	8675	-20.9	ML9-3	53	2383	-16.6
ML9-4	61	2726	-15.3	ML9-3	61	14,095	-20.5	ML9-4	61	1848	-16.7
ML9-6	89	2665	-14.9	ML9-4	89	14,548	-20.7	ML9-6	89	2338	-16.8
ML13-1	30	2276	-18.3	ML9-6	30	6829	-20.1	ML13-1	30	555	-12.0
ML13-2	60	2676	-18.1	ML13-1	60	10,334	-20.6	ML13-2	60	1455	-17.0
ML13-3	68	1890	-17.9	ML13-2	68			ML13-3	68	903	-14.7
ML13-4	81	2456	-18.2	ML13-3	81	11,568	-19.9	ML13-4	81	1528	-18.0

C isotope compositions of soil organic matter and carbonate minerals are also given in Table 1. The organic matter in the GR1 site of the Huron watershed had carbon isotopic ratios ( $\delta^{13}\text{C}_{\text{SOM}}$ ) ranging from  $-29.4$  to  $-24.7\%$ , with an average value of  $-26.8\%$ . The  $\delta^{13}\text{C}_{\text{SOM}}$  compositions at soil monolith sites of the Kalamazoo watershed range from  $-22.6$  to  $-22.3\%$ , with an average value of  $-22.4\%$  and between the isotopic signatures of  $\text{C}_3$  and  $\text{C}_4$  vegetation (Deines, 1980; Mariotti, 1991; Vogel, 1993). This may reflect the crop rotation (soybean/wheat/corn) at KBS, as corn is a  $\text{C}_4$  plant while soybeans and wheat are  $\text{C}_3$  plants. The  $\delta^{13}\text{C}_{\text{SOM}}$  values measured in this study are only a snapshot in time and would be expected to vary, as crops are rotated and residual organic matter composition changes. Thus, it is impossible to quantify the contributions of different organic matter sources to the soil  $\text{CO}_2$ . Calcite and dolomite (inorganic carbon) within the Huron and Kalamazoo watersheds are from Devonian/Silurian limestone and dolostone transported from northern Michigan during last glaciation.  $\delta^{13}\text{C}$  values of carbonate carbon ( $\delta^{13}\text{C}_{\text{CaCO}_3}$ ) are close to  $0\%$  and do not differ significantly between the two watersheds (Huron:  $0.4 \pm 0.3\%$ ; Kalamazoo:  $-0.2 \pm 0.2\%$ ; Table 1).

#### 4.2. Soil gas $\text{CO}_2$ concentrations and $\delta^{13}\text{C}_{\text{CO}_2}$

Soil gas  $\text{CO}_2$  concentrations and carbon isotopic ratios ( $\delta^{13}\text{C}_{\text{CO}_2}$ ) from HH (Huron) and soil monoliths (Kalamazoo) are reported in Table 2. Depth profiles of soil  $\text{pCO}_2$  are plotted in Fig. 3A and B for the HH2 and soil monolith sites, respectively. At HH2 site,  $\text{pCO}_2$  increases with depth sharply over the first 100 cm and then remains relatively constant after that. The  $\text{pCO}_2$  values clearly show seasonal variations, with maxima observed in summer months (August/September) and minima in winter months (February). At soil monolith sites, the  $\text{pCO}_2$  levels at September are also much higher than those in colder

months (December and April). Depth variation at the monolith sites was observed only in September and it was very likely that maximum  $\text{pCO}_2$  had not been reached at 100 cm where the deepest samples were collected. In the absence of carbonate precipitation, the major sources of  $\text{CO}_2$  in the vadose zone are root respiration and microbial respiration of organic matter (Berner and Berner, 1996); thus  $\text{CO}_2$  concentrations are controlled by availability of organic carbon, density and activity of roots, temperature, and soil moisture (Bacon and Keller, 1998). Temporal variations of soil  $\text{pCO}_2$  in both watersheds reflect the temperature-dependence of these biological processes. In the HH2 site,  $\text{pCO}_2$  at the deep soils is about 13–25 times higher than atmospheric  $\text{CO}_2$  and in the monolith sites  $\text{pCO}_2$  is 5–70 times higher than atmospheric  $\text{CO}_2$ .

A previous study in southern Texas (U.S.A.) has shown that in soil zones,  $\text{CO}_2$  concentrations vary significantly with season, but  $\delta^{13}\text{C}_{\text{CO}_2}$  remains relatively constant with time (Wood and Petraitis, 1984). The  $\delta^{13}\text{C}_{\text{CO}_2}$  values in the Huron watershed vary with depth and also with season (Fig. 4A). Carbon isotopic ratios in soil  $\text{CO}_2$  were about 4.7 to 5.3‰ enriched relative to organic matter at that site. The  $\delta^{13}\text{C}_{\text{CO}_2}$  values of deeper soil gas samples ( $>50$  cm) ranged from  $-22$  to  $-20\%$  and showed seasonal variation, becoming more  $^{13}\text{C}$ -enriched in warmer months. Similar seasonal variation in  $\delta^{13}\text{C}_{\text{CO}_2}$  has been observed indirectly in riverine  $\delta^{13}\text{C}_{\text{DIC}}$  in a small granitic catchment in France (Amiotte-Suchet et al., 1999). Soil gas samples from the top 20 cm lie in a mixing line between deeper soil gas and air (Pawellek and Veizer, 1994).

The  $\delta^{13}\text{C}_{\text{CO}_2}$  values in the Kalamazoo watershed site showed more variation than those in the Huron site, ranging from  $-22$  to  $-14\%$  (Fig. 4B). Here, soil gas samples were collected from relatively shallow soil zones ( $<100$  cm), where the soil  $\text{CO}_2$  has mixed organic matter sources under the corn–soybean–wheat rotation. In April and December, the  $\text{pCO}_2$  was much lower and  $\delta^{13}\text{C}_{\text{CO}_2}$  much higher than in September. The significantly different  $\delta^{13}\text{C}_{\text{CO}_2}$  observed at different seasons could be either that there are seasonally varying organic matter sources and/or that mixing with atmosphere is more significant in the low  $\text{CO}_2$  production season.

#### 4.3. Soil water/groundwater chemistry and $\delta^{13}\text{C}_{\text{DIC}}$ values

Elemental and isotope chemistry of groundwaters in the vicinity of the Huron study sites are reported in Table 3. Soil water chemistry from the Huron and the Kalamazoo study sites has been previously reported in our chemical weathering studies (Jin et al., 2008a,b). Where soil water DIC and  $\delta^{13}\text{C}_{\text{DIC}}$  are presented for this study, the pH and concentrations of alkalinity, major cations ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) and anions ( $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ) of these soil waters are presented as well (Huron soil waters in Table 4; Kalamazoo soil water in Table 5). Water chemistry and isotope data of newly collected soil waters are also presented in Tables 4 and 5 for the Huron and the Kalamazoo sites, respectively.

Briefly, carbonate minerals are absent from shallow soil horizons, where silicate weathering is the predominant control on soil water chemistry, low or even slightly negative alkalinity (e.g. net acidity) was observed in soil waters (Fig. 5A). When carbonate dissolution occurs in the deeper soil layers, divalent cation concentrations ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) and alkalinity increase sharply as do soil water pH and DIC values. The groundwaters have very similar chemistry to the deep soil waters in the Huron watershed, suggesting that carbonate dissolution approaches equilibrium with respect to dolomite in the soil zones (Fig. 5A; Jin et al., 2008a). In contrast, the Kalamazoo soil waters have slightly lower  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations and alkalinity, and saturation state calculations show that soil waters are still undersaturated with respect to dolomite while at equilibrium with calcite (Jin et al., 2008b).

