Impact of Carbonate Precipitation on Riverine Inorganic Carbon Mass Transport from a Mid-continent, Forested Watershed

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Abstract. Physiochemical controls on the carbonate geochemistry of large river systems are important regulators of carbon exchange between terrestrial and marine reservoirs on human time scales. Although many studies have focused on large-scale river carbon fluxes, there are few investigations of mechanistic aspects of carbonate mass balance and transport at the catchment scale. We determined elemental and carbonate geochemistry and mass balances for net carbonate dissolution fluxes from the forested, mid-latitude Huron River watershed, established on carbonate-rich unconfined glacial drift aquifers. Shallow groundwaters are near equilibrium with respect to calcite at pCO$_2$ values up to 25 times atmospheric values. Surface waters are largely groundwater fed and exhibit chemical evolution due to CO$_2$ degassing, carbonate precipitation in lakes and wetlands, and anthropogenic introduction of road salts (NaCl and CaCl$_2$). Because the source groundwater Mg^{2+}/HCO$_3^-$ ratio is fairly constant, this parameter permits mass balances to be made between carbonate dissolution and back precipitation after groundwater discharge. Typically, precipitation does not occur until IAP/K calcite values exceed 10 times supersaturation. Stream chemistry changes little thereafter even though streams remain highly supersaturated for calcite. Our data taken together with historical United States Geological Survey (USGS) data show that alkalinity losses to carbonate precipitation are most significant during periods of lowest discharge. Thus, on an annual basis, the large carbon flux from carbonate dissolution in soil zones is only decreased by a relatively small amount by the back precipitation of calcium carbonate.

Key words: calcite saturation, carbon, Michigan, rivers, alkalinity

1. Introduction

The dissolution and precipitation of carbonate minerals in aqueous surficial environments play an important role in the transformation of terrestrial organic to inorganic carbon reservoirs. Given the great reactivity and solubility of carbonates, the flux from carbonate dissolution to ground and surface waters is limited largely by the volume of water and soil zone pCO$_2$ in

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open systems (e.g., Reardon et al., 1979; Van Breenan and Protz, 1988). Enhanced mineral weathering is one likely response to predicted global warming, enhanced biosphere carbon cycling, and changes in land use, (e.g., Mackenzie et al., 1993; Mackenzie et al., 1998). Enhanced carbonate and silicate mineral dissolution has recently been documented in experimental tree growth mesocosms maintained at elevated CO_2 and nitrogen fertility levels (Andrews and Schlesinger, 2001; Hamilton et al., 2002; Williams et al., 2003). Here, soil zone pCO_2 profiles are controlled by root and microbial respiration rates which increase with enhanced growth under elevated CO_2 (the "fertilization effect") and with N-fertility (Pregitzer et al., 2000).

An increase in the mass of terrestrial carbon reservoirs through CO_2 fertilization, enhanced biosphere carbon transformation rates, and changes in land use in turn may increase the amount of inorganic carbon carried in rivers and discharged into the world's oceans. Early investigations of riverine fluxes focused on inorganic carbon contents and speciation in major world rivers (e.g., Kempe, 1982 and references therein) and solute sources and mass balances from major world river basins (e.g., Meybeck, 1987 and references therein). Recent studies on large-scale riverine solute fluxes have focused on two main aspects of the weathering process, CO_2 consumption from silicate weathering (e.g., Aucour et al., 1999; Gaillardet et al., 1999; Mortatti and Probst, 2003) and the separation of organic vs. inorganic carbon sources using carbon and strontium isotopic tracers (e.g., Barth et al., 2003; Karim and Veizer, 2000; Telmer and Veizer, 1999).

In classic treatments of riverine carbonate chemistry (Berner and Berner, 1987; Garrells and Mackenzie, 1971; Holland, 1978), the relation between dissolved Ca^{+2} and HCO_3^- concentrations is considered relative to theoretical CO_2 partial pressures and equilibrium with respect to calcite. In this case the Ca^{2+}–HCO_3^- relations in most world rivers were considered to reflect near-equilibrium conditions with respect to calcite, requiring supersaturation with respect to atmospheric CO_2. This assumption was supported by the fact that calcite saturation indices for major world river systems are nearly all at or below equilibrium with respect to calcite (Kempe, 1982). In landscapes where carbonate groundwaters discharge into river systems, degassing of CO_2 typically leads to calcite saturation and calcium carbonate precipitation (e.g., Herman and Lorah, 1987; Jacobson and Usdowski, 1975; Lu et al., 2000).

Investigations of streams draining carbonate-bearing watersheds have observed a decrease in alkalinity concentrations at low and high discharge conditions (Grosbois et al., 2000; Roy et al., 1999), but few have characterized the carbonate saturation dynamics of riverine systems on smaller catchment scale.

Recently, Telmer and Veizer (1999) suggest that different catchments in the St. Lawrence River drainage have variable soil zone pCO_2 values due

to different thickness of soils in each basin. This could produce a higher pCO_2 value of the weathering zone in some basins, in turn generating higher dissolved inorganic carbonate loads from such regions. Importantly, a recent study of the Mississippi River drainage system has revealed a significant increase in alkalinity concentrations and fluxes over the past 50 years (Raymond and Cole, 2003). With the use of data from smaller catchments in the Mississippi drainage, patterns of land use are considered to drive this increase with agricultural catchments having the highest alkalinity concentrations. However, the possibility of retention of carbonate alkalinity within a catchment was not considered and may also play a role. Because many glaciated mid-continent watersheds contain calcareous wetlands (fens) and marl lakes (e.g., Almendinger and Leete, 1998a,b; Dustin et al., 1986; Glaser et al., 1990, Komor, 1994), it is reasonable to expect some decrease in net export of HCO_3^- by carbonate precipitation in these environments. Thus, without a reasonable geochemical mass balance of dissolved solutes in source waters and sinks, it is difficult to attribute changes in riverine alkalinity values unequivocally to changes in carbon cycling of landscapes and land use types.

In this paper, we present results of a study of ground and surface water elemental and carbonate system geochemistry in catchments of the Huron River watershed located in the relatively recently deglaciated mid-continent region of the United States. The relation of topographic gradients and internal permeability differentials in glacial drift aquifer systems produce a very close coupling between unconfined groundwaters and surface water drainages (Grannemann et al., 2000). This permits us to establish fundamental geochemical characteristics of groundwaters and to follow the chemical evolution of surface waters in catchments as they pass through carbonate fens and marl lakes into the main channel of the Huron River. Using these geochemical data, we arrive at mass balances of dissolution and precipitation and investigate how these are related to degree of carbonate mineral saturation and pCO_2. Finally, we integrate these mass balances with historical discharge and chemical data available from United States Geological Survey (USGS) Huron River gauging stations to evaluate how significantly carbonate precipitation reduces net riverine inorganic carbon fluxes.

2. Materials and Methods

2.1. THE HURON WATERSHED AND SITE CHARACTERIZATION

The Huron River watershed is located in the southeastern corner of the Lower Peninsula of Michigan (Figure 1a and b) and has a mean annual temperature of 10 °C and average annual precipitation of 84 cm. The Huron
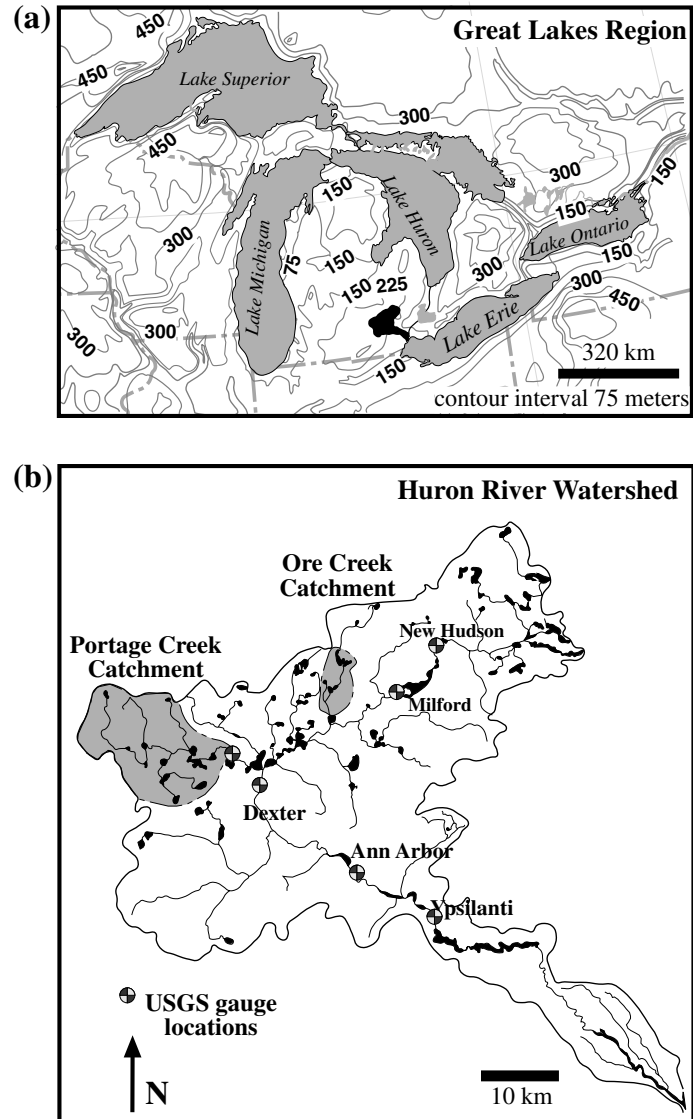
Figure 1. (a) A map of the mid-continent Pleistocene sediment thickness over bedrock. This map does not show the over all topography of the region, however due to the nature of the underlying bedrock, the surface topography is mainly controlled by the varying thickness of the glacial drift. The shaded area indicates the Huron River watershed in Michigan, USA. (b) The Huron River watershed. Portage and Ore Creek catchments are shaded in gray. The USGS gauge locations are indicated with the circle symbols.

River drainage is established on Wisconsinan age glacial drift deposits, with kettle and kame topography, up to 160 m thick composed of carbonate bearing sand, gravel and silt that mantle a low relief bedrock surface

Table I. Huron River USGS Gauge data

Huron River USGS gauge name	Station (number)	Drainage area (km^2)	Total volume (10^{10} l/year)	Normalized discharge ($1/km^2$-s)	Data (years)	Ave. HCO_3^- (meq/1)
At Milford, MI	4170000	383	9.1	7.5	53	3.93
Near New Hudson, MI	4170500	342	10.3	9.6	53	3.63
Near Dexter, MI	4173000	1352	31.7	7.4	26	3.71
At Ann Arbor, MI	4174500	1888	40.5	6.8	87+	3.85
At Ypsilanti, MI	4174800	2090	57.5	8.7	13	3.76

Data source: NWISWeb, 2001.

(Farrand, 1982). The Huron River watershed is comprised of lakes and extensive wetlands, including marshes, bogs, and fens. This landscape structure is a result of ice and debris left behind after the retreat of the last glacial maximum in southern Michigan approximately 13,000 years ago.

The soils of the southeastern Lower Peninsula of Michigan began formation about 13,000 years ago and unaltered parent drift materials are typically encountered within 1–2 m of the surface. Soils are mainly alfisols, which form in temperate humid regions under deciduous forests (Brady and Weil, 1996). Clays within these soils are dominantly kaolinite making cation exchange capacities (CEC) relatively low.

The watershed has a drainage area above the city of Ann Arbor of 1,888 km^2. The USGS has maintained multiple river discharge gauges in the Huron River watershed. The locations of the 5 main gauge sites with long-term data are shown in Figure 1b and Table I summarizes site information, drainage area, and discharge statistics. Our study of the Huron watershed focused on two catchments, the Portage Creek (205 km^2) and the Ore Creek (86 km^2) drainages (Figures 1b and 2a and b). Portage Creek flows through a forested and agriculturally rich area that has less urban development than the remaining drainage area, including the Ore Creek region. These two catchments have well developed carbonate rich wetlands called fens which are common in the Pleistocene glaciated landscapes of the mid-continent of the United States (Almendinger and Leete, 1998a,b; Komor, 1994). The Portage Creek catchment (Figure 2b) has a fen (Figure 2c) located along Tiplady Rd., near Hell, Michigan (W83° 59′ 08″ and N42° 26′ 36″). This fen has surface sediments consisting of both organic (peat) and inorganic low Mg calcite (marl) soils. The Ore Creek catchment (Figure 2a) has a fen located in the Brighton recreation area along Bauer Rd., near Brighton, Michigan (W83° 49′ and N42° 31′ 40″). This fen has marl sediments below a thin surface cover (approximately 1 cm) of organic matter. In both cases, the fens are associated with
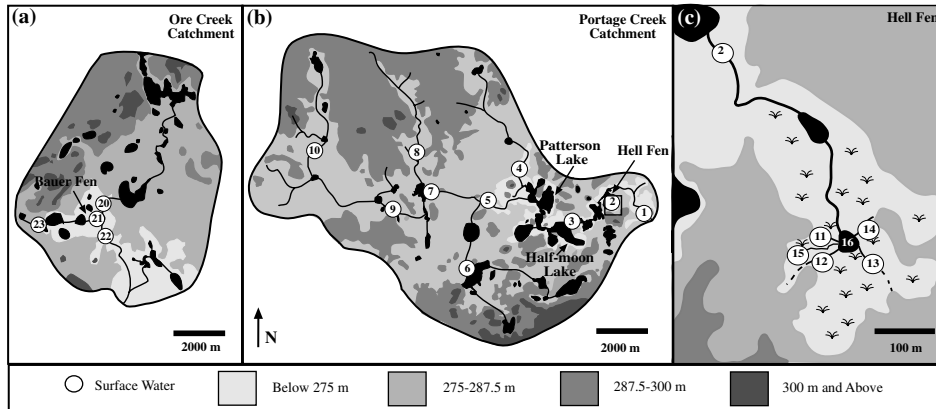
Figure 2. (a) Generalized topography map of the Ore Creek catchment. Topography is represented with darker to lighter shading as the elevation decreases. The locations of the sampling sites are indicated with circles and sample numbers on the maps. (b) Generalized topography map of the Portage Creek catchments. Lakes sampled in the study are indicated. The box on the Portage Creek drainage indicates the location of the Tiplady road fen that is shown in (c). (c) A schematic diagram of the drainage and topography for Hell fen on Tiplady road in the Portage Creek catchment. Sample sites and numbers are also indicated, note that sample number 2 is the same as in (b).

focused groundwater recharge from the topographically high areas surrounding the fen.

