

Evidence for carbon sequestration by agricultural liming

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[1] Agricultural lime can be a source or a sink for CO₂, depending on whether reaction occurs with strong acids or carbonic acid. Here we examine the impact of liming on global warming potential by comparing the sum of Ca²⁺ and Mg²⁺ to carbonate alkalinity in soil solutions beneath unmanaged vegetation versus limed row crops, and of streams and rivers in agricultural versus forested watersheds, mainly in southern Michigan. Soil solutions sampled by tension indicated that lime can act as either a source or a sink for CO₂. However, infiltrating waters tended to indicate net CO₂ uptake, as did tile drainage waters and streams draining agricultural watersheds. As nitrate concentrations increased in infiltrating waters, lime switched from a net CO₂ sink to a source, implying nitrification as a major acidifying process. Dissolution of lime may sequester CO₂ equal to roughly 25–50% of its C content, in contrast to the prevailing assumption that all of the carbon in lime becomes CO₂. The ~30 Tg/yr of agricultural lime applied in the United States could thus sequester up to 1.9 Tg C/yr, about 15% of the annual change in the U.S. CO₂ emissions (12 Tg C/yr for 2002–2003). The implications of liming for atmospheric CO₂ stabilization should be considered in strategies to mitigate global climate change.

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1. Introduction

[2] The future course of global climate change depends critically on near-term CO₂ mitigation measures, including the sequestration of CO₂-C in organic or inorganic forms [Caldeira *et al.*, 2004]. On a global scale, one of the most important chemical weathering reactions is the dissolution of carbonate minerals by reaction with carbonic acid, which consumes CO₂ to yield dissolved inorganic carbon in the form of carbonate alkalinity [Stumm and Morgan, 1996]. In humid and subhumid climates, carbonate alkalinity is subsequently transported through groundwater flow paths and eventually into streams and rivers, with little back-precipitation [Reardon *et al.*, 1979; Gaillardet *et al.*, 1999; Drees *et al.*, 2001; Szramek and Walter, 2004], and ultimately reaches the oceans. On geological timescales this alkalinity input to the oceans may be approximately balanced by precipitation of carbonate minerals [Milliman,

1993; Berner, 1999]. However, in relation to the immediate problem of anthropogenic CO₂ as a driver of global climate change, the timescale for transport from the sites of mineral weathering in soils through groundwater and ultimately to the oceans is long (centuries), and this balance may be disrupted by increases in atmospheric CO₂ [Andersson and Mackenzie, 2004]. Thus changing rates of carbonate mineral weathering and subsequent reprecipitation play an important role in today's atmospheric CO₂ balance, a major driver of climate change.

[3] The weathering of indigenous carbonate minerals has been augmented by the widespread use of agricultural “lime,” most often applied as calcite or dolomite (CaCO₃ or CaMg(CO₃)₂, respectively). Periodic liming is necessary to counteract soil acidification in cultivated soils, which usually results mainly from nitrogen and sulfur fertilizers, cultivation of N-fixing crops, and crop harvest [Helyar and Porter, 1989; Fisher *et al.*, 2003]. Liming has long been a foundation of agriculture in humid regions throughout the world, and has increased with agricultural intensification. In the United States alone, ~30 Tg/yr of lime are applied to agricultural fields [West and McBride, 2005], which is equivalent to about 3.7 Tg/yr of carbon. While not large compared to other terms in the global or U.S. CO₂ budget, this lime carbon flux represents 31% of the annual change in the U.S. CO₂ loading rate (12 Tg C/yr for 2002–2003), and thus is potentially significant from the standpoint of atmospheric CO₂ stabilization. Moreover this flux is also significant when compared to the potential maximum carbon sequestration associated with mitigation measures such as

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Table 1. Relative Global Warming Potential Impact for Different Management Systems Based on Soil Carbon Sequestration, Agronomic Inputs, and Trace Gas Fluxes, In Part From *Robertson et al.* [2000]^a

Ecosystem Management	CO ₂ Equivalents				N ₂ O	CH ₄	Net GWP: Lime as Source ^c	Net GWP: Lime as Sink ^d
	Soil-C	N-fertil.	Lime ^b	Fuel				
	Annual Crops (Corn/Soy/Wheat)							
Conventional	0	27	23	16	52	−4	114	68
No-till	−110	27	34	12	56	−5	14	−54
Low input with legume cover	−40	9	19	20	60	−5	63	25
Organic with legume cover	−29	0	0	19	56	−5	41	41
	Perennial Crops							
Alfalfa	−161	0	80	8	59	−6	−20	−180
Poplar	−117	5	0	2	10	−5	−105	−105

^aUnits are CO₂-equivalents (g m^{−2} yr^{−1}) based on IPCC conversion factors. Negative global warming potential (GWP) impact indicates a global warming mitigation potential. Net GWP impact is calculated on the basis of the alternative assumptions that lime acts as either a CO₂ source or sink proportional to its carbon content.

^bEquivalent CO₂ in lime amendments, which were applied following standard best management practices.