The  $\delta^{13}\text{C}_{\text{DIC}}$  values of soil waters and groundwaters are distinctively different in the shallow and deep soil zones of the Huron watershed

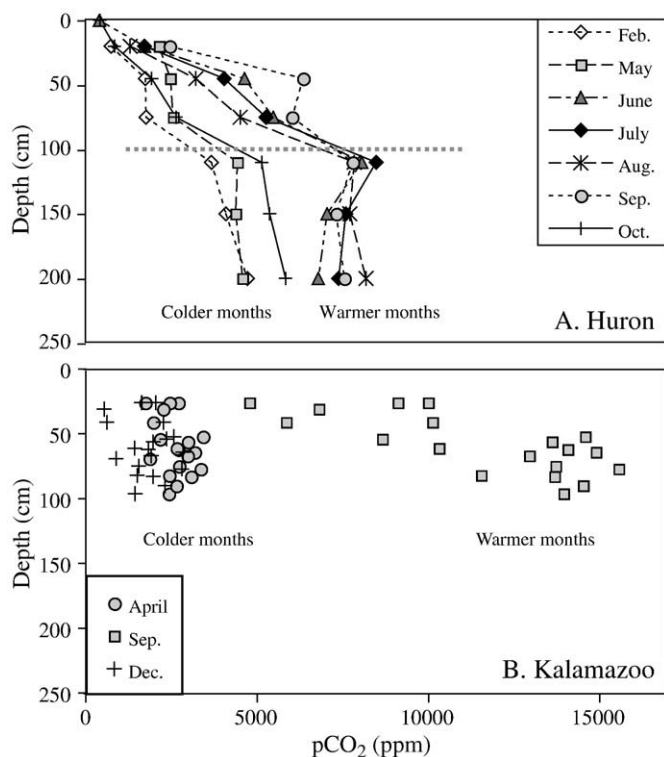
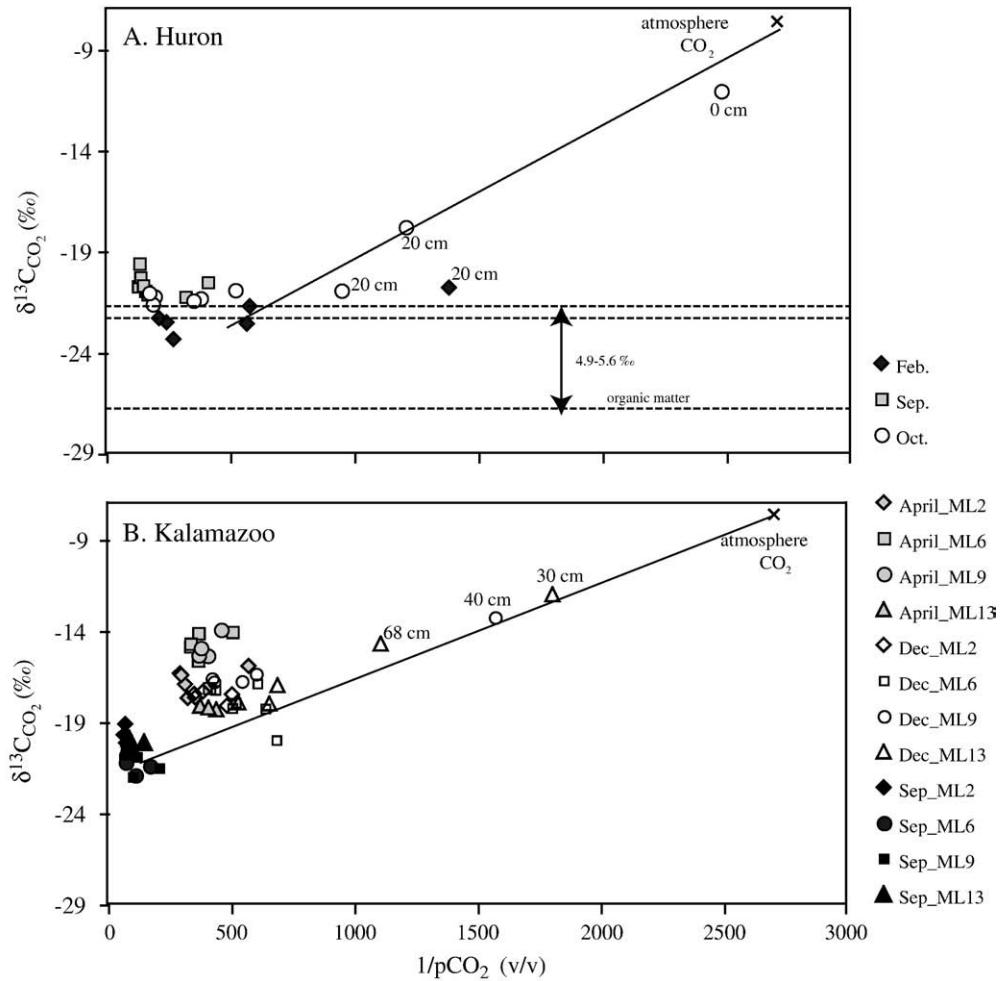


Fig. 3. Seasonal and spatial variations of soil  $\text{pCO}_2$  in the Huron (HH site; A) and in the Kalamazoo (KBS site; B) watersheds. In both watersheds, higher  $\text{CO}_2$  concentrations are observed in the warmer months and lower concentrations in the colder months. In the Huron watershed, soil  $\text{CO}_2$  remains relatively constant in soils deeper than 100 cm (grey dashed line).



**Fig. 4.** The Keeling plots ( $\delta^{13}\text{C}_{\text{CO}_2}$  values vs.  $1/p\text{CO}_2$ ) in the Huron (A) and Kalamazoo (B) watersheds. The atmospheric  $\text{CO}_2$  is plotted for reference. In the Huron watershed, the C isotope composition of  $\text{CO}_2$  is enriched relative to that of the organic matter and the measured values are within the calculated range (4.9–5.6‰; dashed lines) according to Cerling (1984). Shallow gas samples plot along the mixing line between atmospheric  $\text{CO}_2$  and the deep soil gases (solid lines).

(Fig. 5B).  $\delta^{13}\text{C}_{\text{DIC}}$  of soil waters from shallow, carbonate-free soil zones have a wide range from  $-25$  to  $-15\%$ , while soil waters from deeper soils and groundwaters have relatively constant  $\delta^{13}\text{C}_{\text{DIC}}$  values around  $-11\%$ . The  $\delta^{13}\text{C}_{\text{DIC}}$  of soil waters in the Kalamazoo watershed covers a wide range from  $-15$  to  $-2\%$  (Fig. 5B) even though all these soil waters were collected from carbonate-bearing soil horizons.

**4.4. Time scales for C isotope equilibrium: sampling protocols**

To the best of our knowledge, there are only a few studies on the carbon isotopes of gas and water in the vadose zone, and on C sources involved in chemical weathering (e.g., Reardon et al., 1979). One of the difficulties in such field investigations is the sampling

technique, which should not fractionate the carbon isotope composition of the original samples. Experiments carried out to determine the fractionation factors between aqueous phase ( $\text{HCO}_3^-$ ) and gas  $\text{CO}_2$  have shown that at least 24 h were required to reach equilibrium conditions between two phases even in the well-stirred system (Lesniak and Zawadzki, 2006). Contamination and fractionation by exchange with atmospheric gases could be minimized by limiting the exposure of sample to the atmosphere and also by increasing the sample size (Davidson, 1995). Theoretical calculations using diffusion models to estimate the time needed for riverine DIC to degas and reach equilibrium with atmosphere show that at least 8 h is required for waters with high DIC such as Michigan rivers (Kanduc et al., 2007). All these laboratory and field

**Table 3**  
Elemental and isotope geochemistry of the Huron groundwaters.

Sample	Date	Alk	pH	DIC	$\delta^{13}\text{C}_{\text{DIC}}$	$\text{Na}^+$	$\text{K}^+$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{Cl}^-$	$\text{SO}_4^{2-}$	$\text{NO}_3^-$
GW1	5/6/06	5.49	7.82	5.61	-11.5	484	44.3	1864	940	76.6	124	27.8
GW2	5/6/06	4.43	7.98	4.27	-10.5	159	31.8	1636	806	30.4	162	21.2
GW3	5/6/06	7.24	8.14	7.28	-11.5	408	83.6	2467	1218	40.3	11.2	10.3
GW4	5/6/06	5.53	7.58	5.66	-11.1	131	28.7	2417	935	43.7	379	29.2
GW5	5/6/06	5.54	7.68	4.77	-11.7	113	27.4	2276	1017	96.0	289	36.5
GW6	5/6/06	5.19	7.57	4.99	-9.4	855	26.3	1687	659	13.1	55.0	34.2

Alk (alkalinity) in meq/l; DIC in mmol/l;  $\delta^{13}\text{C}_{\text{DIC}}$  in ‰; major ions in  $\mu\text{mol/l}$ .