In addition to the fens, lakes form an important part of the drainage system in the Huron River watershed. In this study, two lakes, Halfmoon and Portage were sampled for water chemistry. Halfmoon Lake is the larger of the two with an average depth of 14 m and a volume of 13×10^6 m^3, while Patterson Lake is 9 m deep and has a volume of 5.7×10^6 m^3. Many of the lakes in the region have bottom sediments comprised of organic muck and carbonate mud, Halfmoon and Patterson Lakes are excellent examples of these marl lakes. Seepage lakes typically have high groundwater input to their basins (Dustin et al., 1986; Wachniew and Rozanski, 1997). Similar to fens, discharging groundwaters could degas in the lake basin and potentially precipitate calcium carbonate. Even more importantly, biologic processes of respiration and photosynthesis also can significantly modify the carbonate equilibria in lake waters. Both the fens and lakes are active sites of carbon transformation and would be expected to moderate to some degree the mass transport of inorganic carbon mobilized from soil zones to the main channel of the Huron River.

2.2. SAMPLING PERIODS AND PROTOCOLS

Surface water samples were collected, time and weather permitting, on a monthly basis over the course of 21 months from August 1999 to May 2001.

Table II. Totals for Ann Arbor, MI (4174500)

12 month: Time period	Discharge Total (10^{10} l per year)	Rain total (cm)	Snow depth total (cm)
July 1998–June1999	31.3	97.6	171.7
July 1999–June 2000: Year 1	22.9	85.7	109.2
July 2000–June 2001: Year 2	59.4	116.0	181.9

Data source: NOAA- National Climatic Data Center.

Sampling times were spread out to capture seasonality and the resulting changes in discharge, and are separated into 2 years of study, Year 1 (July 1999–June 2000) and Year 2 (July 2000–June 2001). The characteristics of Huron River discharge and climate data for the study time period are given in Table II. The USGS site 4174500 (Huron River @ Ann Arbor) is the only real time gauging site with data pertinent to the chemical and discharge mass balance of our study sites. Eighty-seven years of discharge data at Ann Arbor indicate an average value of 4.05×10^{10} l per year (see Table I). During the year previous and Year 1 of the study, the discharge was well below the annual average, at 3.1 and 2.3×10^{10} l, respectively. In contrast, Year 2 of the study has a discharge well above the annual average at 5.9×10^{10} l.

Surface water sampling locations were selected based on the relationship to confluences with the main stream, at points before and after the stream passed through a lake system, and with regard to the ease of obtaining the sample (see Figure 2a–c). In addition to these considerations, sample locations were also positioned upstream of large roads and developments to limit potential contamination from local runoff. Groundwater samples were collected from glacial drift aquifers, which comprise the vast majority of tapped aquifers in the Huron watershed (Twenter et al., 1976). Well depths varied from 16 to 60 m in depth below the surface and most were unconfined (e.g., no water wells with locally perched water tables were included). Full hydrogeological information on each groundwater sampling site (e.g., elevation, water level, location map) is available in Szramek et al., (2004), a related study of the sources and sinks of toxic levels of arsenic in glacial drift aquifer systems.

2.3. FIELD MEASUREMENTS

Temperature, conductivity, dissolved oxygen (DO), and pH measurements were made in the field. Temperature and DO were measured using a YSI model 58 m and a YSI 5239 DO probe with high sensitivity membrane, directly at the source, either in the stream or at the groundwater well head.

Conductivity was measured using a Corning 316 m with a two point calibration 0 and 1413 μs, to provide a rapid geochemical reference point. Dissolved oxygen measurements were precise to $\pm 5\%$ saturation and conductivity measurements to within $\pm 5\%$.

A Corning 315 high sensitivity pH meter with an Orion Ross combination pH electrode calibrated with low ionic strength buffers of 4.1 and 6.97 (corrected for temperature) was used to measure pH in the field as close to the ambient water temperature as possible. Because pH is sensitive to degassing and warming, water samples were collected in a large volume, airtight container and pH was measured at least twice to verify electrode stability. The reproducibility of field pH determinations is ± 0.02 pH units.

Sample aliquots collected for later chemical analysis in the laboratory were immediately passed through a 0.45 μm nylon filter into their respective bottles and kept refrigerated until analyzed. Acid washed HDPE bottles were used to collect anion and cation aliquots. DD water rinsed HDPE and glass bottles were used to collect alkalinity and dissolved organic carbon aliquots, respectively. Acid washed glass serum bottles capped with Teflon liners were used to store aliquots for dissolved inorganic carbon (DIC) analyses. These were poisoned in the field against biological activity using $CuCl_2$ and were filled to the top with no headspace before capping. Sample aliquots for dissolved organic carbon (DOC) and cations were preserved in the field with concentrated HCl and HNO_3 respectively. Sample aliquots for DIC.

2.4. LABORATORY ANALYSIS

Major element chemistry was measured by ICP-OES for cations and ion chromatography for anions. A Leeman Labs Inc. Plasma-Spec ICP-AES 2.5 was used to analyze for Ca, Mg, Na, K, Sr, Ba, Mn, Fe, Zn, Si, and B with a precision of $\pm 2\%$ for major and $\pm 5\%$ for minor elements. Anions (Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-}, F^-, and Br^-) were analyzed on a Dionex 4000I series ion chromatograph (IC) with an AS14 column with a precision of $\pm 2\%$. PO_4^{3-}, Br^- and F^- were found to be consistently below detection (less than 1 μM).

Total alkalinity was measured by electrometric endpoint titration using a Radiometer TitraLab automated titration system with a TIM900 titration manager and ABU91 or ABU93 autoburette. Due to the given measurement precision (± 0.01 meq/kg), the pH range of the samples, and the ionic composition of the solutions, HCO_3^- was calculated as equivalent to total alkalinity. Charge balance calculations were performed on water chemistry data to check for internal analytical consistency, using the relationship:

$$\text{CB} = \frac{\sum c_{\text{cations}} - \sum c_{\text{anions}}}{\sum c_{\text{cations}} + \sum c_{\text{anions}}} \times 100,$$

where c is the concentration in charge equivalents/l of solution, the data were always within $\pm 5\%$.

The DIC contents of 30 ml samples were analyzed on a UIC Coulometrics CO_2 coulometer with a precision of $\pm 2\%$. The measured DIC and titration alkalinity values of the samples agreed to within the precision of the two measurements, thereby supporting this assumption. The DOC contents were measured using a high-temperature platinum-catalyzed carbon analyzer via combustion followed by infrared detection of CO_2 (Shimadzu TOC-5000A) with an uncertainty of $\pm 2\%$.

2.5. AQUEOUS SPECIATION AND CARBONATE MINERAL EQUILIBRIA

Aqueous speciation and mineral saturation state modeling was conducted on the data using the USGS program Solmineq.88 (Kharaka et al., 1988). Major elements (Ca^{+2}, Mg^{+2}, Na^+, K^+, Sr^{+2}, Si, Cl^-, SO_4^{2+}, NO_3^-), alkalinity (HCO_3^-), pH and temperature were input into the program. Calculated values for pCO_2 and IAP/K calcite (Ωc) were obtained from the Solmineq.88 output. The error in the pCO_2 values provided by Solmineq.88 is related to the precision of the pH. Given a precision of ± 0.02 pH units and the uncertainty in the titration alkalinity, the uncertainty in the pCO_2 is about 10%. Errors in cation measurements and the precision in measuring the carbonate parameters (alkalinity, pH) determine the error in the IAP/K for calcite to be within 25%.

The geochemical evolution of the saturation state of a typical groundwater by progressive CO_2 degassing was also modeled, assuming no change in temperature after discharge and a constant alkalinity value. The initial groundwater modeled had the following geochemical parameter values: $T = 11.1\ °C$, pH 7.61, log $pCO_2 = -2.15$ atm., $Ca^{+2} = 1.79$ mM, $Mg^{+2} = 0.93$ mM, Alk = 5.39 meq/l, $Na^+ = 1.02$ mM, $Cl^- = 0.69$ mM, and $SO_4^{-2} = 0.23$ mM. Speciation under the new pCO_2 conditions was calculated using the CO_2 saturation option of Solmineq.88 and three different log pCO_2 values, -2.5, -3.0 and -3.5 atm.

2.6. DATA RETRIEVAL FROM THE USGS STREAM DATABASE

The five USGS stream gauge sites in the Huron River watershed listed in Table I were used in this data analysis. Historical discharge and chemical databases were downloaded from USGS National Water Information System (NWISWeb, 2001). The Huron River @ Milford

(4170000), the HR near New Hudson (4170500), the HR near Dexter (4173000) and the HR @ Ypsilanti (4174800) all have historical discharge (usually collected on a daily basis), but much more limited sampling for chemical analyses (typically 1 sample per year). Chemical data available varied in the number of samples and the solutes reported The Huron River @ Ann Arbor (4174500) is the only site with discharge data available from our the study time period, but no chemical data were gathered at this site. Data reported as total dissolved were used for all solutes, except alkalinity. Alkalinity is mainly reported as $CaCO_3$, HCO_3^- and as acid neutralizing capacity (ANC) and all were converted to HCO_3^- alkalinity in meq/l.

Two of our routine field sampling sites (Portage at Tiplady, Site 1; Huron River near Dexter) coincided with USGS historical gauges (sites 4172500 and 4173000, respectively). Both of these sites have been decommissioned. However, because historical discharge data were taken concurrently at these two sites with that from the functioning gauge site in Ann Arbor (4174500), interpolation of relative discharge proportions at each site was used to arrive at discharge values. This involved calculating the ratio of the annual discharge values from each site and normalizing them to drainage area (see Table 1). The ratios were remarkably constant, with estimated discharges ±10% of observed values. This is supported by the relatively constant area normalized discharge data for each segment of the Huron River drainage shown in Table I.

3. Results

3.1. ELEMENTAL GEOCHEMISTRY

A complete geochemical data set of field, laboratory and calculated geochemical parameters is presented in Tables III–VII, including a subset of data previously shown in Szramek et al. (2004) for ease of comparison and completeness. Table III is divided by type of sample: (a) groundwater, (b) lake, (c) Huron River, (d) stream, and (e) fen. The surface water samples are represented in Tables and Figures in terms of Years 1 and 2 of the study period because of the different geochemical patterns observed for the low discharge Year 1 vs. the higher discharge Year 2 (Table II). Surface water temperatures range from 4 to 30 °C, while groundwaters are much more uniform at about 11 °C. Minor element data for potassium and silica are not presented, as they do not contribute to charge balance significantly and are not involved with the major geochemical processes addressed here.

The Fe and Mn concentrations are presented as they differ significantly between ground, surface and lake waters. Fe and Mn concentrations for the

Table III. Groundwater geochemical data

	Field				Laboratory							Calculated		
	Temp. (°C)	Cond. (μs)	O_2 (%)	pH	Alk_t (meq/l)	DOC (mM)	Ca^{2+} (mM)	Mg^{2+} (mM)	Na^+ (mM)	Cl^- (mM)	SO_4^{2-} (mM)	log pCO_2 (atm)	IAP/K (calcite)	Mg^{2+}/HCO_3^- (molar)
Portage creek catchment														
11704 River Bank	11.2	530	0.5	7.57	5.12	n.m.	1.89	0.878	0.275	0.040	0.291	−2.13	1.83	0.17
11331 Country L.	12.0	567	0.7	7.43	5.32	n.m.	1.98	0.900	0.470	0.175	0.327	−1.98	1.46	0.17
11239 Country L.	12.2	712	0.7	7.46	5.65	n.m.	2.57	1.13	0.328	1.23	0.395	−1.99	2.07	0.20
11600 Longden	11.0	597	1.1	7.56	5.42	n.m.	1.77	0.973	0.613	0.321	0.129	−2.10	1.77	0.18
11367 Country L.	11.5	550	1.5	7.52	5.49	0.12	1.91	0.967	0.301	0.194	0.401	−2.06	1.74	0.18
9626 Silver Hill	11.2	488	0.8	7.55	5.32	0.12	1.66	0.810	0.544	0.194	0.151	−2.11	1.58	0.15
3475 Patatterson	10.9	479	1.5	7.67	4.88	0.06	1.61	0.823	0.444	0.119	0.170	−2.25	1.90	0.17
11471 Silver Hill	11.1	493	0.4	7.63	5.44	0.09	1.63	1.04	0.526	0.061	0.087	−2.17	1.95	0.19
11471 Silver Hill	10.6	514	<0.8	7.86	5.28	0.41	1.79	0.926	0.461	0.061	0.086	−2.42	3.42	0.18
11471 Silver Hill	11.6	538	<6	7.80	5.43	0.32	1.78	0.946	0.500	0.084	0.090	−2.34	3.16	0.17
3549 Tiplady	10.6	541	0.9	7.72	5.09	0.10	2.10	0.950	0.127	0.070	0.280	−1.99	5.09	0.19
3549 Tiplady	10.9	585	1.5	7.60	5.37	0.90	1.94	0.909	0.164	0.093	0.273	−2.16	1.92	0.17
11256 Country L.	13.8	508	1.8	7.40	5.00	0.08	1.73	0.856	0.435	0.163	0.166	−1.97	1.24	0.17
11273 Country L.	13.7	518	0.9	7.44	5.04	0.10	1.79	0.872	0.465	0.120	0.238	−2.01	1.40	0.17
4485 Monks	14.2	582	0.8	7.23	5.70	0.33	2.29	0.831	0.239	0.224	0.171	−1.74	1.24	0.15
Ore Creek Catchment														
6225 Windmere	10.9	523	0.6	7.65	5.79	0.14	1.61	0.882	0.748	0.054	0.240	−2.16	2.10	0.15
6225 Windmere	11.1	514	0.4	7.61	5.81	0.32	1.70	0.905	0.774	0.071	0.006	−2.12	2.07	0.16
6243 Windmere	11.5	591	0.4	7.57	5.73	0.12	2.31	1.13	0.461	0.817	0.239	−2.09	2.42	0.20
6258 Cunningham	10.4	601	1.0	7.61	5.58	0.11	2.29	1.03	0.315	0.472	0.359	−2.14	2.46	0.19
6193 Nottingham	11.3	540	1.3	7.57	5.48	0.07	1.94	0.875	0.348	0.303	0.148	−2.11	2.01	0.16