^cCalculated by *Robertson et al.* [2000], assuming all carbon in lime becomes CO₂.

^dCalculated with the alternative assumption that all lime dissolves via carbonic acid weathering.

no-till agriculture that increase soil organic matter; such measures are estimated to be capable of sequestering at most 100–150 Tg C/yr in the United States during several decades [Council for Agricultural Science and Technology, 2004]. Projections of the worldwide expansion of intensive agriculture suggest that global lime use may increase nearly threefold in the next 50 years [Tilman et al., 2001]. Thus it becomes even more important to consider the implications of liming for terrestrial carbon sequestration when contemplating the impact of agriculture on global climate change [West and McBride, 2005].

[4] Liming of agricultural soils takes on greater importance when other greenhouse gas fluxes in addition to carbon are considered. In an analysis of the global warming potential (GWP) impact of different agricultural systems, *Robertson et al.* [2000] found agricultural liming to be the second most important source of GWP impact in their annual crop systems (after N₂O release), and the most important source in their alfalfa system. *Robertson et al.*'s calculations assumed that the inorganic carbon in these minerals eventually becomes CO₂ as the lime is consumed, following IPCC emissions guidelines [Intergovernmental Panel on Climate Change, 1997]. Lime is typically applied every few years to agricultural soils to keep soil pH within a range favorable for crop growth; assuming all of this lime dissolves to CO₂ prior to the next lime application, then on average 23–34 g CO₂-C/m² per year was released in their conventionally farmed annual crops and 80 g C/m² per year was released in their alfalfa system. This contrasts with N₂O emissions of around 58 g C-equivalents/m² per year in all cropping systems, and in the no-till system it negated a significant portion of the mitigation potential associated with soil organic carbon storage, ~110 g C m^{−2} yr^{−1} (Table 1), a typical value for midwest U.S. no-till cropping systems [Lal et al., 1999]. CO₂ contributions from liming are thus large relative to other sources of GWP impact in these agricultural systems and also relative to estimates of CO₂ originating from carbonate precipitation caused by

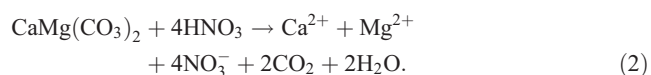
dryland irrigation with alkaline groundwater (~12 g C m^{−2} yr^{−1} [Schlesinger, 1999, 2000]).

[5] Notwithstanding the IPCC assumption that all lime C ultimately becomes CO₂, biogeochemical theory suggests that the dissolution of carbonate minerals can act as either a net source or sink for CO₂. In moderately acid (pH 5–6.5), neutral and alkaline soils, most of the dissolution of carbonate minerals can be ascribed to carbonic acid weathering, which is the major natural process of limestone weathering and the primary source of alkalinity to most surface and groundwaters [Stumm and Morgan, 1996]. Dissolved CO₂ from root and microbial respiration exists in equilibrium with the weak acid H₂CO₃, and hereafter we refer to the sum of these forms as “soil CO₂.” Soil CO₂ reacts with solid carbonates as shown in this reaction using dolomite as an example,



Note that carbonic acid weathering is a *sink* for soil CO₂ because every mole of lime-derived C that dissolves yields 2 moles of HCO₃[−] alkalinity (the dominant form of carbonate alkalinity at the pH of most soil waters). Dissolution is enhanced in soils with high biological activity because respiratory CO₂ typically accumulates to partial pressures 1 to 2 orders of magnitude above atmospheric levels, with consequent increases in carbonic acid [Jones and Mulholland, 1998].

[6] Alternatively, in the presence of a strong acid such as HNO₃ produced by the nitrification of NH₄⁺ to NO₃[−], the dissolution of carbonate minerals acts as a CO₂ source rather than a CO₂ sink,