**Table 4**  
Soil water composition in the Huron watershed ( $\mu\text{mol/l}$  for major ions).

Site	Date	Depth (cm)	pH	Alk (meq/l)	DIC (mmol/l)	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	
GR1	7/19/05	280	7.59	5.03			2073	679	0.8	19	
GR1	8/31/05	280	7.74	4.68		-10.1	2048	648	30.9	179	
GR1	11/2/05	280	7.64	4.43		-9.9	1775	561	46.4	190	
GR3	6/19/04	40	5.48	0.19	0.55		-19.8	163	89	148.1	93
GR3	7/26/04	40	5.95	0.14			-22.0	120	63	8.9	102
GR3	7/30/04	40	5.79	0.10	0.54		-21.8	124	66	6.1	111
GR3	7/19/05	175	7.38	4.59		4.65	-11.4	1992	579	35.5	188
GR4	5/2/05	13	6.73	0.35	0.29		-15.8	200	74	131.0	62
GR4	7/19/05	13	6.15	0.34				111	49	11.9	298
GR4	7/30/04	25						299	211		
GR4	6/19/04	250						301	212		
GR4	10/26/04	250	6.84	0.30				273	187	1.7	312
GR4	7/19/05	250	6.71	0.56				278	164	2.3	576
GR4	8/31/05	250						271	152	11.1	299
GR4	7/26/04	400	5.53	0.10		-21.6	393	275	6.0	540	
GR4	7/30/04	400	5.57	0.17	0.42		-21.4	384	272	5.9	542
GR4	10/26/04	400	6.81	0.29		-16.1	385	279	4.9	458	
GR4	5/2/05	400	5.74	0.24	0.44		-21.7	377	263	1.5	559
GR4	7/19/05	400	5.85	0.31	0.50		-22.7	388	270	1.3	47
GR4	8/31/05	400	6.36	0.12				400	277	3.4	592
HH1	6/19/04	23	6.65	0.55	0.73		-20.4	227	114	3.8	55
HH1	5/2/05	23	6.44	0.50			-19.1	197	94	16.3	99
HH1	11/20/03	50	6.18	0.01	0.18		-20.7	105	72	0.9	134
HH1	5/17/04	95	6.17	0.19	0.67			108	71	1.8	143
HH1	5/2/05	95	6.03	0.18	0.31		-17.7	72	37	1.6	95
HH2	5/17/04	25	6.50	0.35	0.73			32	49	4.0	51
HH2	6/19/04	25	5.63	0.03	0.21		-23.9	20	30	0.7	33
HH2	5/2/05	25	6.14	0.21	0.14		-20.0	29	46	0.6	65
HH2	6/19/04	50	5.86	0.02	0.18		-22.8	38	47	1.1	81
HH2	4/28/05	50	5.92	0.09			-18.8	25	28	0.7	53
HH2	5/2/05	50	5.86	0.17	0.12		-17.1	25	26	2.1	52

studies suggest that our sampling techniques should be able to preserve carbon isotope signatures of soil water/groundwaters and soil gas samples. This was further confirmed by the different  $\delta^{13}\text{C}_{\text{DIC}}$  values observed between shallow and deep soil waters of the Huron watersheds, suggesting no contamination from the atmospheric  $\text{CO}_2$ .

## 5. Discussion

### 5.1. Soil $\text{CO}_2$ fluxes and $\delta^{13}\text{C}_{\text{CO}_2}$ variations at the Huron watershed sites

Soil  $\text{CO}_2$  is an important reaction agent for both silicate and carbonate dissolution and its isotope composition ( $\delta^{13}\text{C}_{\text{CO}_2}$ ) is controlled by its sources (i.e., respiration of  $\text{C}_3$  vs.  $\text{C}_4$  plant organic matter) and processes that may fractionate its isotope ratios. The organic matter in the Huron watershed has carbon isotopic ratios ( $\delta^{13}\text{C}_{\text{SOM}}$ ) averaging  $-26.8\%$ , reflecting  $\text{C}_3$  plants and consistent with the forest vegetation present at this site (Deines, 1980; Mariotti, 1991). For samples collected from top 15 cm at GR1 site,  $\delta^{13}\text{C}_{\text{SOM}}$  is over 2‰ heavier in the deeper soils (11 cm) than in the shallow soils (2 cm) (Table 1). Relatively enriched soil organic matter in the deeper and older soils has been previously observed and several mechanisms behind this have been proposed, including an isotopic change in atmospheric  $\text{CO}_2$  over time, an increased contribution from microbial biomass in the deeper soils, and kinetic fractionation during respiration and preferential decomposition of certain organic components in soils (Mariotti, 1991; Amiotte-Suchet et al., 1999; Trumbore, 2000; Wynn et al., 2005; Boström et al., 2007).

Temporal and spatial variations of soil  $\text{CO}_2$  reflect the balance between  $\text{CO}_2$  production and consumption. Assuming  $\text{CO}_2$  is at steady state in an unsaturated soil, the amount of  $\text{CO}_2$  produced in the soil horizons would be balanced by the amount of  $\text{CO}_2$  lost to overlying air through molecular diffusion, assuming  $\text{CO}_2$  consumed in mineral

weathering reactions to be a minor flux (see later discussion). This relationship has been previously modeled according to the following equation (Cerling, 1984; Cerling and Quade, 1993):

$$\frac{\partial C_s^*}{\partial t} = 0 = D_s^* \frac{\partial^2 C_s^*}{\partial z^2} + \phi^* \quad (4)$$

where  $D_s^*$  is the molecular diffusion coefficient for  $\text{CO}_2$  in the soils [ $\text{cm}^2 \text{s}^{-1}$ ],  $C_s^*$  is soil  $\text{CO}_2$  concentration [ppmv],  $t$  is time (h) and  $z$  is soil depth [cm].  $\phi^*$  is the respiratory  $\text{CO}_2$  production rate [ $\text{mol m}^2 \text{h}^{-1}$ ], and will be assumed to be constant at a given time. Steady state assumption also requires constant isotopic composition of soil  $\text{CO}_2$ , thus,  $C^*$  could be  $^{12}\text{C}$  or  $^{13}\text{C}$ . Boundary conditions are:

$$\text{At } z = 0 \text{ (soil surface): } C_s^* = C_a^* \quad (5)$$

$$\text{At } z = L \text{ (a certain depth): } \frac{\partial C_s^*}{\partial z} = 0 \quad (6)$$

where  $C_a^*$  is atmospheric  $\text{CO}_2$  concentration. By solving differential Eq. (4) at boundary conditions (5) and (6) we can obtain the following equation:

$$C_s^* = \frac{\phi^*}{D_s^*} \left( Lz - \frac{z^2}{2} \right) + C_a^* \quad (7)$$

Thus, if  $D_s^*$  is known,  $\phi^*$  can be calculated from  $\text{CO}_2$  depth profiles. Even though  $p\text{CO}_2$  was measured in both the Huron and the Kalamazoo sites, Eq. (7) can only be applied to the Huron watershed, where soil gas samples were collected deep enough to reach steady state conditions with the constant  $\text{CO}_2$  partial pressures. The  $\text{CO}_2$  soil production and modeling parameters are presented in Table 6. At steady state,  $\text{CO}_2$  is produced in (and emitted from) the Huron soils at 1 to 4  $\text{mmol m}^{-2} \text{h}^{-1}$ . Similar rates have also been observed in soils at Sicily, Italy (Camarda et al., 2007). The  $\text{CO}_2$  production rates are highest at around 4  $\text{mmol m}^{-2} \text{h}^{-1}$  in the summer, within the typical respiration rate in temperate and subtropical ecosystems (4–10  $\text{mmol m}^{-2} \text{h}^{-1}$  during the growing seasons; Dorr and Munnich, 1980).