Table III. Continued

	Field			pH	Laboratory							Calculated		
	Temp. (°C)	Cond. (μs)	O_2 (%)		Alk_t (meq/l)	DOC (mM)	Ca^{2+} (mM)	Mg^{2+} (mM)	Na^+ (mM)	Cl^- (mM)	SO_4^{2-} (mM)	log pCO_2 (atm)	IAP/K (calcite)	Mg^{2+}/HCO_3^- (molar)
Cabin 3	<11.4	484	<25	7.89	4.65	0.10	1.65	0.827	0.164	0.318	0.316	−2.50	3.05	0.18
5620 Bauer	10.8	502	0.2	7.62	5.06	0.07	1.74	0.913	0.416	0.134	0.267	−2.19	1.86	0.18
5620 Bauer	10.6	526	1.5	7.57	5.07	0.17	1.79	0.926	0.375	0.300	0.256	−2.14	1.68	0.18
Horse staging	11.2	542	65.0	7.55	5.38	0.11	1.99	0.917	0.205	0.079	0.374	−2.10	1.89	0.17
Family Cabin 2	10.2	471	3.7	7.76	4.80	0.13	1.59	0.745	0.448	0.100	0.153	−2.35	2.22	0.16
Horse Camp	10.1	522	18.0	7.59	5.64	0.09	1.63	1.01	0.382	0.082	0.143	−2.11	1.76	0.18
6271 Cunningham	11.4	677	0.7	7.62	5.25	0.17	2.44	1.14	0.539	1.56	0.435	−2.18	2.55	0.22
6247 Nottingham	11.6	589	1.5	7.72	5.47	3.47	1.81	0.996	0.557	0.513	0.138	−2.26	2.66	0.18

Table IV. Lake water geochemical data

Date	Field				Laboratory								Calculated			
	Depth (m)	Temp. (°C)	Cond. (µs)	O_2 (%)	pH	Alk_t (meq/l)	DOC (mM)	Ca^{2+} (mM)	Mg^{2+} (mM)	Na^+ (mM)	Cl^- (mM)	SO_4^{2-} (M)	log pCO_2 (atm)	IAP/K (calcite)	Mg^{2+}/ HCO_3 (molar)	Alk loss (molar/1)
Patterson Lake																
11/14/98	0.0	8.4	n.m	59	7.86	4.04	n.m	1.60	0.843	0.648	2.70	0.381	−2.57	2.32	0.21	0.7
11/14/98	2.5	8.1	n.m	89	7.93	4.05	n.m	1.67	0.868	0.544	2.71	0.380	−2.57	2.40	0.21	0.9
11/14/98	5.0	8.0	n.m	86	7.93	4.02	n.m	1.62	0.847	0.683	2.71	0.380	−2.57	2.31	0.21	0.8
10/20/01	0.0	11.3	561	80	8.29	3.88	1.07	1.75	0.876	0.609	1.00	0.495	−2.99	6.38	0.23	1.1
10/20/01	1.5	11.6	562	77	8.30	3.36	1.03	1.76	0.885	0.618	0.938	0.502	−3.05	5.75	0.26	1.7
10/20/01	5.0	11.2	567	72	7.82	3.72	1.21	2.02	0.876	0.592	0.928	0.495	−2.53	2.47	0.24	1.3
Half-Moon Lake																
06/17/99	0.0	23.0	n.m	77	8.52	3.71	n.m	1.81	0.893	0.583	0.805	0.559	−3.21	14.2	0.24	1.4
06/17/99	2.5	23.0	n.m	72	8.51	3.76	n.m	1.83	0.905	0.596	0.805	0.556	−3.21	14.6	0.24	1.4
06/17/99	5.0	17.0	n.m	69	8.28	3.75	n.m	1.86	0.901	0.583	0.811	0.555	−3.01	8.07	0.24	1.4
6/19/01	0.0	26.4	508	99	8.58	4.06	1.23	1.93	0.831	0.570	0.766	0.403	−3.25	21.3	0.20	0.7
6/19/01	2.5	24.9	511	93	8.58	4.06	1.17	1.92	0.831	0.570	0.760	0.401	−3.26	20.4	0.20	0.7
6/19/01	5.0	15.5	518	57	8.25	4.04	1.12	1.97	0.802	0.561	0.761	0.417	−2.92	7.93	0.20	0.5

Table V. Huron R. near Dexter (4173000) geochemical data

Date	Field			pH	Laboratory							Calculated			
	Temp. (°C)	Cond. (μs)	O_2 (%)		Alk_t (meq/l)	DOC (mM)	Ca^{2+} (mM)	Mg^{2+} (mM)	Na^+ (mM)	Cl^- (mM)	SO_4^{2-} (mM)	log pCO2 (atm)	IAP/K (calcite)	Mg^{2+}/HCO_3^- (molar)	Alk loss (meq/l)
8/16/99	22.2	693	n.m.	8.16	3.51	n.m.	1.42	0.995	2.46	2.83	0.401	−2.88	5.00	0.28	2.1
2/3/00	5.0	n.m.	n.m.	8.04	4.68	n.m.	2.02	1.08	1.26	3.03	–	−2.65	4.28	0.23	1.5
3/9/00	3.7	719	n.m.	8.26	4.18	n.m.	1.88	1.19	2.00	2.42	0.445	−2.94	5.08	0.29	2.6
4/22/00	10.9	627	n.m.	8.29	4.00	n.m.	1.67	1.13	1.92	2.33	0.446	−2.98	6.04	0.28	2.4
7/26/00	25.9	622	103	8.51	3.73	0.92	1.75	0.749	1.57	2.05	0.352	−3.21	15.4	0.20	0.5
8/1/00	20.0	610	81	8.37	3.72	1.68	1.66	0.913	1.52	1.93	0.351	−3.08	9.18	0.25	1.5
9/1/00	17.9	720	n.m.	7.95	4.12	n.m.	1.92	0.963	1.87	2.60	0.347	−2.61	4.28	0.23	1.3
3/11/01	3.6	621	91	7.98	3.91	n.m.	1.77	0.798	1.49	1.94	0.330	−2.67	2.49	0.20	0.6
6/26/01	26.0	657	94	8.27	4.12	n.m.	1.73	0.845	1.71	1.92	0.315	−2.91	10.1	0.21	0.7

Table VI. Stream water geochemical data

Date	Field				Laboratory							Calculated			
	Temp. (°C)	Cond. (μs)	O_2 (%)	pH	Alk_t (meq/l)	DOC (mM)	Ca^{2+} (mM)	Mg^{2+} (mM)	Na^+ (mM)	Cl^- (mM)	SO_4^{2-} (mM)	log pCO_2 (atm.)	IAP/K (calcite)	Mg^{2+}/HCO_3^- (molar)	Alk loss (meq/l)
Portage Creek Catchment															
(1) *Portage @ Tiplady* (4172500)															
9/25/99	13.3	479	n.m.	8.09	4.26	n.m.	1.63	0.971	0.596	0.720	0.355	−2.74	4.57	0.23	1.2
3/9/00	7.9	483	n.m.	8.44	3.60	n.m.	1.66	1.05	0.609	0.852	0.512	−3.18	6.97	0.29	2.4
4/22/00	12.0	438	n.m.	8.30	3.56	n.m.	1.53	1.09	0.696	0.870	0.492	−3.03	5.46	0.30	2.6
7/26/00	23.7	552	95	8.22	4.07	1.23	1.81	0.811	0.592	0.839	0.493	−2.87	8.89	0.20	0.5
8/1/00	20.0	503	57	7.95	3.77	2.36	1.81	0.938	0.600	0.831	0.502	−2.64	4.06	0.25	1.6
8/21/00	20	528	73	8.17	4.10	1.13	1.87	0.784	0.579	0.686	0.733	−2.81	8.45	0.19	0.4
9/4/00	23.9	507	93	8.44	3.95	1.10	1.76	0.852	0.538	0.815	0.418	−2.12	34.5	0.22	0.9
10/15/00	15.1	509	98	8.30	3.97	0.99	1.63	0.798	0.618	0.850	0.462	−2.98	7.21	0.20	0.6
3/11/01	4.3	513	111	7.98	3.86	0.90	1.87	0.848	0.531	0.772	0.451	−2.68	2.69	0.22	1.0
5/2/01	20.8	517	100	8.19	3.97	0.89	1.85	0.842	0.592	0.771	0.321	−2.86	7.71	0.21	0.8
6/26/01	26.1	553	86	8.19	4.11	1.00	1.76	0.805	0.539	0.726	0.344	−2.82	8.83	0.20	0.5
(2) *Hell Fen Outlet*															
9/13/99	20.0	n.m.	n.m.	8.19	4.10	n.m.	1.47	1.04	0.337	0.441	0.193	−2.84	6.35	0.25	1.8
10/11/99	15.1	443	n.m.	7.94	4.49	n.m.	1.65	1.08	0.289	0.447	0.214	−2.57	5.42	0.24	1.7
12/11/99	3.8	509	n.m.	8.36	4.57	n.m.	2.05	1.04	0.309	0.473	0.399	−2.99	7.82	0.23	1.4
4/22/00	11.0	411	n.m.	7.90	4.12	n.m.	1.50	0.934	0.212	0.278	0.229	−2.56	2.55	0.23	1.2
8/1/00	20.0	436	85	8.16	3.87	0.94	1.51	0.749	0.173	0.269	0.200	−2.83	5.90	0.19	0.4
8/21/00	24.1	434	n.m.	8.27	4.43	0.85	1.73	0.711	0.218	0.260	0.173	−2.88	10.9	0.16	−0.4

Table VI. continued

Date	Field				Laboratory							Calculated			
	Temp. (°C)	Cond. (µs)	O_2 (%)	pH	Alk_t (meq/l)	DOC (mM)	Ca^{2+} (mM)	Mg^{2+} (mM)	Na^+ (mM)	Cl^- (mM)	SO_4^{2-} (mM)	log pCO_2 (atm.)	IAP/K (calcite)	Mg^{2+}/HCO_3^- (molar)	Alk loss (meq/l)
10/14/00	14.7	478	86	8.12	4.78	0.60	1.74	0.773	0.253	0.348	0.171	−2.72	6.25	0.16	−0.4
3/11/01	5.4	435	53	7.66	4.02	0.28	1.79	0.683	0.200	0.293	0.232	−2.33	1.40	0.17	−0.1
5/2/01	23.3	466	53	8.23	4.32	0.47	2.01	0.820	0.272	0.358	0.415	−2.86	10.5	0.19	0.3
6/26/01	28.9	429	103	8.34	4.07	0.65	1.59	0.779	0.208	0.591	0.223	−2.97	12.3	0.19	0.4
(3) HML Outlet															
12/11/99	8.4	474	n.m.	8.41	3.69	n.m.	1.69	0.934	0.679	0.914	0.494	−3.14	6.93	0.25	1.6
3/9/00	5.9	534	n.m.	8.41	3.81	n.m.	1.76	1.14	0.652	0.924	0.532	−3.13	6.75	0.30	2.7
4/22/00	10.5	460	n.m.	8.33	3.73	n.m.	1.59	1.11	0.635	0.894	0.515	−3.01	5.94	0.30	2.6
7/26/00	26.1	517	86	8.66	3.88	1.30	1.85	0.827	0.596	0.834	0.534	−3.36	22.5	0.21	0.8
10/14/00	17.0	514	75	8.35	3.89	1.01	1.66	0.823	0.626	0.879	0.492	−2.98	7.19	0.21	0.8
3/11/01	4.5	550	72	7.69	3.86	1.07	1.97	0.786	0.483	0.759	0.459	−2.38	1.47	0.20	0.6
5/2/01	21.6	516	98	8.49	3.89	1.11	1.96	0.762	0.535	0.749	0.435	−3.18	15.3	0.20	0.4
6/26/01	28.4	487	119	8.60	3.99	1.17	1.78	0.830	0.535	0.716	0.385	−3.27	21.4	0.21	0.7
(4) Livermore Creek															
8/16/99	18.3	415	n.m.	8.14	5.09	n.m.	1.99	1.02	0.744	0.854	0.331	−2.71	8.47	0.20	0.7
12/11/99	1.2	697	n.m.	8.10	4.33	n.m.	2.69	1.17	0.718	0.989	1.45	−2.76	4.42	0.27	2.3
8/1/00	19.6	579	62	8.12	5.12	1.36	2.36	1.01	0.648	0.929	0.470	−2.69	21.2	0.20	0.6
9/4/00	17.9	597	76	8.25	5.35	1.17	2.40	1.06	0.571	0.729	0.386	−2.81	13.1	0.20	0.7
5/2/01	21.9	583	119	8.26	4.62	1.35	2.14	0.820	0.526	0.720	0.354	−2.87	12.1	0.18	0.0
6/26/01	22.4	564	111	8.20	5.24	1.07	2.27	0.954	0.622	0.816	0.362	−2.75	12.7	0.18	0.2