The  $\delta^{13}\text{C}_{\text{CO}_2}$  can be modeled quantitatively, similar to  $p\text{CO}_2$ , where both isotopes are involved (i.e.,  $C^*$  could be  $^{12}\text{C}$  or  $^{13}\text{C}$ ). It is still under debate whether carbon isotopes are fractionated during respiratory conversion from organic matter to  $\text{CO}_2$  (Fritz et al., 1978; Mariotti, 1991; Amiotte-Suchet et al., 1999), but this fractionation factor would be small. Most likely, slight fractionation between  $\text{CO}_2$  and its organic matter sources results from kinetic fractionation associated with molecular diffusion. The diffusion coefficients of soil gas  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$  are different and this would produce a minimum of  $+4.4\%$  enrichment in  $\delta^{13}\text{C}_{\text{CO}_2}$  relative to  $\delta^{13}\text{C}_{\text{SOM}}$  (Craig, 1953; Cerling et al., 1991):

$$^{12}D_s = 1.0044^{13}D_s \quad (8)$$

Based on Cerling et al. (1991), the diffusion fractionation is further modeled by Davidson (1995). In this calculation, both  $^{12}\text{C}_{\text{CO}_2}$  and  $^{13}\text{C}_{\text{CO}_2}$  are assumed at steady state and balanced by production and diffusive loss. The fractionation between soil  $\text{CO}_2$  and organic matter can be derived, according to the following equation:

$$\Delta = \delta_{\text{CO}_2} - \delta_{\text{SOM}} = 0.0044\delta_{\text{SOM}} + \frac{C_a^*}{C_s^*} (\delta_a - 1.0044\delta_{\text{SOM}} - 4.4) + 4.4 \quad (9)$$

where  $\delta_{\text{CO}_2}$ ,  $\delta_{\text{SOM}}$  and  $\delta_a$  are carbon isotope compositions of soil  $\text{CO}_2$ , organic matter in soil, and atmospheric  $\text{CO}_2$ , respectively.  $C_s^*$  and  $C_a^*$  are  $\text{CO}_2$  concentrations in soil gas and atmosphere. Applying this



**Table 5**  
Soil water composition in the Kalamazoo watershed ( $\mu\text{mol/l}$  for major ions).

Site	Date	Depth (cm)	pH	Alk (meq/l)	DIC (mmol/l)	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$
<i>Monolith #2</i>										
2 drip	11/25/03	200	8.21	2.50		−4.9	1197	308	464	122
2 drip	6/10/04	200	7.97	3.66	3.62	−14.4	1599	409	217	133
2 drip	7/27/04	200	8.01	4.36		−13.2	1916	491	238	143
2 drip	10/21/04	200	8.36	4.11	4.06	−9.1	1560	496	141	147
2 drip	12/22/04	200	8.13	2.64	2.60	−5.4	1193	304	99	122
2 drip	4/15/05	200	8.19	2.35		−8.3	955	235	24	29
2 drip	5/5/05	200	7.98	2.49	2.28	−7.3	1039	254	76	107
2 drip	8/26/05	200	7.98	4.18	4.12	−8.4	1793	451	171	118
2 tub	6/10/04	200	7.61		3.18	−14.1	1491	379	225	130
2 tub	10/21/04	200	8.39	4.41	4.25	−10.3	1608	521	138	147
2 tub	4/14/05	200	8.10	2.13	2.07	−6.6	904	226	69	185
2 tub	5/5/05	200	7.82	2.51	2.46	−7.9	999	247	87	108
2 tub	8/26/05	200	7.78	3.53	3.31	−9.8	1557	385	159	109
<i>Monolith #6</i>										
6 drip	11/25/03	200	8.03	2.65		−6.3	1200	370	347	180
6 drip	6/10/04	200	7.94	2.90	2.79	−11.0	1304	389	352	188
6 drip	7/27/04	200	8.12	4.20		−11.7	1866	557	307	180
6 drip	10/21/04	200	8.39	3.89	3.66	−9.0	1518	555	272	202
6 drip	12/22/04	200	8.24	2.47	2.48	−6.1	1170	344	139	195
6 drip	4/15/05	200	8.32	2.29	2.08	−6.0	996	283	68	182
6 drip	5/5/05	200	8.07	2.28	2.03	−5.7	978	284	68	184
6 drip	8/26/05	200	8.05	5.08	4.67	−6.8	2142	623	93	210
6 tub	6/10/04	200	7.71	2.56	2.49	−10.2	1200	357	361	187
6 tub	10/21/04	200	8.34	4.21	3.86	−9.9	1624	601	285	198
6 tub	4/14/05	200	8.11	2.18	1.98	−7.5	904	261	80	105
6 tub	5/5/05	200	7.86	2.26	2.10	−7.1	998	286	62	182
6 tub	8/26/05	200	7.61	3.73	3.39	−9.1	1611	448	89	203
<i>Monolith #9</i>										
9 drip	11/25/03	200	8.01	3.79		−5.7	1587	442	292	150
9 drip	6/10/04	200	7.82	3.78	3.49	−9.2	1663	465	227	144
9 drip	7/27/04	200	8.16	5.24		−10.6	2238	616	219	110
9 drip	10/21/04	200	8.42	4.52	4.15	−7.7	1633	612	184	131
9 drip	12/22/04	200	8.23	3.55	3.24	−5.2	1562	427	96	135
9 drip	4/15/05	200	8.40	3.11	2.94	−5.0	1195	311	46	129
9 drip	5/5/05	200	8.04	3.28	3.08	−6.3	1267	338	47	128
9 drip	8/26/05	200	7.70	5.87		−8.2	2487	646	98	110
9 tub	6/10/04	200	7.59	3.63	3.43	−8.6	1594	419	205	137
9 tub	10/21/04	200	8.21	5.04	4.69	−9.4	1734	673	185	136
9 tub	4/14/05	200	8.07	3.20	2.88	−7.7	1234	334	53	124
9 tub	5/5/05	200	8.09	3.17	2.86	−6.3	1244	324	45	127
9 tub	8/26/05	200	7.54	4.63	4.64	−10.3	2003	503	91	131
9A*	11/25/03	180	7.37	3.83		−6.0	1638	429	462	137
9A	7/27/04	180	7.51	5.20		−10.5	2338	600	283	112
9A	12/22/04	180	7.72	3.71	3.43	−4.7	1625	422	116	123
9A	4/15/05	180	7.85	3.36		−6.0	1262	335	38	79
9A	5/5/05	180	7.64	3.46	3.25	−5.7	1290	346	41	83
9A	8/26/05	180	7.32	5.54		−6.1	2400	601	113	99
9B	11/25/03	180	7.45	3.78		−3.9	1798	423	541	157
9B	6/10/04	180	7.63	4.38	4.28	−10.2	1904	423	123	171
9B	7/27/04	180	7.52	5.20		−9.5	2421	541	231	146
9B	12/22/04	180	7.75	3.65	3.33	−5.3	1721	402	158	137
9B	4/15/05	180	7.81	3.50	3.51	−5.2	1300	313	55	129
9B	5/5/05	180	7.65	3.55	3.45	−5.5	1302	324	47	122
9B	8/26/05	180	7.32	5.48	5.45	−2.9	2407	521	88	142
<i>Monolith #13</i>										
13 drip	11/25/03	200	7.64	3.03		−7.9	1416	403	414	177
13 drip	6/10/04	200	8.01	4.34	4.29	−13.9	2051	563	383	164
13 drip	7/27/04	200	8.32	5.15		−11.5	2169	634	341	167
13 drip	10/21/04	200	8.48	4.09	3.91	−8.4	1549	596	217	206
13 drip	12/22/04	200	8.19	3.15	2.96	−5.4	1423	406	62	202
13 drip	4/15/05	200	8.36	3.12	2.52	−8.0	1233	334	28	179
13 drip	5/5/05	200	8.09	3.25	2.92	−8.1	1289	357	29	179
13 tub	6/10/04	200	7.66	4.55	4.21	−13.6	1954	529	384	160
13 tub	10/21/04	200	8.16	4.90	4.61	−9.8	1705	667	237	199
13 tub	4/14/05	200	8.22	2.86	3.02	−8.1	1167	315	26	175
13 tub	5/5/05	200	8.03	3.29	2.98	−8.3	1269	348	29	177
13 tub	8/26/05	200	7.73	4.67	4.66	−10.6	2026	528	69	199
13A	11/25/03	180	7.48	3.46		−7.7	1517	479	472	151
13A	6/10/04	180	7.64	4.37		−14.5	1914	556	445	158

(continued on next page)

Table 5 (continued)

Site	Date	Depth (cm)	pH	Alk (meq/l)	DIC (mmol/l)	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$
Monolith # 13										
13A	7/27/04	180	7.42	4.96		-12.7	2148	657	465	154
13A	12/22/04	180	7.79	3.65	3.54	-7.5	1635	489	179	174
13A	4/15/05	180	7.87	3.24		-8.9	1283	386	52	182
13A	5/5/05	180	7.67	3.26	3.08	-6.5	1274	382	42	174
13A	8/26/05	180	7.41	4.87	5.20	-7.7	2108	593	113	195
13B	11/25/03	180	7.48	2.53		-8.0	1261	354	585	151
13B	7/27/04	180	7.51	5.04		-12.1	2246	608	284	188
13B	12/22/04	180	7.75	2.92	2.59	-7.6	1317	375	29	215
13B	4/15/05	180	7.89	3.21		-8.6	1282	353	2	39
13B	5/5/05	180	7.71	3.27		-8.5	1296	357	22	187
13C	11/25/03	180	7.55	2.21		-8.7	1139	372	469	251
13C	7/27/04	180	7.45	4.69		-11.3	1985	624	153	252
13C	12/22/04	180	7.81	2.52	2.38	-5.8	1215	360	21	294
13C	5/5/05	180	7.60	3.13	2.95	-8.3	1271	371	25	238
13C	8/26/05	180	7.40	4.72		5.1	2086	607	79	223

\*9 (or 13) A, B, and C: collected from duplicate Prenart lysimeters at 180 cm. Drip samples are instantaneous soil solutions collected in about 3 h.

equation to the Huron data, the difference between  $\delta^{13}\text{C}_{\text{CO}_2}$  and  $\delta^{13}\text{C}_{\text{SOM}}$  can be calculated:

$$\Delta = \frac{5520}{\text{pCO}_2} + 4.28 \quad (10)$$

where  $\text{pCO}_2$  varies with season. For the HH2 site of the Huron watershed, the isotopic difference between soil organic matter and

$\text{CO}_2$  is expected to range between 4.9 and 5.6‰. At forested sites of the Huron watershed, the  $\delta^{13}\text{C}_{\text{SOM}}$  had an average value of  $-26.8\%$  while the  $\delta^{13}\text{C}_{\text{CO}_2}$  averaged about  $-21 \pm 1\%$ . This difference in C isotope ratios between soil  $\text{CO}_2$  and its organic matter sources is within the calculated range. Thus,  $\delta^{13}\text{C}_{\text{CO}_2}$  not only varies with  $\delta^{13}\text{C}_{\text{SOM}}$  but also with  $\text{CO}_2$  production rate ( $\text{pCO}_2$ ).

Dissolved organic carbon (DOC) is also potentially important in inorganic carbon cycling. DOC concentrations have been shown to decrease with depth, following the depth trend of solid organic matter at the Huron watershed (Jin et al., 2008a). Only a few studies have characterized the C isotopic composition of DOC and its isotopic relationship with solid organic matter sources. In a study performed in the Morvan Mountains of France, it was found that C isotopic composition of the soil water DOC was slightly depleted relative to the soil organic matter (Amiotte-Suchet et al., 2007). This depletion was greater in a deciduous forest catchment (by about 1‰) compared to a coniferous forest catchment where no significant isotopic differentiation was observed between the DOC and its presumed source (solid organic matter). Furthermore, watershed studies have shown  $\delta^{13}\text{C}_{\text{DOC}}$  values of  $-27\%$  that are similar to that of  $\text{C}_3$  plants composing the vegetation cover in the study area (Schiff et al., 1990). Generally, DOC is degraded to  $\text{CO}_2$  by bacterial respiration, a process that has been shown not to fractionate C isotopes (Barth and Veizer, 1999), in agreement with the observed decrease of DOC with depth in the soil profiles (Jin et al., 2008a). In the Huron watershed sites, the C isotopic composition of DOC was not measured, because DOC is not a direct source of soil water/groundwater DIC.

## 5.2. Speciation of soil water DIC

DIC is the sum of three C-bearing species,  $\text{H}_2\text{CO}_3^0$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ . Another term commonly used in carbon systematics is carbonate alkalinity, defined as  $[\text{HCO}_3^-] + 2 * [\text{CO}_3^{2-}]$ , where  $[\text{HCO}_3^-]$  and  $[\text{CO}_3^{2-}]$  are concentrations in molar equivalents. Carbonate alkalinity and DIC can be converted from one to another if water temperature and pH values are known. At the near-neutral pH range, typical of most surface waters,  $\text{HCO}_3^-$  is the major species and DIC concentrations are virtually identical to carbonate alkalinity. However, the titrated alkalinity does not necessarily equal carbonate alkalinity because weak organic acids can also be titrated and this could be especially problematic when water samples are collected from shallow soil zones, where pH values are low and dissolved organic matter concentrations are high (Clark and Fritz, 1997).

At a given temperature,  $\text{H}_2\text{CO}_3^0$  concentrations are determined by  $\text{pCO}_2$  through Henry's law and DIC (or carbonate alkalinity) values controlled by pH, and by carbonate solubility (Fig. 6). Groundwater

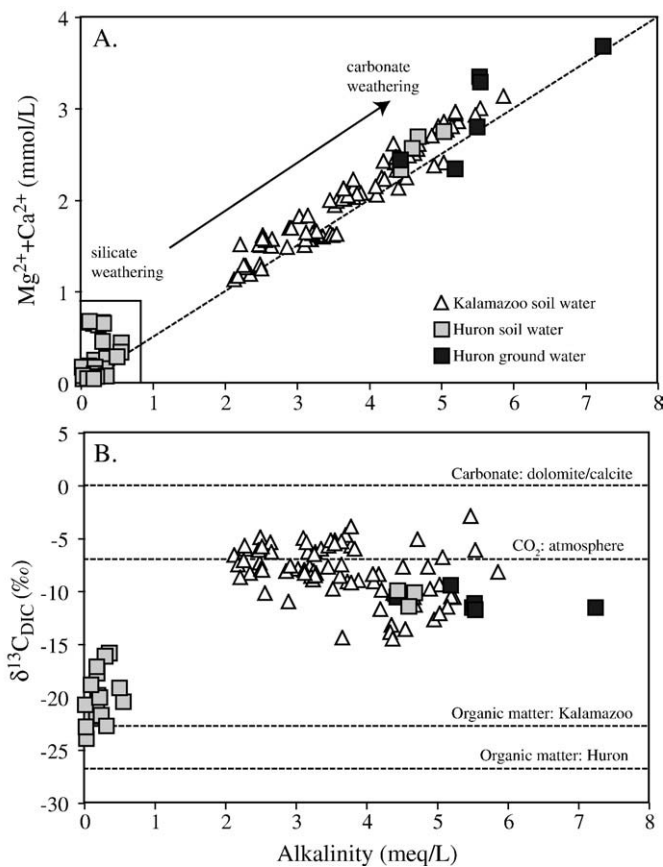


Fig. 5. Elemental chemistry (A) and carbon isotope ratios of DIC (B) in soil waters and groundwater of the Huron and the Kalamazoo watersheds.  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  are the major cations and alkalinity includes the major anion ( $\text{HCO}_3^-$ ) in these soil water and groundwater samples (dashed line in A represents 1:2 ratio, according to charge balance). A sharp transition exists from silicate weathering to carbonate weathering with increasing depth in the soil profile in both DIC concentrations and stable isotope compositions. Isotopic compositions of all C reservoirs are shown for reference (dashed lines in B).

**Table 6**  
CO<sub>2</sub> production rates at a soil profile of the Huron watershed.

Month	CO <sub>2</sub> production rate (mmol/m <sup>2</sup> /h)
Feb	1.0
June	3.6
July	3.3
Aug	2.6
Oct	1.5

$L = 100$  cm;  $^{12}\text{Ca} = 370$  ppm.  
 $^{12}D_s = 0.02$  cm<sup>2</sup> s<sup>-1</sup> from Cerling (1984).

and soil water from the Huron watershed are at equilibrium with soil gas CO<sub>2</sub> at values of approximately 10 to 20 times those of atmospheric CO<sub>2</sub> (Fig. 6) and within the range of CO<sub>2</sub> measured in the soil gas samples. This consistency between calculated pCO<sub>2</sub> from inorganic carbon chemistry and measured pCO<sub>2</sub> from soil gas samples suggests that soil waters and groundwaters in the Huron watershed sites were at equilibrium with gaseous CO<sub>2</sub> in the soil atmosphere.