Table VI. continued

Date	Field			Laboratory								Calculated			
	Temp. (°C)	Cond. (μs)	O_2 (%)	pH	Alk_t (meq/l)	DOC (mM)	Ca^{2+} (mM)	Mg^{2+} (mM)	Na^+ (mM)	Cl^- (mM)	SO_4^{2-} (mM)	log pCO_2 (atm.)	IAP/K (calcite)	Mg^{2+}/HCO_3^- (molar)	Alk loss (meq/l)
(5) Portage @ Unadilla															
8/16/99	19.1	450	n.m.	8.02	3.59	n.m.	1.50	1.07	0.787	1.05	0.674	−2.73	3.61	0.30	2.5
12/11/99	2.8	729	n.m.	8.52	4.16	n.m.	2.05	1.22	0.974	1.23	0.719	−3.21	9.68	0.29	2.8
3/9/00	7.1	687	n.m.	8.36	4.39	n.m.	2.46	1.35	0.813	1.21	1.01	−3.02	9.25	0.31	3.3
7/26/00	23.0	658	74	8.36	4.79	1.41	2.27	0.901	0.618	0.966	0.665	−2.96	16.3	0.19	0.3
8/1/00	20.0	635	61	8.24	4.56	1.36	2.27	1.11	0.696	1.01	0.707	−2.86	10.9	0.24	1.7
8/21/00	20.6	665	66	8.28	5.04	1.45	2.36	0.913	0.613	0.944	0.683	−2.86	13.8	0.18	0.1
9/4/00	20.6	605	68	8.33	4.62	1.31	2.19	1.06	0.684	1.01	0.602	−2.95	13.3	0.23	1.4
5/2/01	18.4	599	79	8.23	4.42	1.20	2.22	0.995	0.705	0.961	0.615	−2.86	9.79	0.22	1.2
6/26/01	24.4	630	69	8.31	4.70	1.46	2.16	0.965	0.666	0.923	0.554	−2.91	14.6	0.21	0.8
(6) S. Lake @ Boyce															
3/9/00	7.8	420	n.m.	8.18	3.46	n.m.	1.36	0.967	0.465	0.659	0.235	−2.92	3.27	0.28	2.0
7/26/00	22.8	378	51	7.67	3.21	0.81	1.22	0.667	0.404	0.576	0.184	−2.40	1.50	0.21	0.6
8/21/00	27.0	394	68	7.77	3.26	1.09	1.25	0.654	0.411	0.571	0.184	−2.48	2.22	0.20	0.5
9/4/00	21.4	379	41	7.68	3.26	0.85	1.24	0.770	0.414	0.576	0.172	−2.41	1.73	0.24	1.1
6/26/01	26.6	n.m.	n.m.	7.60	3.17	0.85	1.18	0.688	0.427	-	-	−2.32	1.37	0.22	0.7
(7) Portage @ Williams															
12/11/99	5.0	606	n.m.	8.79	4.11	n.m.	1.84	1.13	0.870	1.23	0.727	−3.50	15.7	0.28	2.3
9/4/00	23.4	592	23	8.39	4.42	1.44	2.14	1.04	0.649	0.980	0.638	−2.02	15.4	0.24	1.5
5/2/01	19.7	620	123	8.62	4.27	1.16	2.11	0.958	0.622	0.939	0.656	−3.29	21.1	0.22	1.2
6/26/01	25.4	645	85	8.64	4.70	n.m.	2.18	0.965	0.635	0.888	0.570	−3.26	28.7	0.21	0.8

Table VI. continued

Date	Field			Laboratory								Calculated			
	Temp. (°C)	Cond. (μs)	O_2 (%)	pH	Alk_t (meq/l)	DOC (mM)	Ca^{2+} (mM)	Mg^{2+} (mM)	Na^+ (mM)	Cl^- (mM)	SO_4^{2-} (mM)	log pCO_2 (atm.)	IAP/K (calcite)	Mg^{2+}/HCO_3^- (molar)	Alk loss (meq/l)
(8) Vansyckle Creek															
7/26/00	17.5	734	92	8.34	6.46	2.76	2.84	1.22	0.366	0.671	0.759	−2.83	20.8	0.19	0.5
9/4/00	17.1	761	70	8.32	6.72	0.77	2.97	1.37	0.375	0.679	0.616	−2.79	21.3	0.20	1.1
5/2/01	16.9	713	106	8.27	6.11	1.17	2.79	1.21	0.392	0.654	1.03	−2.78	16.2	0.20	0.8
6/26/01	16.6	741	81	8.18	6.26	n.m.	2.69	1.22	0.339	0.695	0.574	−2.67	13.6	0.19	0.6
(9) Portage @ McIntyre															
7/26/00	25.6	673	113	8.60	4.55	1.36	2.39	1.05	0.918	1.19	0.940	−3.24	26.5	0.23	1.4
8/21/00	25.4	723	145	8.78	5.03	1.74	2.67	1.05	0.887	1.26	1.00	−3.41	45.1	0.21	0.9
9/4/00	21.6	711	65	8.36	4.73	1.30	2.54	1.24	1.091	1.40	0.924	−2.97	16.4	0.26	2.3
5/2/01	21.8	691	161	8.68	4.48	1.28	2.32	1.04	0.822	1.14	0.884	−3.34	27.8	0.23	1.4
6/26/01	25.4	650	163	8.52	4.36	1.24	2.19	1.09	0.957	1.22	0.802	−3.17	21.0	0.25	1.8
(10) Portage @ Rock															
12/11/99	0.5	729	n.m.	8.32	6.02	n.m.	3.04	1.37	0.399	0.711	1.07	−2.85	10.9	0.23	1.7
6/26/01	21.2	519	56	7.75	4.01	1.23	1.75	0.976	0.444	0.784	0.387	−2.40	2.77	0.24	1.5
6/26/01	19.6	864	74	8.02	5.46	n.m.	2.74	1.13	1.179	1.48	0.935	−2.56	9.10	0.21	1.0
Ore Creek Catchment															
(20) Up Ore															
10/14/00	13.7	546	80	8.26	3.83	0.58	1.31	0.699	1.23	1.74	0.188	−2.95	5.07	0.18	0.1
4/26/01	15.8	588	86	8.49	3.74	0.49	1.53	0.740	1.54	2.02	0.242	−3.21	9.86	0.20	0.5

Table VI. continued

Date	Field				Laboratory							Calculated			
	Temp. (°C)	Cond. (μs)	O_2 (%)	pH	Alk_t (meq/l)	DOC (mM)	Ca^{2+} (mM)	Mg^{2+} (mM)	Na^+ (mM)	Cl^- (mM)	SO_4^{2-} (mM)	log pCO_2 (atm.)	IAP/K (calcite)	Mg^{2+}/HCO_3^- (molar)	Alk loss (meq/l)
(21) Murry Lake															
7/30/00	24.6	460	79	8.10	3.73	0.64	1.45	0.901	0.605	0.914	0.201	−2.78	5.43	0.24	1.4
8/1/00	23.1		n.m.	7.91	3.72	0.63	1.43	0.856	0.609	0.955	0.194	−2.59	3.37	0.23	1.1
10/14/00	14.6	477	90	8.23	4.07	0.52	1.51	0.777	0.613	0.860	0.193	−2.90	5.96	0.19	0.3
4/26/01	16.8	518	94	8.33	4.19	0.42	1.68	0.828	0.748	1.05	0.218	−2.99	8.89	0.20	0.5
(22) Down Ore															
7/30/00	25.6	504	78	8.14	3.78	0.81	1.43	0.884	0.861	1.30	0.207	−2.81	6.05	0.23	1.2
10/14/00	14.4	489	80	8.20	5.61	0.46	1.52	0.868	0.770	1.01	0.192	−2.73	7.38	0.15	−0.7
4/26/01	16.2	629	92	8.32	3.95	0.52	1.61	0.784	1.49	1.98	0.248	−3.00	7.64	0.20	0.5
(23) Cunningham Lake															
7/30/00	20.6	386	66	7.89	3.64	0.84	1.52	0.712	0.232	0.303	0.184	−2.58	2.97	0.20	0.4
8/1/00	20.0	426	n.m.	7.99	4.20	0.54	1.59	0.856	0.194	0.331	0.141	−2.62	4.58	0.20	0.7
10/14/00	12.4	485	79	7.98	5.00	0.34	1.79	0.864	0.261	0.263	0.235	−2.56	4.50	0.17	−0.1
4/26/01	15.4	479	94	8.26	4.59	0.40	1.81	0.806	0.293	0.343	0.242	−2.88	8.59	0.18	−0.0

Table VII. Fen drainage water geochemical data

Date	Field				Laboratory							Calculated			
	Temp. (°C)	Cond. (μs)	O$_2$ (%)	pH	Alk$_t$ (meq/l)	DOC (mM)	Ca^{2+} (mM)	Mg^{2+} (mM)	Na$^+$ (mM)	Cl$^-$ (mM)	SO$_4^{2-}$ (mM)	log pCO$_2$ (atm.)	IAP/K (calcite)	Mg^{2+}/HCO$_3^-$ (molar)	Alk loss (meq/l)
Portage Creek Catchment															
(11) *Hell Fen Lake*															
9/13/99	20.0	n.m	n.m	8.02	4.66	n.m	1.78	1.05	0.266	0.529	0.253	−2.62	5.82	0.23	1.3
9/24/99	19.0	471	n.m	8.09	4.94	n.m	1.77	1.07	0.418	0.536	0.259	−2.67	6.85	0.22	1.1
10/11/99	15.5	480	n.m	8.00	5.08	n.m	2.00	1.14	0.268	0.533	0.272	−2.57	5.74	0.22	1.4
12/11/99	4.5	422	n.m	8.39	5.06	n.m	1.97	0.958	0.298	0.581	0.401	−2.98	9.10	0.19	0.4
8/21/00	21.3	557	n.m	7.75	5.22	0.54	2.20	0.831	0.273	0.434	0.261	−2.29	4.51	0.16	−0.5
9/4/00	22.2	537	115	8.15	5.17	0.45	2.16	1.02	0.229	0.463	0.255	−2.70	25.0	0.20	0.6
10/14/00	13.6	514	n.m	7.65	4.93	0.61	1.85	1.02	0.279	0.505	0.263	−2.23	2.24	0.21	0.9
5/2/01	20.5	531	n.m	8.17	4.75	0.36	1.99	0.875	0.249	0.554	0.197	−2.76	9.35	0.18	0.2
6/26/01	27.7	505	82	8.12	4.51	0.60	1.82	0.921	0.237	-	-	−2.71	9.14	0.20	0.7
(12) *Western w/aspens*															
9/25/99	20.0	571	n.m	8.03	5.73	n.m	2.22	1.04	0.244	0.590	0.315	−2.54	8.71	0.18	0.2
12/11/99	3.8	596	n.m	7.89	5.66	n.m	2.42	1.12	0.345	0.539	0.342	−2.42	3.90	0.20	0.7
3/9/00	5.8	588	n.m	7.74	5.67	n.m	2.37	1.26	0.377	0.456	0.362	−2.27	2.92	0.22	1.5
8/21/00	7.4	600	n.m	7.60	5.86	0.15	2.31	1.04	0.279	0.424	0.367	−2.11	2.29	0.18	0.0
9/4/00	11.2	600	44	7.72	5.77	n.m	2.47	0.957	0.231	0.437	0.366	−2.24	3.61	0.17	−0.3
10/14/00	8.6	582	n.m	7.65	5.66	0.00	2.20	0.971	0.281	0.499	0.319	−2.18	2.49	0.17	−0.2
5/2/01	11.1	611	n.m	7.57	5.65	0.13	2.48	1.03	0.267	0.585	0.552	−2.10	2.47	0.18	0.2
6/26/01	10.9	629	36	7.49	5.68	n.m	2.47	1.04	0.225	0.795	0.310	−2.01	2.09	0.18	0.2

Table VII. continued

Date	Field				Laboratory							Calculated			
	Temp. (°C)	Cond. (μs)	O_2 (%)	pH	Alk_t (meq/l)	DOC (mM)	Ca^{2+} (mM)	Mg^{2+} (mM)	Na^+ (mM)	Cl^- (mM)	SO_4^{2-} (mM)	log pCO_2 (atm.)	IAP/K (calcite)	Mg^{2+}/HCO_3^- (molar)	Alk loss (meq/l)
(13) *Western Inlet*															
9/13/99	20.0	n.m	n.m	7.77	5.95	n.m	2.30	0.991	0.387	0.560	0.124	-2.26	5.30	0.17	-0.3
10/11/99	15.5	461	n.m	7.70	5.41	n.m	2.32	1.17	0.381	0.818	0.219	-2.24	3.55	0.22	1.2
3/9/00	5.8	588	n.m	7.74	4.86	n.m	2.28	1.10	0.369	0.463	0.560	-2.33	2.42	0.23	1.4
8/21/00	22.9	568	n.m	7.41	5.97	0.78	2.50	0.838	0.288	0.434	0.141	-1.88	2.81	0.14	-1.2
9/4/00	16.5	589	10	7.60	6.12	n.m	2.47	1.14	0.223	0.441	0.074	-2.08	3.53	0.19	0.3
5/2/01	13.7	552	n.m	7.52	5.08	0.42	2.26	0.835	0.259	0.448	0.310	-2.09	2.07	0.16	-0.4
6/26/01	17.9	575	25	7.40	5.90	0.58	2.31	0.867	0.235	0.408	0.094	-1.89	2.17	0.15	-1.0
(14) *Eastern inlet*															
9/13/99	20.0	n.m	n.m	7.94	5.18	n.m	2.18	1.09	0.379	0.936	0.331	-2.49	6.37	0.21	1.0
10/11/99	15.5	539	n.m	7.55	5.79	n.m	2.48	1.11	0.274	0.532	0.319	-2.06	2.86	0.19	0.5
3/9/00	4.9	620	n.m	7.92	5.21	n.m	2.44	1.26	0.341	0.737	0.572	-2.49	3.95	0.24	2.0
8/21/00	12.6	598	n.m	7.83	4.98	0.27	2.35	0.926	0.356	0.706	0.407	-2.41	3.06	0.19	0.3
9/4/00	12.9	595	69	8.06	5.33	0.20	2.33	1.09	0.336	0.718	0.344	-2.62	7.16	0.20	0.8
5/2/01	12.9	609	n.m	7.74	5.21	0.32	2.26	0.966	0.345	0.732	0.353	-2.30	3.35	0.19	0.3
6/26/01	14.1	608	68	7.75	5.24	0.10	2.30	1.00	0.334	0.702	0.334	-2.31	3.65	0.19	0.5
(15) *ECF*															
12/11/99	3.8	486	n.m	8.28	5.19	n.m	2.07	1.08	0.197	0.302	0.421	-2.85	7.43	0.21	0.9
3/9/00	7.5	520	n.m	8.21	5.21	n.m	2.05	1.21	0.281	0.308	0.385	-2.78	7.19	0.23	1.7
9/4/00	21.1	526	12	8.23	5.00	0.26	2.10	1.11	0.129	0.333	0.352	-2.80	11.7	0.22	1.3
6/26/01	29.6	534	56	7.95	5.02	0.16	2.04	0.983	0.164	0.300	0.319	-2.48	8.05	0.20	0.6