However, soil waters from the KBS sites plot across a relatively low CO<sub>2</sub> range (less than 20 times greater than atmospheric CO<sub>2</sub>; Fig. 6), much lower than those from direct measurement on soil gas samples in the stratum just above the carbonate minerals. As the soil gas samples were only collected from the top 100 cm while soil waters were collected at 150 cm or deeper below soil surface, the calculated and measured pCO<sub>2</sub> cannot be compared directly. Much lower CO<sub>2</sub> concentrations in the deeper KBS soils could be caused by a clayey layer in the B-horizon which could block soil gas movement towards the deep monolith, or because carbonate dissolution consumes CO<sub>2</sub> and thus lowers pCO<sub>2</sub>. All the soil water from the Kalamazoo monoliths (depth range, 180–200 cm) and deep soil waters/groundwaters from the Huron watershed sites (depths > 150 cm at GR1 and GR3) were saturated with respect to calcite (Fig. 6; Jin et al., 2008a,b).

### 5.3. Is carbonate dissolution in soil profiles always an open system with respect to CO<sub>2</sub>?

If the soil CO<sub>2</sub> reservoir is large enough and gas–water exchange is at equilibrium, carbonate dissolution would not draw down soil CO<sub>2</sub>, a situation known as open-system dissolution (Deines et al., 1974). In closed-system dissolution, water is equilibrated with a specified pCO<sub>2</sub>, and then is isolated from CO<sub>2</sub> replenishment as carbonate dissolution proceeds (Deines et al., 1974). In this case, H<sub>2</sub>CO<sub>3</sub><sup>0</sup> will decrease due to consumption by carbonate weathering. Open- vs. closed-system dissolution are conceptual end-members and a given environment could lie in between these two scenarios, effectively being partially closed. Considering a 4-meter soil profile with 30% porosity, the amount of CO<sub>2</sub> present in the whole soil profile is between 0.2 and 0.4 mol/m<sup>2</sup> at STP conditions, based on typical pCO<sub>2</sub> partial pressures of 4000 and 8000 ppm(v) in the winter and summer months, respectively. CO<sub>2</sub> production and emission rates for Michigan soils were estimated in the previous section to be about 1–4 mmol/m<sup>2</sup>/h, and they mainly vary with temperature. With this production rate in Michigan soils, the soil CO<sub>2</sub> turnover time is on the order of 2 to 14 days.

The soil CO<sub>2</sub> produced by respiration is lost through diffusion to the overlying air, as discussed previously. However, soil CO<sub>2</sub> can also be lost by reacting with minerals in the soil profiles. This is particularly important when carbonate minerals are present, which are more reactive and soluble (e.g., Jacobson et al., 2002; Szramek et al., 2007; Williams et al., 2007). In the study sites of the Huron and Kalamazoo watersheds, chemical weathering processes have been previously characterized (Jin et al., 2008a,b) and it has been shown that carbonate mineral weathering rates are dominantly controlled by pCO<sub>2</sub>-dependent carbonate solubility. Thus, the amount of CO<sub>2</sub> con-

sumed by carbonate dissolution is proportional to carbonate weathering rates and water discharge. A typical soil water alkalinity in the Huron and the Kalamazoo watersheds is 3.5 meq/l, which is almost entirely derived from carbonate mineral dissolution and thus half of that alkalinity originated from soil CO<sub>2</sub>. It is estimated that in the case of a 2-inch infiltration event that percolates through the soil zones and equilibrates with carbonate minerals, about 0.09 mol/m<sup>2</sup> of CO<sub>2</sub> will be consumed. This is significant compared to the total amount of CO<sub>2</sub> present in the whole soil profile (0.2–0.4 mol/m<sup>2</sup>).

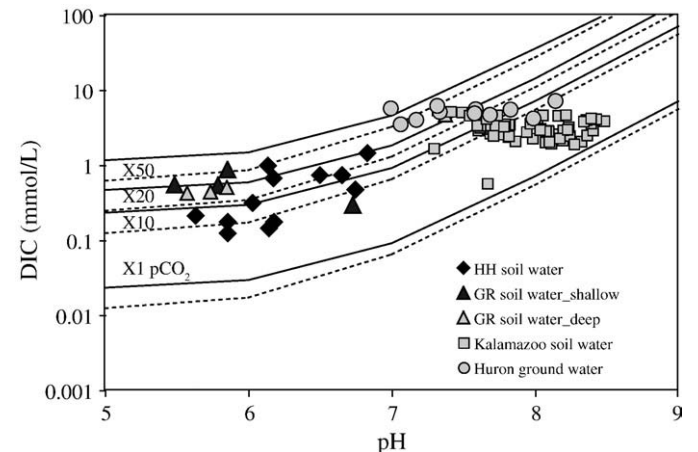
Previous consideration of CO<sub>2</sub> dissolution under open- vs. closed-system conditions has been based on physical properties of soils, taking into consideration the position of the carbonate minerals relative to water table and root zone (e.g., Reardon et al., 1979, 1980). In both the Huron and Kalamazoo watershed sites, most carbonate weathering occurs well above the water table and fairly close to the root zone, all of which seem to favor an open system. However, mass balance calculations discussed above suggest that CO<sub>2</sub> in the lower part of the soil profile could be exhausted by chemical reaction with the abundant carbonate minerals, and therefore the vadose zone is not necessarily an open system with respect to CO<sub>2</sub>. At the shallow soil horizons where silicate weathering is present and carbonate weathering is absent, the vadose zone would remain as an open system in which soil CO<sub>2</sub> is not significantly drawn down by mineral weathering reactions.

### 5.4. Kinetic vs. equilibrium controls on $\delta^{13}\text{C}_{\text{DIC}}$ in the Huron watershed

The  $\delta^{13}\text{C}_{\text{DIC}}$  is controlled by the relative concentrations of the three dissolved carbon species and their carbon isotopic composition (Clark and Fritz, 1997):

$$\delta^{13}\text{C}_{\text{DIC}} = \left( \delta^{13}\text{C}_{\text{H}_2\text{CO}_3^0} * [\text{H}_2\text{CO}_3^0] + \delta^{13}\text{C}_{\text{HCO}_3^-} * [\text{HCO}_3^-] + \delta^{13}\text{C}_{\text{CO}_3^{2-}} * [\text{CO}_3^{2-}] \right) / \text{DIC} \quad (11)$$

This equation could be simplified depending on whether the system is controlled by equilibrium or kinetic factors. In an open system where isotopic equilibrium is obtained, soil CO<sub>2</sub> is a large carbon reservoir and all dissolved C-bearing species are at isotopic equilibrium with CO<sub>2</sub>. Thus,  $\delta^{13}\text{C}_i$  ( $i = \text{H}_2\text{CO}_3^0, \text{HCO}_3^-, \text{CO}_3^{2-}$ ) is determined by  $\delta^{13}\text{C}_{\text{CO}_2}$  and a temperature-dependent equilibrium fractionation factor between dissolved C-bearing species and gaseous CO<sub>2</sub> (e.g., Zhang et al., 1995). Among all, the largest equilibrium fractionation (~9‰) occurs between HCO<sub>3</sub><sup>-</sup> and CO<sub>2</sub>(g). Since DIC



**Fig. 6.** Soil water and groundwater DIC and pH. Theoretical DIC values as a function of pH and pCO<sub>2</sub> (X1, X10, X20, X50 pCO<sub>2</sub>; expressed as degree of excess over atmospheric pCO<sub>2</sub>) are plotted at 5 °C (solid lines) and 25 °C (dashed lines).

speciation is a function of  $p\text{CO}_2$  and pH, the overall  $\delta^{13}\text{C}_{\text{DIC}}$  depends only on pH, temperature and  $\delta^{13}\text{C}_{\text{CO}_2}$  in an open system at isotopic equilibrium. Theoretical  $\delta^{13}\text{C}_{\text{DIC}}$  values were calculated and plotted against pH at equilibrium conditions with soil  $\text{CO}_2$  ( $\delta^{13}\text{C}_{\text{CO}_2}$  of  $-22\%$  and  $-20\%$ , respectively) and also with atmospheric  $\text{CO}_2$  ( $\delta^{13}\text{C}_{\text{CO}_2}$  of  $-8.0\%$ ) at  $5^\circ\text{C}$  (dashed lines in Fig. 7A). Another temperature ( $10^\circ\text{C}$ ) is considered when DIC is at isotopic equilibrium with soil  $\text{CO}_2$ , and no significant difference in  $\delta^{13}\text{C}_{\text{DIC}}$  is observed with those at  $5^\circ\text{C}$ , especially at low pH environments.

In a kinetically controlled system where isotope equilibrium was not attained,  $\delta^{13}\text{C}_{\text{DIC}}$  will be solely determined by the source of DIC (including atmospheric  $\text{CO}_2$ , soil gas  $\text{CO}_2$  or carbonate C; Clark and Fritz, 1997). When only silicate minerals are present, the DIC is entirely derived from aqueous  $\text{CO}_2$  (Eq. (12)). In contrast, if soils contain carbonate minerals, then DIC becomes dominated by bicarbonate alkalinity derived equally from aqueous  $\text{CO}_2$  and carbonate minerals (at circumneutral pH and in the absence of strong acid

loading). Thus, the  $\delta^{13}\text{C}$  of  $\text{HCO}_3^-$  will be a 1:1 mixture of  $\delta^{13}\text{C}_{\text{H}_2\text{CO}_3}$  and  $\delta^{13}\text{C}_{\text{CaCO}_3}$  (Eq. (13)):

$$\text{Silicate weathering: } \delta^{13}\text{C}_{\text{DIC}} = \delta^{13}\text{C}_{\text{H}_2\text{CO}_3} \quad (12)$$

$$\text{Carbonate weathering by carbonic acid reaction:} \quad (13)$$

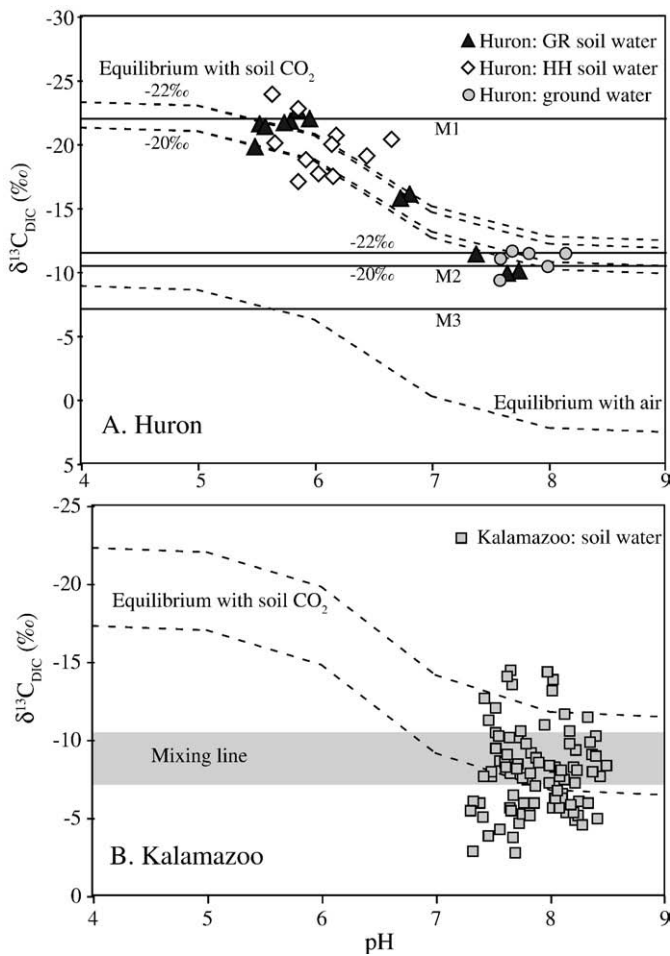
$$\delta^{13}\text{C}_{\text{DIC}} = (\delta^{13}\text{C}_{\text{H}_2\text{CO}_3} + \delta^{13}\text{C}_{\text{CaCO}_3}) / 2.$$

Three non-equilibrium mixing lines are plotted in Fig. 7A: soil  $\text{CO}_2$  reacting with silicate minerals (M1), soil  $\text{CO}_2$  reacting with carbonate minerals (M2, with  $\delta^{13}\text{C}_{\text{CO}_2}$  of  $-22\%$  and  $-20\%$ , respectively), and atmospheric  $\text{CO}_2$  reacting with silicate minerals (M3).

$\delta^{13}\text{C}_{\text{DIC}}$  of soil waters and shallow groundwaters in the Huron watershed show two trends (Fig. 7A). In shallow soil horizons where silicate mineral dissolution dominates the soil water chemistry, soil water  $\delta^{13}\text{C}_{\text{DIC}}$  values vary significantly with pH but lie on the equilibrium line with soil  $\text{CO}_2$ . This implies that soil  $\text{CO}_2$  is the only source of DIC in the shallow soils, and the atmospheric  $\text{CO}_2$  contribution is not significant. Furthermore, this is an open system with respect to soil gas  $\text{CO}_2$ , consistent with our previous mass balance calculation and the fact that silicate dissolution consumes little  $\text{CO}_2$ . The deep soil waters and shallow groundwaters, however, have pH between 7 and 8.5, and relatively constant  $\delta^{13}\text{C}_{\text{DIC}}$  values around  $-11\%$ . The hydrochemical evolution of these deep soil waters and shallow groundwaters is controlled by carbonate dissolution. These natural waters lie close to both the mixing line between carbonate carbon and soil  $\text{CO}_2$  and the equilibrium line with soil  $\text{CO}_2$  ( $\delta^{13}\text{C}_{\text{CO}_2}$  of  $-20\%$ ), and will be discussed below.

When  $\delta^{13}\text{C}_{\text{CO}_2}$  is around  $-22\%$ , soil waters and groundwaters with  $\delta^{13}\text{C}_{\text{DIC}}$  of  $-11\%$  plot closer to the mixing line of soil carbonate and respiratory  $\text{CO}_2$  than the equilibrium line (Fig. 7A). Several field conditions could favor this non-equilibrium scenario: (1) Rapid carbonate dissolution rates (especially for calcite) have been observed in our study sites, where soil waters have similar chemistry as the shallow groundwaters and saturation is always attained in soils irrespective of rainfall intensity (Jin et al., 2008a,b). Thus, carbonate mineral weathering is a solubility-controlled instead of kinetic-controlled process. (2) Rapid water infiltration to the water table and short residence times of solutes in vadose zone. A LiBr tracer experiment conducted at the KBS monoliths demonstrated that there are preferential flowpaths in the vadose zone (Jin et al., 2008b). (3) A partially closed system with respect to  $\text{CO}_2$ . As discussed in the section above,  $\text{CO}_2$  consumption by carbonate dissolution could occur faster than new infiltration and respiratory processes can replace soil  $\text{CO}_2$ . This is most likely in the colder months, when the  $\text{CO}_2$  production rate is low. (4) Spatial heterogeneity of soils, which leads to limited gas–water exchange. Direct measurement of  $\text{O}_2$  content by microelectrodes within soil aggregates has shown that pores were variably aerated, thus correlating to different denitrification rates (Sextstone et al., 1985). Synchrotron imaging and computer microtomographic images provide direct evidence of heterogeneity of pore diameters and connectivity within soil macroaggregates (Smucker et al., 2007). These studies suggest that soil gas and soil water are not well mixed, and that gas exchange could be limited.