Table VII. continued

Date	Field				Laboratory							Calculated			
	Temp. (°C)	Cond. (μs)	O$_2$ (%)	pH	Alk$_t$ (meq/l)	DOC (mM)	Ca^{2+} (mM)	Mg^{2+} (mM)	Na$^+$ (mM)	Cl$^-$ (mM)	SO$_4^{2-}$ (mM)	log pCO$_2$ (atm.)	IAP/K (calcite)	Mg^{2+}/ HCO$_3^-$ (molar)	Alk loss (meq/l)
(16) 2 West 2															
5/2/01	10.0	701	n.m	7.38	5.76	0.07	2.59	1.06	0.452	1.14	0.304	-1.90	1.66	0.18	0.3
6/26/01	18.9	688	83	8.04	5.83	n.m	2.62	1.11	0.461	1.46	0.304	-2.55	10.0	0.19	0.5
6/26/01	9.2	718	33	7.34	5.79	0.10	2.52	1.07	0.457	1.21	0.291	-1.86	1.46	0.18	0.3
Ore Creek Catchment															
(24) Bauer lake															
8/1/00	23.2	555	n.m	8.29	4.00	1.90	1.57	0.962	1.10	1.67	0.181	-2.95	8.83	0.24	1.5
10/14/00	7.6	606	n.m	8.06	4.75	0.56	1.70	0.884	1.20	1.74	0.137	-2.65	5.71	0.19	0.3
4/3/01	8.1	576	n.m	7.81	4.80	n.m.	2.77	1.27	1.45	2.01	0.280	-2.42	3.60	0.26	2.4
4/26/01	18.2	693	n.m	8.30	4.82	0.40	2.09	0.969	1.46	2.01	0.267	-2.90	11.7	0.20	0.7
(25) Bauer #1															
8/1/00	22.9	550	n.m	8.37	5.12	0.81	1.93	0.950	0.753	n.m.	n.m.	–	–	0.19	0.3
10/14/00	12.5	521	n.m	8.18	5.53	0.73	1.77	0.909	0.513	0.589	0.006	-2.72	7.73	0.16	-0.4
4/26/01	25.5	580	n.m	8.23	4.14	0.91	1.55	0.835	1.14	1.68	0.159	-2.87	8.55	0.20	0.6
(26) Bauer #2															
8/1/00	22.2	401	n.m	8.07	3.64	1.72	1.57	0.790	0.321	0.571	0.201	-2.76	5.05	0.22	0.8
10/14/00	17.8	514	n.m	7.82	5.14	0.81	1.74	0.736	0.661	0.679	0.046	-2.37	3.82	0.14	-1.0
4/26/01	23.8	706	n.m	8.17	5.00	0.63	2.08	0.955	1.43	2.09	0.255	-2.73	10.8	0.19	0.4
(27) Bauer Cattails															
8/1/00	22.5	529	n.m	7.69	5.64	1.24	2.19	0.761	0.248	0.282	0.135	-2.19	4.44	0.13	-1.3
8/1/00	22.2	622	n.m	7.97	6.18	1.15	2.28	1.00	1.04	n.m.	n.m.	–	–	0.16	-0.5
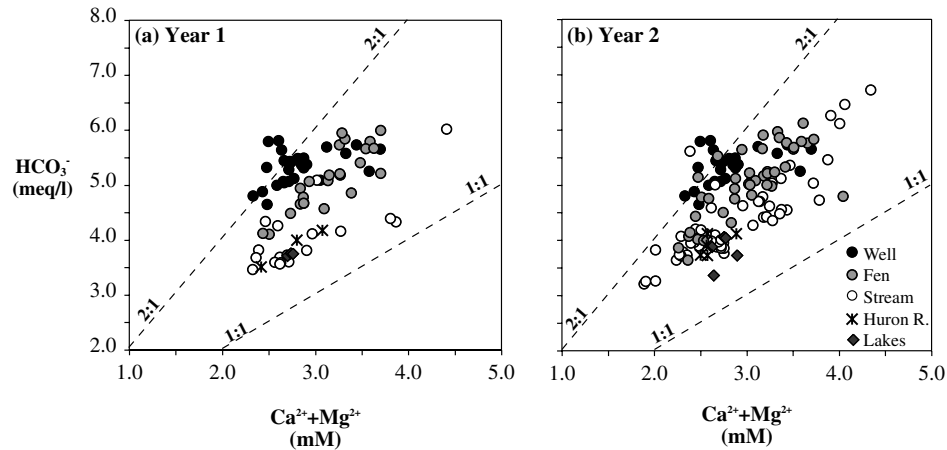
Figure 3. HCO_3^- vs. $Ca^{2+} + Mg^{2+}$ for both ground and surface waters during Years 1 and 2 for the Portage and Ore creek catchments in the Huron River Watershed. Groundwaters fall around the $2(Ca^{2+} + Mg^{2+}) = HCO_3^-$ line, indicating the water chemistry is controlled by carbonate mineral dissolution. The surface waters fall below this line, indicating HCO_3^- loss relative to $Ca^{2+} + Mg^{2+}$.

surface, fen and lake samples are very low, usually less than 5 μM for Fe and 3 μM for Mn. These samples are all in contact with the atmosphere, which would cause removal of most of the Mn and all of the Fe through the formation of hydroxides. Arsenic is also shown to be present in the groundwaters, however arsenic is absent from the surface waters due to its incorporation into the hydroxides (Szramek et al., 2004). The groundwater samples are approximately an order of magnitude higher in Fe (~30 μm) and within the same range as other waters for Mn. The trend of higher dissolved Fe and Mn in the groundwaters relative to the surface waters is consistent with the very low dissolved oxygen concentrations and Fe mobilization from buried paleosoil zones in the drift deposits (Szramek et al., 2004).

In general all sample types are predominantly Ca^{2+}–Mg^{2+}–HCO_3^- waters (Figure 3a and b), where HCO_3^- is the single most abundant dissolved species. The stoichiometric relationship between HCO_3^- and $Ca^{2+} + Mg^{2+}$ in the samples from our study indicates that the waters are essentially a result of carbonate dissolution and groundwaters fall around the 2:1 line of $2(Ca^{2+} + Mg^{2+}) = HCO_3^-$ (Figure 3a and b). Given that that groundwater is the major water source to streams during most of the year, surface, fen and lake waters all appear to have lost HCO_3^- or gained divalent cations relative the groundwater source.

The relationships between Na^+ and Cl^- concentrations shown in Figure 4a and b explain this excess Ca^{2+}. Na^+ and Cl^- concentrations increase due to anthropogenic salt inputs. These salts include about 20,000 lbs of halite from the Morton Company salt mine near Detroit
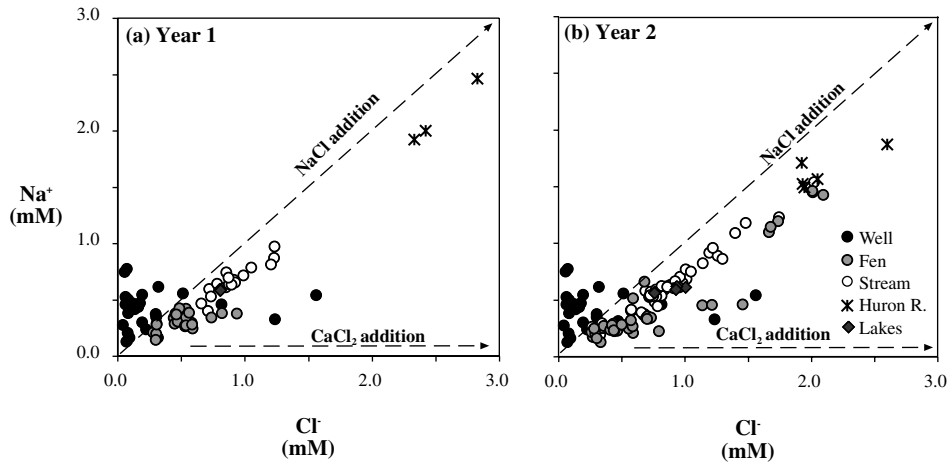
Figure 4. Na$^+$ vs. Cl$^-$ for Years 1 and 2 of the Portage and Ore Creek catchment ground and surface waters. A 1:1 line indicates the stoichiometric dissolution of halite (NaCl). The groundwaters fall above the 1:1 line with higher concentrations of Na$^+$ relative to Cl$^-$. The surface waters fall below the 1:1 line indicating that the additional Cl$^-$ has multiple sources, including NaCl and CaCl$_2$. A line indicating the direction water samples would move from the 1:1 line with the addition of CaCl$_2$ is shown.

Michigan added each year by the Washtenaw County transportation department for deicing roads (Mulcahy, 2003). The Portage Creek catchment (Figure 4a) has a few groundwaters with higher than average Na$^+$–Cl$^-$ concentrations, but in general the groundwaters are dilute in comparison and typically have a molar excess of Na$^+$ increasing the Na$^+$/Cl$^-$ ratios in these groundwaters. Since these are all shallow groundwaters contained in permeable glacial drift material rich in aluminosilicates, the Na$^+$ excess likely is derived from plagioclase feldspar dissolution. The surface waters on the other hand range from more dilute waters to relatively high Na$^+$ and Cl$^-$ concentrations at 3 mM each. In most cases the surface, fen and lake waters do not have a 1:1 relationship between Na$^+$ and Cl$^-$; this would be expected if halite dissolution were adding all the excess Na$^+$ and Cl$^-$ in the water.

Along with NaCl (halite), CaCl$_2$ (basinal and man-made brines) is also being added to deice residences and roads in the winter and to assist dust control on dirt roads in the summer months. Gypsum (CaSO$_4$) dissolution or sulfide oxidation processes can also contribute excess calcium, but since sulfate concentrations of 90% of the surface water samples are below 0.5 mM, these processes make a relatively small contribution to the overall excess calcium budget relative to CaCl$_2$ salts (see Tables III–VII).

3.2. GENERAL PATTERNS OF ELEMENTAL CHEMISTRY AT USGS GAUGE STATIONS

Historical area-normalized discharge values and chemical data (HCO_3^-, $Ca^{2+} + Mg^{2+}$, and Cl^- concentrations) for four USGS gauging stations are shown in Figure 5a–c. Although the historical data available are not extensive, the historical data are quite similar to the values observed in our study for the Huron River near Dexter. There is no systematic difference among the four sites for the carbonate-related parameters. In contrast, chloride concentrations vary widely among sites due to differences in proximity to developed highways and residential areas where road salting is common.

The Cl^- values appear to decrease with increasing discharge value at most of the gauge sites. However, periods of elevated discharge do not significantly differ in $Ca^{2+} + Mg^{2+}$ or HCO_3^- values at any of the four gauging sites, except the extreme discharges at the Ypsilanti gauge where the values decrease. Because the soils developed on the glacial drift in the Huron Watershed are very rich in carbonate minerals, runoff from snowmelt and/or storm events is very similar to the overall chemical stoichiometry observed in shallow groundwaters (compare to Figure 3 values from the present study).

Alkalinity and discharge relationships for the four sites suggest that the lowest discharge periods also have some of the lower alkalinity concentrations. The highest alkalinity values are observed during discharge conditions near the long term average values (see Table I) for each gauging site. Significantly, watersheds developed on carbonate landscapes in Europe (Seine, Loire Rivers) have similar patterns of alkalinity concentration with discharge, with minima occurring at low and high discharge values (Grosbois et al., 2000; Roy et al., 1999).

3.3. NORMALIZATION OF WATER CHEMISTRY TO GROUNDWATER Mg^{2+}/HCO_3^- VALUE

Previous studies have examined carbonate mass balances in carbonate precipitating springs and streams, using the stoichiometric loss of Ca^{2+} and HCO_3^- (Drysdale et al., 2002; Herman and Lorah, 1987; Jacobson and Usdowski, 1975; Lorah and Herman, 1988; Zaihua et al., 1995). This approach allows the amount of carbonate dissolved or precipitated to be evaluated independently of dilution effects. However, in the Huron watershed, Ca^{2+} has another source, anthropogenic $CaCl_2$, so Ca^{2+} concentrations in combination with alkalinity values cannot be used to arrive at accurate estimates of amounts of carbonate precipitation.

Although the carbonate related divalent cation Sr^{2+} has proven useful as a Ca^{2+} tracer in stream waters (e.g. Blum et al., 1998; Jacobson et al., 2002), the
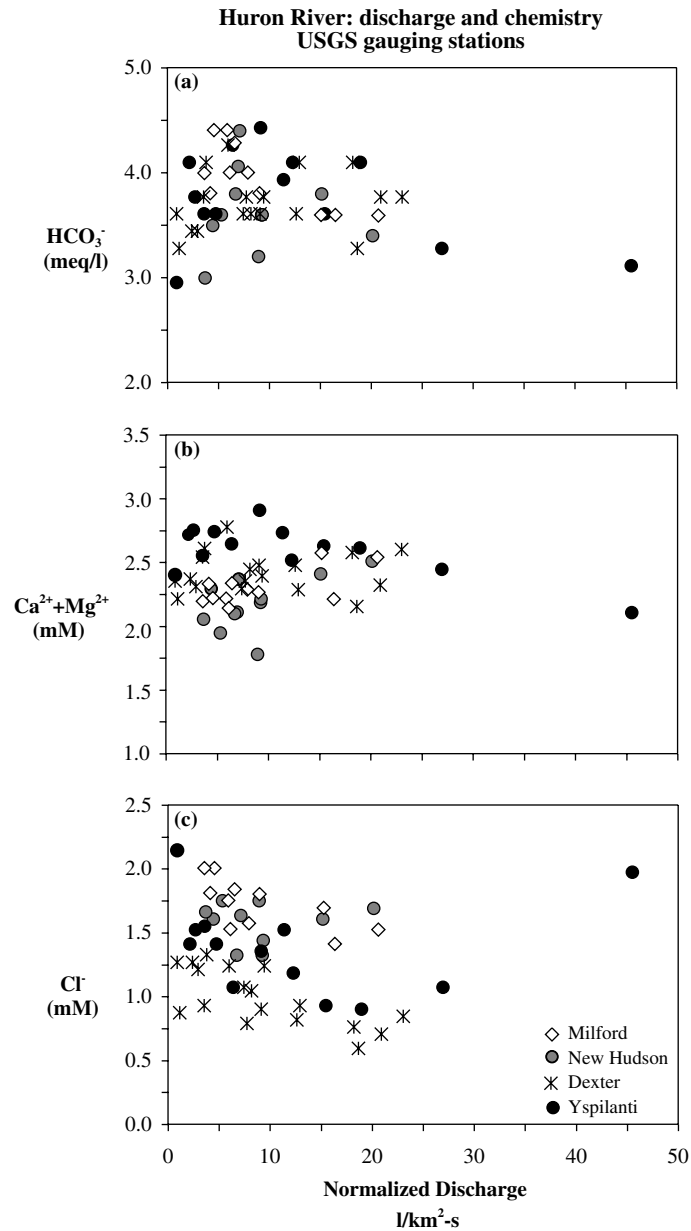
Figure 5. Discharge and chemistry (HCO_3^- (meq/l), $Ca^{2+} + Mg^{2+}$ (mM), and Cl^- (mM)) relations for 4 USGS gauge sites on the Huron River located in Figure 1. Table I reports the station # and drainage area for each location.

basinal brine-derived $CaCl_2$ salts from the Michigan Basin have a Sr^{2+}/Ca^{2+} ratio almost 1000 times higher than in our groundwaters (see McIntosh et al., GSA Bull, 2004, in press). To better quantify the amount of carbonate back

precipitation, a "conservative" element derived only from carbonate mineral dissolution with no significant geochemical sink is required.