Recharge mostly occurs in early spring and late fall in southern Michigan, when soil  $\text{CO}_2$  production rate is low and when most of our soil waters and groundwaters were collected. We propose that conditions for non-equilibrium carbonate dissolution could be met in Michigan soils during these cooler months. If so, the stable isotope data also suggest that the DIC isotopic signature produced by silicate weathering at the shallow soils becomes masked by carbonate dissolution at the deeper horizons. One of the most important assumptions in the  $^{14}\text{C}$ -dating technique using groundwaters is that half of the DIC is contributed by “dead” carbonate carbon and the



**Fig. 7.** C isotopic compositions of DIC in soil waters and groundwaters as a function of pH in the Huron watershed (A) and in the Kalamazoo watershed (B). Solid lines and dashed lines are theoretic  $\delta^{13}\text{C}_{\text{DIC}}$  values as a function of pH at isotopic non-equilibrium and equilibrium conditions, respectively. Solid line M1: non-equilibrium, soil  $\text{CO}_2$  as the only carbon source ( $\delta^{13}\text{C}_{\text{DIC}} = \delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ ); line M2: non-equilibrium, mixing of carbonate carbon and soil  $\text{CO}_2$  carbon ( $\delta^{13}\text{C}_{\text{DIC}} = 1/2 \delta^{13}\text{C}_{\text{CO}_2(\text{aq})} + 1/2 \delta^{13}\text{C}_{\text{CaCO}_3}$ ) with  $\delta^{13}\text{C}_{\text{CO}_2}$  as  $-22\%$  and  $-20\%$ , respectively; line M3: non-equilibrium, atmospheric  $\text{CO}_2$  as the only carbon source ( $\delta^{13}\text{C}_{\text{DIC}} = \delta^{13}\text{C}_{\text{atm CO}_2(\text{aq})}$ ). The dashed lines represent C isotope compositions at equilibrium conditions, with the soil  $\text{CO}_2$  ( $-22\%$  and  $-20\%$ ) and with atmospheric  $\text{CO}_2$  ( $-8.0\%$ ) at  $5^\circ\text{C}$ . Another temperature ( $10^\circ\text{C}$ ) is considered when DIC is at isotopic equilibrium with soil  $\text{CO}_2$ , and no significant difference in  $\delta^{13}\text{C}_{\text{DIC}}$  is observed with those at  $5^\circ\text{C}$ , especially at low pH environments. For the Kalamazoo watershed (B),  $\delta^{13}\text{C}_{\text{DIC}}$  values are modeled in two conditions: non-equilibrium mixing between  $\text{CO}_2$  and carbonate (grey area) and equilibrium with soil  $\text{CO}_2$  (between dashed lines).

other half by “modern” soil CO<sub>2</sub> (e.g., Fontes and Garnier, 1979; Clark and Fritz, 1997). If soil carbonate is dissolving under partially closed-system conditions, then this assumption may not be valid.

In the warmer months of Michigan, soil CO<sub>2</sub> is much higher and close to –20‰ in its carbon isotopic composition. The rain that falls on the ground is mostly lost through evapotranspiration with little being recharged to the water table. In this case, residence times of water in the unsaturated zone will be long enough to reach isotope equilibrium with soil CO<sub>2</sub>. The discussion above suggests that whether Michigan soil water and groundwater DIC can reach isotope equilibrium with soil CO<sub>2</sub> depends mainly on (1) whether carbonate dissolution is an open or partially closed system with respect to CO<sub>2</sub>; and (2) the recharge rate of soil waters, and thus the contact time between DIC and soil CO<sub>2</sub>.

### 5.5. $\delta^{13}\text{C}_{\text{DIC}}$ in agricultural ecosystems of the Kalamazoo watershed

The  $\delta^{13}\text{C}_{\text{DIC}}$  values of soil waters in the KBS site of the Kalamazoo watershed neither exhibit a simple mixing relationship nor do they fall on the equilibrium line (Fig. 7B). Instead, C isotope compositions vary seasonally, becoming more depleted in summer and enriched in winter. These soil waters were collected from soil depths of 180 and 200 cm, within the carbonate-bearing horizons, where water chemistry is dominated by carbonate dissolution and seasonal variation in  $\delta^{13}\text{C}_{\text{DIC}}$  is controlled by  $\delta^{13}\text{C}_{\text{CO}_2}$ . The seasonal variation of  $\delta^{13}\text{C}_{\text{DIC}}$  is in agreement with the observed trend of  $\delta^{13}\text{C}_{\text{CO}_2}$ , as organic matter sources of CO<sub>2</sub> are different over time (Fig. 4B). However, there is some significant deviation between measured and modeled data.

In natural environments, carbonate and silicate minerals are dissolved by carbonic acid, as well as by strong acids such as sulfuric acid and nitric acid (Karim and Veizer, 2000). Therefore, the isotopic composition of DIC will not only depend on the relative proportions of silicate and carbonate minerals being weathered, but also on the source of acids (strong acids vs. CO<sub>2</sub>) and the relative proportions of inorganic C forms (bicarbonate and CO<sub>2</sub>). The pH values of soil waters range between 7.5 and 8.5, where over 95% of DIC is bicarbonate. Pyrite is common in Michigan bedrock strata and its oxidation produces sulfate (Jin et al., 2008b). At KBS, nitrate and sulfate concentrations are high in surface and subsurface waters (Tables 4 and 5; Hamilton et al., 2007; Jin et al., 2008a,b). Atmospheric inputs as well as in situ production of these ions by nitrification and pyrite oxidation would be accompanied by protons that are subsequently neutralized in reaction with carbonate minerals in deeper soils. If DIC is produced entirely from carbonate minerals reacting with strong acid (Eq. (1)), this would result in a (SO<sub>4</sub> + NO<sub>3</sub>)/DIC ratio by equivalents of 1. If DIC is produced from carbonate minerals reacting with CO<sub>2</sub> (Eq. (2)), this would result in a (SO<sub>4</sub> + NO<sub>3</sub>)/DIC ratio by equivalents of 0. The (SO<sub>4</sub> + NO<sub>3</sub>)/DIC ratios in the Kalamazoo soil waters were  $0.14 \pm 0.05$  ( $n = 40$ ), suggesting that about 20% of carbonate minerals dissolved in the soil water can be accounted for by reaction with strong acids as opposed to carbonic acid. The higher ratios observed in the winter months can partially explain the more <sup>13</sup>C-enriched DIC than predicted by the model. In summary, C isotopes measured in KBS soil waters reflect soil acidification introduced by human activities and this effect may be global (e.g., Raymond and Cole, 2003; Hamilton et al., 2007).

## 6. Conclusions and implications

This study has examined inorganic carbon concentrations and stable isotope ratios of various carbon reservoirs along the hydrologic flow path from surface soils enriched in organic matter but leached of carbonate minerals, into underlying glacial parent material containing abundant carbonate minerals. The dramatic change in inorganic carbon biogeochemistry over just a few meters of increasing depth in the soil profiles illustrates the strong interactions of silicate and

carbonate minerals with biogenic CO<sub>2</sub> generated predominantly in overlying organic soils, as well as with nitric and sulfuric acids from precipitation and internal sources such as nitrification. Stable C isotopes and soil pCO<sub>2</sub> concentrations revealed the role of vegetation as a source of organic matter for the respiratory CO<sub>2</sub> production that drives mineral weathering in these soils. The pCO<sub>2</sub> concentrations in the soil profile are also controlled by diffusion towards the ground surface and consumption through carbonate dissolution.

In shallow soil zones where only silicate minerals are weathered, C isotope equilibrium exists between soil CO<sub>2</sub> and soil water DIC. Here amount of CO<sub>2</sub> consumed by silicate weathering is insignificant compared to the CO<sub>2</sub> production rates; thus, the shallow soil zone remains as an open system with respect to CO<sub>2</sub> and soil water DIC is controlled by soil CO<sub>2</sub>, and soil water pH, and thus indirectly by silicate weathering intensity. Within a short distance into the carbonate mineral-bearing zone, infiltrating waters acquire the inorganic carbon and chemical composition typical of groundwater aquifers in the study region, suggesting that the hydrochemical evolution from precipitation to groundwater takes place rapidly under the influence of carbonate mineral weathering. Isotopic composition of soil water and groundwater DIC is less diagnostic, because  $\delta^{13}\text{C}_{\text{DIC}}$  derived from carbonate dissolution is similar during open- and closed-system evolution. Mass balance calculations reveal that dissolution of carbonate minerals could potentially consume a substantial fraction of the soil CO<sub>2</sub> reservoir and hence the deep carbonate-bearing zone may act as a partially closed system. Such conditions, coupled with quick recharge to the water table and limited gas–water exchange due to spatial heterogeneity of soils, could potentially prevent the dissolved inorganic carbon system from reaching isotopic equilibrium with the solid carbonate minerals.

We suggest that the carbonate-rich soils close to the lower boundary of the carbonate-leached zone may act as a partially closed system with respect to CO<sub>2</sub> and carbonate dissolution. The extent to which this applies in other soil profiles has yet to be investigated and it will have important implications for our understanding of soil carbonate fluxes and for how we interpret stable and radioactive carbon isotope tracers. Our results are of interest to understand how groundwaters and rivers fed by groundwaters acquire their chemical and isotopic composition. The massive amounts of inorganic carbon in lithospheric reservoirs pose a potential feedback mechanism that could mitigate or amplify atmospheric CO<sub>2</sub> increases via changes in the balance between carbonate dissolution and precipitation.

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