The Mg^{2+} in the waters from the Huron River watershed is derived largely from the dissolution of dolomite commonly present in the glacial drift. The Mg^{2+}/Ca^{2+} of the groundwaters is on average 0.49 ± 0.05 molar ratio, indicating that approximately one mole of calcite dissolves for every mole of dolomite. Once released from dolomite, the Mg^{2+} has no other significant sink as the calcites forming in the fens and lakes have Mg^{2+} contents between 2 and 5 mol% (Komor, 1994), consistent with what is known of the partitioning of Mg^{2+} into calcites (e.g. Morse and Mackenzie, 1990). Normalizing losses of alkalinity to the Mg^{2+}/HCO_3^- ratio eliminates the complications presented by rainwater dilution or evapo-concentration.

Figure 6a and b presents the Mg^{2+} to HCO_3^- ratios for the various water types. The average groundwater ratio of Mg^{2+} to HCO_3^- is 0.18 for these two areas. The groundwater Mg^{2+} and HCO_3^- relationships for watersheds in Michigan, including the Huron River water are detailed in Szramek et al. (GSA Bulletin in prep.). Mg^{2+}/HCO_3^- values evolve progressively away from the groundwater, increasing in the surface, lake and fen samples. Note that most of the change in surface water chemistry takes place in the HCO_3^- concentration while Mg^{2+} concentrations tend to be similar to or greater than the original groundwater values. Year 1 shows a more pronounced increase as a result of the preferential loss of HCO_3^- relative to Mg^2 than does Year 2. By the time the waters from the Portage and Ore creek drainages enter into the main stem of the Huron River, HCO_3^- loss has already occurred.

3.4. VARIATION OF CARBONATE SATURATION PARAMETERS WITH MAJOR ELEMENTAL CHEMISTRY

Carbonate system parameters further constrain the conditions required for carbonate precipitation. As the CO_2 partial pressure increases, carbonate mineral solubility in pure water systems also increases (e.g. Drever, 1997; Langmuir, 1997; Morse and Mackenzie, 1990). Typically, ground and soil waters have pCO_2's 10–100 times the atmospheric pCO_2 of $10^{-3.5}$ atm. The relationships between calcite saturation state, alkalinity, Ca^{2+}, and pCO_2 can be shown directly by the following equation for calcite dissolution:

$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^-$$
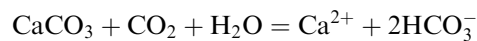
and its related law of mass action:

$$K_{eqcalcite} = \frac{aCa^{2+} a^2 HCO_3^-}{pCO_2}$$
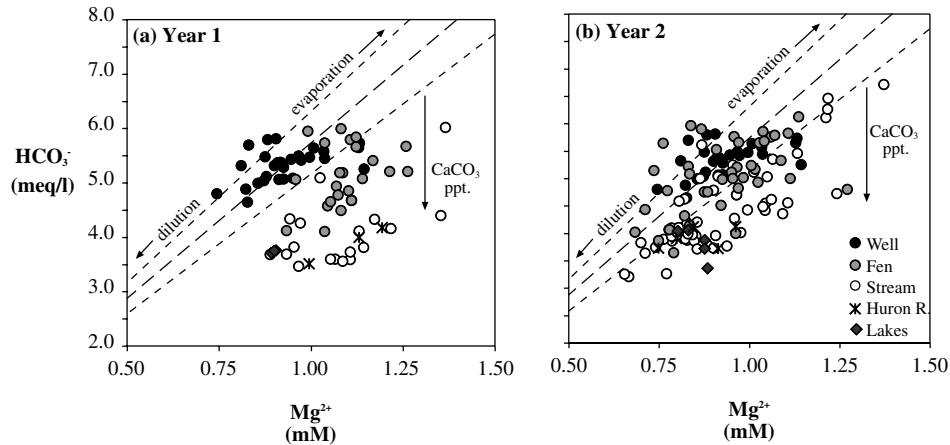
Figure 6. HCO_3^- vs. Mg^{2+} for Years 1 and 2 for ground and surface waters in Portage and Ore Creek catchments. The solid line indicates a best fit through the groundwater data and represents the average Mg^{2+}/HCO_3^- molar ratio (0.174) taken from the groundwater. The dashed lines represent the standard deviation of the Mg^{2+}/HCO_3^- mole ratio. The fen water, stream water, lake water and Huron River all fall off this line indicating the loss of HCO_3^- relative to Mg^{2+} in all the surface waters when compared to the groundwater. Year 1 of the study shows a greater offset from the line than Year 2.

where, a is the ion activity. Groundwaters in this study have an average pCO_2 of $10^{-2.15}$ atm. The surface waters approach a pCO_2 value of $10^{-3.5}$ atm. and approach equilibrium with the atmosphere. The loss of CO_2 is the main driver of increased saturation states for calcite, with changes in temperature and fluid mixing playing relatively small roles.

The stream and fen/lake waters reach approximately 30 times saturation with respect to calcite as a result of CO_2 degassing. Studies of natural freshwater systems have shown that IAP/K values must exceed 5–10 times saturation before calcium carbonate precipitation occurs (Herman and Lorah, 1987; Jacobson and Usdowski, 1975; Lorah and Herman, 1988; Suarez, 1983). Many factors affect carbonate growth kinetics including availability of nucleation sites (Suarez, 1983), inhibition by Mg^{2+} and PO_4^{3-} (Suarez, 1983; Zhang and Dawe, 2000), and DOC concentrations in excess of 0.05 mM (Lebron and Suarez, 1996, 1998). The Huron watershed has an average Mg^{2+}/Ca^{2+} ratio of approximately 0.5, which could have slight effect on the growth rate of calcite. Except for lake waters, PO_4^{3-} concentrations are below detection (1 μM) in most samples and therefore would also be expected to have little effect on the precipitation of calcium carbonate. DOC values for the Huron watershed are in excess of those shown to decrease calcite precipitation rates. The average surface water DOC value is close to 1 mM.
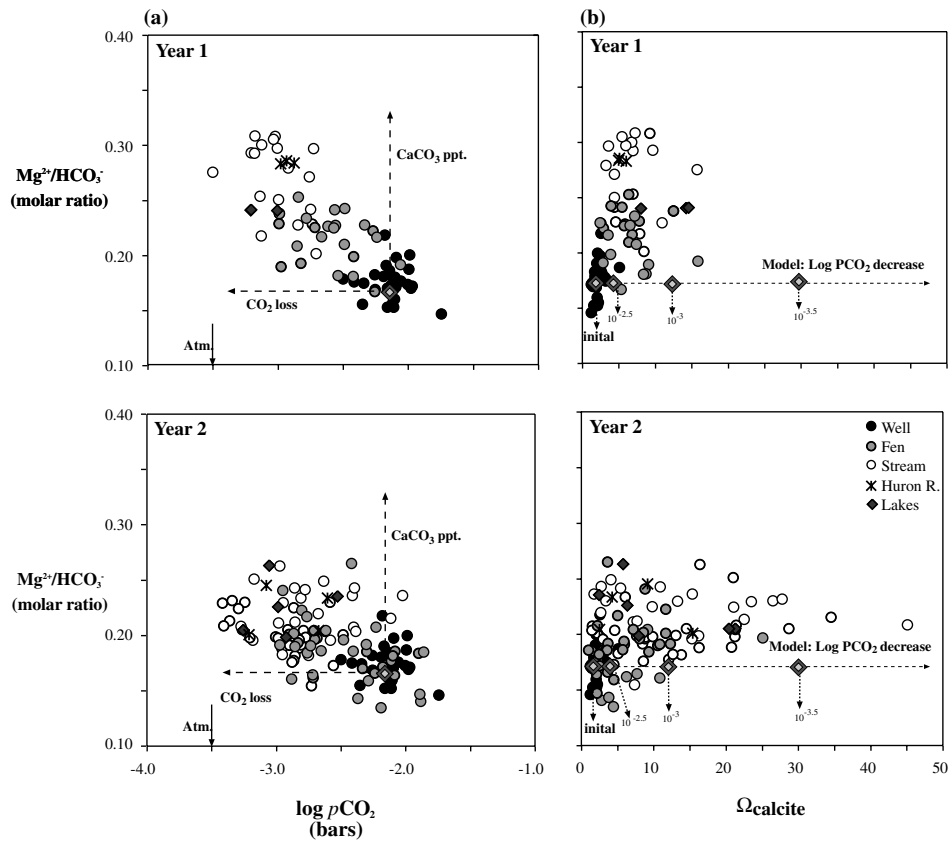
Figure 7. (a) Mg^{2+}/HCO_3^- vs. log pCO_2 relationships for Year 1 show higher Mg^{2+}/HCO_3^- mole ratio than Year 2. A dashed line indicates the direction the Mg^{2+}/HCO_3^- mole ratio moves relative to the removal of HCO_3^- during the precipitation (ppt.) of calcium carbonate. A second dashed line indicates the direction of CO_2 degassing and the decrease in pCO_2 as CO_2 is lost to the atmosphere. (b) Mg^{2+}/HCO_3^- vs. Ω calcite shows that Year 1 of the study does not achieve the degree of supersaturation that Year 2 does, up to 45 times saturation. Year 1 however, has the higher Mg^{2+}/HCO_3^- mole ratios indicating that the saturation states are held in check by the back precipitation of calcium carbonate. A dashed line indicates direction of CO_2 degassing. Diamonds indicate modeled log pCO_2 values for waters that undergo degassing without the back precipitation of calcium carbonate.

Changes in the Mg^{2+}/HCO_3^- ratio are driven by amount of calcium carbonate precipitation and indicate which environments in the catchment are the main loci of precipitation. The relationship between calcium carbonate precipitation and Mg^{2+}/HCO_3^- ratio can be further constrained by comparing the ratio to the values of carbonate parameters of the waters. Figure 7a shows the Mg^{2+}/HCO_3^- ratio versus log pCO_2. As outlined earlier, an increasing Mg^{2+}/HCO_3^- ratio is an indication of HCO_3^- loss. The loss of

CO_2 generally tracks the trend of increasing Mg^{2+}/HCO_3^- ratios. Year 1 shows a stronger increase in Mg^{2+}/HCO_3^- ratios with CO_2 degassing than does Year 2. Groundwaters have the highest pCO_2 values (avg. $10^{-2.15}$ atm.) and the lowest Mg^{2+}/HCO_3^- values (avg. 0.176 ± 0.016). The Mg^{2+}/HCO_3^- ratio of the fen and stream waters increase (~ 0.30) as they evolve towards atmospheric pCO_2 values ($10^{-3.5}$ atm.).

Relations between the amount of precipitation (changes in Mg^{2+}/HCO_3^- ratios) and calcite saturation state are shown in Figure 7b. Samples collected during Year 2 of the study attain and maintain higher supersaturation for calcite than Year 1. Calcite saturation state responds to CO_2 degassing, carbonate precipitation and Ca^{2+} pollution to varying degrees. Year 1 data show carbonate precipitation has relieved calcite supersaturation, although the waters remain significantly supersaturated. The Huron River site at Ann Arbor can be considered an integrator of the processes occurring in the headwater portions of the watershed. In general the waters show the greatest increase in Mg^{2+}/HCO_3^- ratios between Ω calcite values of 5–10 times saturation, the range shown to be the threshold to calcium carbonate precipitation in other natural systems (Herman and Lorah, 1987; Jacobson and Usdowski, 1975; Lorah and Herman, 1988; Suarez, 1983). Year 1 (Figure 7b) shows the highest Mg^{2+}/HCO_3^- ratios at approximately 5–10 times saturated for calcite with a few samples above 10 times saturation.

4. Discussion

4.1. MASS BALANCE CALCULATIONS: CARBONATE PRECIPITATION AND DISCHARGE

Locations of carbonate precipitation in the Huron River watershed and their relations to the drainage system architecture can be quantified by evaluating the mass balance of carbonate precipitated per liter of stream water at sites along the flow path from headwater catchments to the main channel. Alkalinity loss is calculated assuming that the average groundwater Mg^{2+}/HCO_3^- ratio is the starting value for surface waters in the Huron watershed. Changes in the Mg^{2+}/HCO_3^- ratios quantify the amount gained or lost according to the equation:

$$HCO_{3(predictedSWvalue)}^- = \left(\frac{HCO_3^-}{Mg^{2+}}\right)_{(averageGW)} \times Mg^{2+}_{(measuredSW)},$$

where SW is the surface water and GW is the groundwater. The value of the Mg^{2+}/HCO_3^- ratio is 0.176 ± 0.016. The uncertainty in the alkalinity loss mass balance is ± 0.5 meq/l, when analytical uncertainties for cation and alkalinity determinations are included in the error analysis.

Figure 8a–c presents the temporal and spatial influences on the mass balance for alkalinity loss in the Huron River watershed. Figure 8a shows the actual USGS stream gauge discharge data at Ann Arbor for the period just before and during the study interval as well as the average annual values over the entire period of record (87 years). In Figure 8b, the observed alkalinity losses are compared for stream vs. fen locations. Most fen and stream samples during Years 1 and 2 have lost significant amounts of alkalinity, most likely due to the precipitation of calcium carbonate. Only a few samples taken from the fen drainages exhibit an increase in alkalinity, but even these are largely within the uncertainty of the calculations (± 0.5 meq/l). Taken together, the data indicate that both fen and stream waters have experienced significant alkalinity losses. Another way to view the alkalinity loss patterns is to consider the differences in various reservoirs of the drainage system. Figure 8c shows alkalinity losses over the study period comparing the main channel of the Huron River near Dexter, with Halfmoon Lake water and with streams sampled before and after passing through the lake systems. It appears that both fens and lake settings have experienced carbonate precipitation and that these changes have the most profound effect on the main river channel chemistry during Year 1, the period of lowest discharge in the watershed (see Table II and Figure 8a).

These mass balances can also be viewed on a longer temporal scale and better calibrated to location specific discharge values. The USGS discharge and concurrent chemical data shown in Figure 5a–c for the four gauging sites can be used to evaluate the amount of HCO_3^- loss, again assuming that the groundwater ratio for Mg^{2+}/HCO_3^- is the starting point for the stream waters. Figure 9a shows alkalinity loss versus normalized discharge for the Huron River at the four gauging stations, which have both chemical and discharge data for the samples. As suggested by the patterns of alkalinity concentrations shown in Figure 6a, the lower periods of discharge have the greatest alkalinity loss. At higher discharges alkalinity losses are less than half of that observed during low flow conditions. Importantly, the most significant losses in alkalinity are associated with periods when discharge is below long term average values for the catchments (see Table I).

Alkalinity loss data collected in our study for the two historic USGS gauge sites (Portage @ Tiplady and Huron River near Dexter) are plotted against normalized discharge in Figure 9b and c. No current gauge data is collected at these two sites, necessitating the estimation of discharge as detailed in Section 2.6. Year 1 samples exhibit higher alkalinity losses over the range of normalized discharges (2–15 l/km^{2}s), while Year 2 shows lower alkalinity loss values over the a smaller range of discharges (5–15 l/km^{2}s). Thus, the data gathered in this study suggests that low discharge periods are associated with greatest alkalinity losses and the denser data set from the USGS provides additional support for this assertion.
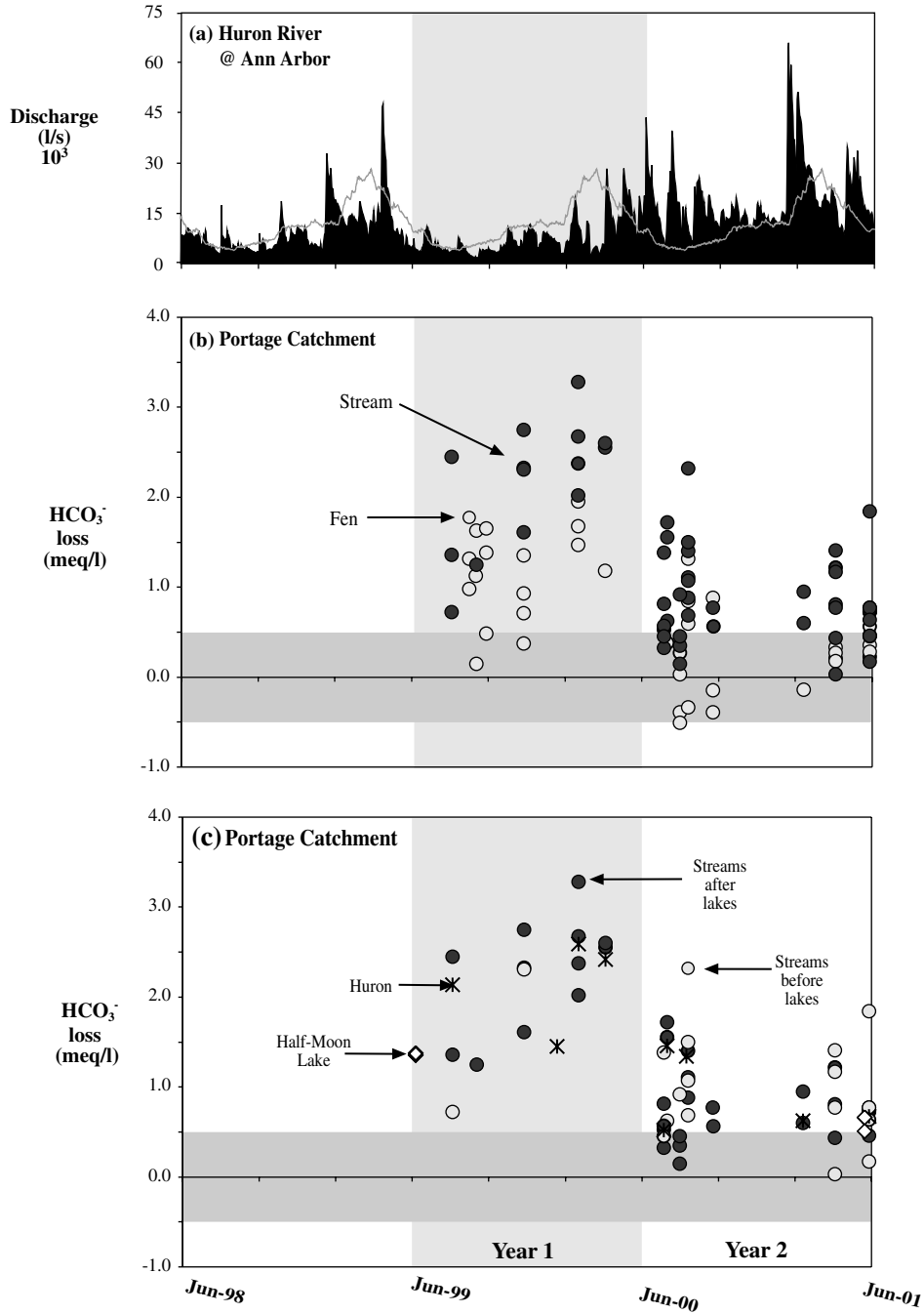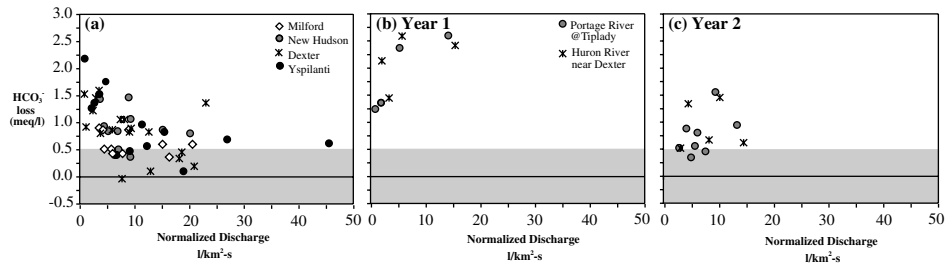
Figure 9. Alkalinity loss (meq/l) vs. normalized discharge (l/km^2 s). (a) The Huron River taken from four USGS sites with both chemical and discharge data. The details of the stations are given in Table I. The data show that the lower flow volumes have higher alkalinity lost values. The gray band indicates the uncertainty in the zero point based on the standard deviation of the Mg^{2+}/HCO_3^- values for the groundwater samples. (b) Data from the Huron River (this study) and Portage @ Tiplady (1) for Year 1. (c) Data from the Huron River (this study) and Portage @ Tiplady (1) for Year 2. Year 1 has higher alkalinity loss values and lower discharge values than Year 2.

4.2. RIVERINE FLUXES VERSUS CARBONATE ACCUMULATION RATES IN LAKES AND FENS

The average amount of calcium carbonate precipitated within the Huron watershed was determined by the average carbonate alkalinity (HCO_3^-) loss (0.86 meq/l) and average discharge (10,050.3 l/s) from historical USGS chemical and discharge data from the Huron River gauge site near Dexter (41730000). The amount of calcium carbonate precipitated from the Huron watershed above the gauge is 1.36×10^{10} g per year. Normalized to the amount of area drained (see Table I), this flux is 1.01×10^7 g per km^2 year. However, the geochemical changes in the stream waters are most pronounced in the headwater portions of the catchments, which are the locus of carbonate precipitating fens and lakes.

Figure 8. (a) Discharge for the Huron River @ Ann Arbor (4174500) for the year previous to the study and Years 1 and Year 2 of the study is shown with the dark shaded area. The light line indicates the average discharge over 87 years of data. Year 1 clearly has discharge below the average, where as Year 2 has discharge above the average. (b) Alkalinity loss (removed) from the Portage Catchment stream and fen waters as determined by the predicted ratio of Mg^{2+}/HCO_3^- from the sampled groundwaters is shown in the second graph. The year June 1999–June 2000 has the greatest degree of alkalinity loss. The increased HCO_3^- loss from the surface waters during Year 1 is accompanied by the lower discharge. (c) The third graph shows HCO_3^- loss with the Huron River, Halfmoon Lake and streams before and after lakes. Stream water that has not passed thorough a lake tends to be as evolved as stream water that has passed through a lake. The Huron River samples are also as evolved as the other samples indicting that the samples are modified before they reach the main channel of the Huron River.

In order to focus on lakes and fens as reservoirs of carbonate accumulation, a mass balance calculation is made of the amount of carbonate loss within the Portage Catchment, the main area of study at the historical USGS gauge located at Portage at Tiplady (4172500). A conservative estimate was calculated using the average alkalinity loss from the Huron River near Dexter (0.860 meq/l) rather than the value calculated during the 2 years of the present study at the Portage at Tiplady sample site. This was done to eliminate the potential bias of data collected in this study to higher carbonate production due to the particularly low discharges of Year 1 of the study.

The average discharge (1384 l/s) along with the average alkalinity loss indicates a loss of 1.88×10^9 g per year (a conservative estimate) this equates 9.2×10^6 g per km^2year in the Portage catchment. The lakes in the Portage catchment comprise approximately 10% (20.4 km^2) of the surface area. If all the carbonate precipitating in the catchment is forming/accumulating in the lakes then 9.17×10^7 grams per km^2 year is accumulating within the lake basins of the Portage Catchment in the Huron River Watershed.

This carbonate production rate is more than twice the short-term accumulation rate of 4.43×10^7 g per year observed in Littlefield Lake in Michigan by Dustin et al. (1986). The authors noted that the short-term rate of calcium carbonate is 3–7 times too low to account for the amount of carbonate accumulated over time in Littlefield Lake. Other authors have noted a similar trend and have indicated that the rates of calcium carbonate production in marl lakes have decreased over the Holocene (Dean, 1999; Dustin et al., 1986; Wetzerl, 1968). The rate of modern day carbonate production appears to have decreased from past rates making accumulation over time difficult to determine.

4.3. EXPORT OF HCO_3^-: INFLUENCE OF CARBONATE PRECIPITATION

The precipitation of calcium carbonate from the Huron River watershed (taken near Dexter) decreases the average HCO_3^- concentration by nearly 20%, from 4.57 meq/l (predicted) to 3.71 meq/l (actual). Although a reduction in the export of alkalinity from the Huron Watershed is observed, this reduction would be nearly impossible to infer from the chemistry downstream in the greater St. Lawrence-Great Lakes Watershed. The alkalinity for the St. Lawrence River is less than 2 meq/l (Holland, 1978; Yang et al., 1996) and is reflective of upstream processes (i.e., carbonate precipitation, dilution). In addition to the low alkalinity concentrations, the St. Lawrence River is typically near saturation for calcite (Holland, 1978; Yang et al., 1996). The type of substrate and the land use with in a watershed can greatly influence the dissolved solutes, saturation states and dissolved CO_2 with in a river system. Telmer and Veizer, (1999) suggest that watersheds operate at different weathering zone pCO_2's, which in turn control the stream chemistry by

regulating rock weathering within the watershed. The recent study of the Mississippi River by Raymond and Cole (2003), indicate that the long-term average of alkalinity concentration of the river is increasing. They attribute this to change in land use within the Mississippi Basin. The thickness of soils (Telmer and Veizer, 1999) and type of land use (i.e., agriculture vs. forested) (Raymond and Cole, 2003) are the main controls on the pCO_2 and in turn the carbonic acid in contact with minerals available to weather. Land use changes and the increases in atmospheric CO_2 in turn will influence the pCO_2 in the shallow soils and potentially increase the amount of solutes, including HCO_3^- draining terrestrial landscapes. However, the back precipitation may limit the predicted export of HCO_3^- to the world's oceans.

The results obtained on the carbonate geochemistry in streams and shallow groundwaters suggest that a more detailed, systematic and temporally controlled study of these systems may provide valuable new insights to the functioning of terrestrial carbonate weathering systems. This study indicates that Holland's (1978) simplified theory on carbonate saturation states within the world's major rivers underestimates the possibility for sustained supersaturation with respect to calcite. Rivers in areas draining carbonates are likely to be at or above saturation for calcite regardless of discharge. Watersheds are commonly characterized by HCO_3^- flux from the mouth of the drainage system, however this relationship limits the understanding of the processes which actually regulate the carbonate dissolution flux.

5. Summary and Conclusions

The suite of geochemical analysis obtained on the surface waters and shallow groundwaters of the Portage and Ore Creek catchments of the Huron River watershed, MI provides a spatially resolved view of processes regulating the dissolved inorganic carbon mass balance within this watershed. The dissolution of calcite and dolomite within the geologically young soils developed on glacial deposits covering the region greatly influence the water chemistry within the watershed. Accordingly, the groundwaters and surface waters in this study are predominantly Ca^{2+}–Mg^{2+}–HCO_3^- waters.

Many other studies that examine the freshwater precipitation of carbonate, mainly as tufa, utilize the Ca^{2+} and alkalinity concentrations in waters to determine the mass balance of carbonate precipitation. The surface waters in the Huron Watershed, however, have excess Na^+, Cl^- and Ca^{2+} relative to groundwaters as a result of anthropogenic NaCl and $CaCl_2$ salts. This means that the Ca^{2+}/HCO_3^- (alkalinity) relationship cannot be used to arrive at an accurate mass balance of carbonate dissolution or precipitation.

The examination of changes in the surface water Mg^{2+}/HCO_3^- ratio relative to the ratio set by the groundwater is the most useful parameter to quantify carbonate production within the Huron River watershed. This is

possible because of the relatively constant value of Mg^{2+}/HCO_3^- in the glacial drift groundwaters and their close hydrogeologic connection to surface waters. The carbonate parameters indicate that the surface waters are highly evolved when compared to the starting conditions set by the groundwater. The increase of Mg^{2+}/HCO_3^- ratio in the surface waters indicates that carbonate precipitation occur as CO_2 degasses. The corresponding Ω calcite indicates that these waters can sustain supersaturation with respect to calcite without back precipitation even though waters exceed 10 fold supersaturation values. Surface water samples from Year 1 of the study have the highest Mg^{2+}/HCO_3^- ratios and Ω calcite values for these waters does not exceed 15 times saturation, a value three times lower than that observed during Year 2 of the study.

The alkalinity loss values for surface water samples attain their maximum values during Year 1 of the study when the discharge of the Huron River was well below normal. Samples from Year 2, a period characterized by riverine discharge values above normal, have more modest alkalinity losses. Importantly the data for the main channel of the Huron River do not show additional alkalinity loss relative to the waters discharged from the smaller headwater catchments, which include fen and lake systems.

The export of dissolved inorganic carbon is decreased from the Huron River watershed by the removal of alkalinity from the surface waters. The relationships for the alkalinity and $Ca^{2+}+Mg^{2+}$ versus discharge indicate that alkalinity and $Ca^{2+}+Mg^{2+}$ values are at their lowest concentrations during the lowest discharges for the Huron River. This is supported by the relationship between alkalinity loss and discharge, where the highest values are observed during the lowest flow periods. These relationships indicate that the flux of carbonate removed from the weathering zone of the soil is decreased only slightly due to the back precipitation of calcium carbonate within the watershed.

The next several centuries will likely see increases in atmospheric CO_2 concentrations and terrestrial carbon cycling due to fertilization effects and changes in land use. All of these tend to intensify the short-term transport of carbon derived from carbonate rock weathering. Our study shows that carbonate weathering flux dynamics within watersheds need to be examined on a small spatial scale. More detailed studies of carbonate saturation state and carbonate precipitation losses within watersheds will permit observed variations in pCO_2 values and HCO_3^- carrying capacity to be related mechanistically to carbonate fluxes from terrestrial environments.

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References

Almendinger J. E. and Leete J. H. (1998a) Peat characteristics and groundwater geochemistry of calcareous fens in the Minnesota River Basin, USA *Biogeochemistry* **43**, 17–41.

Almendinger J. E. and Leete J. H. (1998b) Regional and local hydrogeology of calcareous fens in the Minnesota River Basin, USA. *Wetlands* **18**, 184–202.

Andrews J. A. and Schlesinger W. A. (2001) Soil CO_2 dynamics, acidification, and chemical weathering in a temperate forest with experimental CO_2 enrichment. *Global Biogeochem. Cycles* **15**, 149–162.

Aucour A.-M., Sheppard S. M. F., Guyomar O. and Wattelet J. (1999) Use of ^{13}C to trace origin and cycling of inorganic carbon in the Rhône river system. *Chem Geol.* **159**, 87–105.

Barth J. and Veizer J. (1999) Carbon cycle in St. Lawrence aquatic ecosystems at Cornwall (Ontario), Canada: seasonal and spatial variations. *Chem. Geol.* **159**, 107–128.

Barth J., Cronin A. A., Dunlop J., Kalin R. M. (2003) Influence of carbonates on the riverine carbon cycle in an anthropogenically dominated catchment basin: evidence from major elements and stable carbon isotopes in the Lagan River (N. Ireland). *Chem. Geol.* **200**, 203–216.

Berner E. K. and Berner R. A. (1987) The Global Water Cycle: Geochemistry and Environment: Englewood Cliffs, N. J., Prentice-Hall, 397 pp.

Blum J. D., Grazis C. A., Jacobson A. D. and Chamberlain C. P. (1998) Carbonate versus silicate weathering in the Raikhot Watershed within the High Himalayan Crystalline Series. *Geology* **26**, 411–414.

Brady N. and Weil, R. R. (1996) The nature and properties of soils: Upper Saddle River, NJ, Prentice Hall, 740 pp.

Dean W. E. (1999) The carbon cycle and biogeochemical dynamics in lake sediments. *J. Paleolimnol.* **21**, 375–393.

Dorr Jr. J. A., and Eschman, D. F. (1970) Geology of Michigan. Ann Arbor, Univ. of Michigan Press, 476 pp.

Drever J. I., (1997) The geochemistry of natural waters: surface and groundwater environments: Upper Saddle River, NJ, Prentice Hall, 436 pp.

Drysdale R. N., Taylor M. P. and Ihlenfeld C. (2002) Factors controlling the chemical evolution of travertine-depositing rivers of the Barkly karst, northern Australia. *Hydrol. Process.* **16**, 2941–2962.

Dustin N. M., Wilkinson B. H. and Owen R. M. (1986) Littlefield Lake, Michigan; carbonate budget of Holocence sedimentation in a temperate-region lacustrine system. *Limnol. Oceanography* **31**, 1301–1311.

Farrand W. R. (1982) *Quaternary Geology of Southern Michigan: State of Michigan, Deptartment of Natural Resources, Geological Survey, Lansing, Mich.*

Gaillardet J., Dupre B., Louvat P. and Allegre C. J. (1999) Global silicate weathering and CO_2 consumption rates deduced from the chemistry of large rivers. *Chem Geol.* **159**, 3–30.

Garrels R. M. and Mackenzie F. T. (1971) *Evolution of Sedimentary Rocks: W. W. Norton and Company, New York*, 397 pp.

Glaser P. H., Janssens J. A. and Siegel. D. I. (1990) The response of vegetation to chemical and hydrological gradients in the Lost River peatland, northern Minnesota. *J. Ecol.* **78**, 1021–1048.

Grannemann N. G., Hunt R. J., Nicholas J. R., Reilly T. E., and Winter T. C. (2000) The
    Importance of Ground Water in the Great Lakes Region. USGS Water-Resources Investi-
    gations Report **00-4008**: 1–14.
Grosbois C., Négrel Ph., Fouillac C. and Grimaud D. (2000) Dissolved load of the Loire River:
    Chemical and isotopic characterization. *Chem. Geol.* **170**, 179–201.
Hamilton J. G., DeLucia E. H., George K., Naidu S. L., Finzi A. C. and Schlesinger W. H.
    (2002) Forest carbon balance under elevated CO_2. *Ecosys. Ecol.* **131**, 250–260.
Herman J. S. and Lorah M. M. (1987) CO_2 outgassing and calcite precipitation in Falling Spring
    Creek, Virgina, USA. *Chem. Geol.* **62**, 251–262.
Herman J. S. and Lorah M. M. (1988) Calcite precipitation rates in the field: Measurement and
    prediction for travertine-depositing stream. *Geochim. Cosmochim.* Acta. **52**, 2347–2355.
Holland H. D. (1978) *The Chemistry of the Atmosphere and Oceans:* John Wiley and Sons, New
    York, 351 pp.
Jacobson R. L. and Usdowski E. (1975) Geochemical controls on a calcite precipitating spring.
    Contributions *Mineral. Petrol.* **51**, 65–74.
Jacobson A. D., Blum J. D., Chamberlain C. P., Poage M. A. and Sloan V. F., (2002) Ca/Sr and Sr
    isotope systematics of a Himalayan glacial chronosequence: carbonate versus silicate weath-
    ering rates as a function of landscape surface age. *Geochem. Cosmochim. Acta.* **66**, 13–37.
Kano A., Sakuma K., Kaneko N. and Naka T. (1998) Chemical properties of surface waters in
    the limestone regions of western Japan: Evaluation of chemical conditions for the deposition
    of tufas. *J. Sci. Hiroshima Univ. Ser.* **11**, 11–22.
Karim A. and Veizer J. (2000) Weathering processes in the Indus River Basin: implications from
    riverine carbon, sulfur, oxygen, and strontium isotopes. *Chem. Geol.* **170**, 153–177.
Kempe S. (1982) Long-term records of CO_2 Pressure fluctuations in fresh waters. *In Transport of
    carbon and minerals in major world rivers*, (ed. Degens, E. T. Kempe, S. Soliman, H. and
    Herrerapp, R. pp. 91–323. Hamberg: SCOPE-UNEP.
Kharaka Y. K., Gunter W. D. Aggarwal P. K., Perkins E. H. and DeBraal J. D. (1988)
    SOLMINEQ.88: A computer program for geochemical modeling of water-rock interactions:
    U.S. Geological Survey.
Komor S. C. (1994) Geochemistry and hydrology of a calcareous fen within the Savage Fen
    wetlands complex, Minnesota, USA. *Geochim. Cosmochim.* Acta. **58**, 3353–3367.
Ku T. C. W. (2001) Organic Carbon – Mineral Interactions in Near Surface Environments:
    Implications for the Global Carbon Cycle. Ph. D. thesis: Ann Arbor, University of Michigan.
Langmuir D., (1997) *Aqueous Environmental Geochemistry: N. J., Prentice-Hall*, Englewood
    Cliffs, 600 pp.
Lebron I. and Suarez D. L. (1996) Calcite nucleation and precipitation kinetics as affected by
    dissolved organic matter at 25 °C and pH > 7.5. *Geochem. Cosmochim.Acta* **60**, 2765–2776.
Lebron I. and Suarez D. L. (1998) Kinetics and mechanisms of precipitation of calcite as affected
    by P-CO2 and organic ligands at 25 °C. *Geochim. Cosmochim.* Acta **62**, 405–416.
Lorah M. M. and Herman J. S. (1988) The chemical evolution of a travertine-depositing stream:
    Geochemical processes and a mass transfer reaction. *Water Resourc. Res.* **24**, 1541–1552.
Lu G., Zheng C., Donahoe R. J. and Lyons W. B. (2000) Controlling processes in a $CaCO_3$
    precipitating stream in Huanglong Natural Science District, Sichuan, China. *J. Hydrol.* **230**,
    34–54.
Mackenzie F. T., Lerman A., Ver L. M. B. (1998) Role of the continental margin in the global
    carbon balance during the past three centuries. *Geology* **26**, 423–426.
Mackenzie F. T., Ver L. M., Sabine C., Lane M. and Lerman A. (1993) C, N, P, S global
    biogeochemical cycles and modeling of global change. *In Interactions of C, N, P and S
    Biogeochemical Cycles and Global Change*, (ed. Wollast, R. Mackenzie F. T. and L. Chou),
    pp. 1–62. Springer-Verlag. Berlin.

Meybeck M. (1987) Global chemical weathering of surficial rocks estimated from river dissolved loads. *Am. J. Sci.* **287**, 401–428.

Millot R., Gaillardet J., Dupré B., and Allègre C. J. (2003) Northern latitude chemical weathering rates:Clues from the Mackenzie River Basin, Canada. *Geochim. Cosmochim.* Acta **67**, 1305–1329.

Morse J. W. and Mackenzie F. T. (1990) *Geochemistry of Sedimentary Carbonate*. Elsevier.

Mulcahy J. (2003) *Jury's still out on road brine, The Ann Arbor News*. Ann Arbor, pp. B1, B3.

Pregitzer, K. S., Zak, D. R., Maziasz, J., DeForest, J., Curtis, P. S. and Lussenhop, J. (2000) Interactive effects of atmospheric CO_2 and soil-N availability on fine roots of *Populus tremulodies*. *Ecol. Applications* **10**, 18–33.

Raymond P. A. and Cole J. J. (2003) Increase in the export of alkalinity from North America's largest river. *Science* **301**, 88–91.

Reardon E. J., Allison G. B. and Fritz P. (1979) Seasonal chemical and isotopic variations of soil CO_2 at Trout Creek, Ontario. *J. Hydrol.* **43**, 355–371.

Roy S., Gaillardet J. and Allègre C. J. (1999) Geochemistry of dissolved and suspended loads of the Seine river, France: Anthropogenic impact, carbonate and silicate weathering. *Geochim. Cosmochim.* Acta **63**, 1277–1292.

Suarez D. L. (1983) Calcite supersaturation and precipitation kinetics in the Lower Colorado River, All American Canal and East Highline Canal. *Water Resourc. Res.* **19**, 653–661.

Szramek, K., Walter, L. M. and McCall, P. (2004) Arsenic mobility in groundwater/surface water systems in carbonate-rich Pleistocene glacial drift aquifers (Michigan). *Applied Geochem.* **19**, 1137–1155.

Telmer K. and Veizer J. (1999) Carbon fluxes, pCO_2 and substrate weathering in a large northern river basin, Canada: Carbon isotope perspective. *Chem. Geol.* **159**, 61–86.

Twenter F. R., Knutilla R. L. and Nowlin J. O. (1976) Water Resources of Washtenaw County, Michigan: Ann Arbor, United States Geological Survey in cooperation with the Washtenaw County Metropolitan Planning Commission, pp. 1–143.

U.S. Geological Survey (2001) National Water Information System (NWISWeb) data available on the World Wide Web, accessed [2001], at URL [http://waterdata.usgs.gov/nwis/].

Van Breenan N. and Protz R. (1988) Rates of calcium carbonate removal from soils. *Can. J. Soil Sci.* **68**, 449–454.

Wachniew P. and Rozanski K. (1997) Carbon budget of a mid-latitude, groundwater-controlled lake: Isotopic evidence for the importance of dissolved inorganic carbon recycling. *Geochim. Cosmochim.* Acta **61**, 2453–2465.

Wetzel R. G. (1970), Recent and postglacial production rates of a marl lake. *Limnol. Oceanography* **15**, 491–503.

Williams E. L., Walter L. M., Ku T. C. W., Kling G. W. and Zak D. R. (2003) Effects of CO_2 and nutrient availability on mineral weathering in controlled tree growth experiments. *Global Biogeochem. Cycles* **17** Art. No. 1041.

Yang C., Telmer K. and Veizer J. (1996) Chemical dynamics of the "St. Lawrence" riverine system: δD_{H2O}, $\delta^{18}O_{H2O}$, $\delta^{13}C_{DIC}$, $\delta^{34}_{sulfate}$, and dissolved $^{87}Sr/^{86}Sr$. *Geochem. Cosmochim.* Acta **60**, 851–866.

Zaihua L., Svensson U., Dreybrodt W., Daoxian Y. and Buchmann D. (1995) Hydrodynamic control of inorganic calcite precipitation in Huanglong Ravine, China: Field measurements and theoretical prediction of deposition rates. *Geochem. Cosmochim.*Acta. **59**, 3087–3097.

Zhang Y. and Dawe R. A. (2000) Influence of Mg^{2+} on the kinetics of calcite precipitation and calcite crystal morphology. *Chem. Geol.* **163**, 129–138.