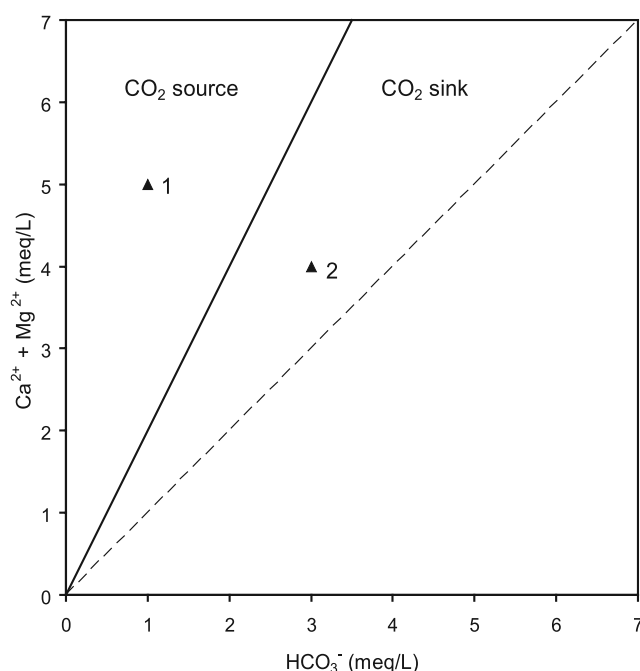


Figure 1. Conceptual model for carbonate mineral dissolution in soils. The dashed line depicts the expected 1:1 ratio of dissolved $\text{Ca}^{2+} + \text{Mg}^{2+}$ to HCO_3^- alkalinity produced by carbonic acid weathering. The solid line represents the elemental stoichiometry in the lime (calcite or dolomite). Hypothetical sample 1 demonstrates a case in which the lime has yielded CO_2 equivalent to 1.5 meq/L, or 60% of its C content, thereby serving as a source of soil CO_2 . Sample 2 has consumed soil CO_2 equivalent to 1 meq/L, or 50% of its C content. Using equation (3), we thus define the “ CO_2 -C sink strength” as -60% for sample 1 (i.e., a CO_2 source) and $+50\%$ for sample 2 (a CO_2 sink).

This reaction becomes important at $\text{pH} < 5$ and greatly enhances the rate of dissolution of carbonate minerals [Plummer *et al.*, 1979]. In this reaction no HCO_3^- alkalinity is produced. Similarly, if the HCO_3^- alkalinity produced by carbonic acid weathering subsequently comes into contact with H^+ , which may occur while associated with exchangeable cations or after downward transport by infiltration, it will be consumed and CO_2 will be produced. The net result of these reactions is for the carbon in lime to become a source of CO_2 in the soil and, ultimately, to contribute to emission of CO_2 to the atmosphere. The lime-derived cations (Ca^{2+} and Mg^{2+}) remain in solution, balanced in charge by the strong acid anions (e.g., NO_3^- in equation (2)).

[7] In this study we seek to better understand the impact of agricultural liming on carbon fluxes and global warming potential. By comparing the chemistry of soil solutions beneath unmanaged vegetation versus limed row crops, and of streams and rivers in agricultural versus forested watersheds, we show how added lime can act as either a source or a sink for atmospheric CO_2 depending on the balance of the reactions described above. We also show that

the chemistry of these waters indicates a predominant role of nitrification as an acidifying process in limed soils.

2. Methods

2.1. Conceptual Model of Carbonate Mineral Dissolution

[8] Figure 1 presents a conceptual model for partitioning carbonate mineral dissolution into C source or sink terms. The model applies to weathering of indigenous carbonate minerals as well as for carbonate minerals used in liming. The dashed line depicts the 1:1 ratio of $\text{Ca}^{2+} + \text{Mg}^{2+}$ to HCO_3^- alkalinity that is expected if dissolution occurs by reaction with carbonic acid. Ratios exceeding unity are produced as the HCO_3^- alkalinity is consumed by acidity. The solid line represents the elemental stoichiometry in the carbonate minerals (calcite or dolomite). Solutions plotting in “ CO_2 sink” area to the right of that line represent dissolution of carbonate minerals plus sequestration of soil CO_2 , while solutions plotting to the left in the “ CO_2 source” area represent dissolution of carbonate minerals and conversion of at least some of the carbonate-C to CO_2 . Most lakes and rivers in watersheds containing carbonate minerals show concentrations of Ca^{2+} , Mg^{2+} and HCO_3^- alkalinity that plot close to the 1:1 line in Figure 1, unless they are also strongly affected by dissolution of evaporite minerals [Wright, 1984; Stallard and Edmond, 1987].

[9] In the absence of carbonate minerals, silicate mineral weathering may be the dominant source of Ca^{2+} , Mg^{2+} and HCO_3^- alkalinity. However, in soils of southern Michigan, silicate weathering generally yields concentrations of Ca^{2+} and Mg^{2+} of no more than 0.2 and 0.14 meq/L, respectively [Jin, 2007], which is a small contribution compared to the weathering of carbonate minerals where they exist. Therefore the model as used in this study does not attempt to correct for solute contributions from silicate weathering, and it is only used in cases where carbonate mineral weathering is the predominant source of these solutes, as indicated by a sum of Ca^{2+} and Mg^{2+} above 2 meq/L (see section 3).

[10] The CO_2 -C sink strength associated with the dissolution of carbonate minerals can thus be estimated from the departure of samples from the source-sink division line, and is expressed as a percentage of the C contained in the carbonate mineral material,

$$\text{CO}_2\text{-C sink strength}(\%) = \frac{[\text{HCO}_3^- - 0.5(\text{Ca}^{2+} + \text{Mg}^{2+})]}{0.5(\text{Ca}^{2+} + \text{Mg}^{2+})} * 100, \quad (3)$$

where concentrations are in meq/L and HCO_3^- represents HCO_3^- alkalinity. This calculation yields positive values when the carbonate minerals are a net CO_2 sink (sequestering CO_2) and negative values when they are a net CO_2 source, as shown in the hypothetical examples in Figure 1.

2.2. Study Sites

[11] We collected hydrochemical samples from soils and streams draining watersheds of different land use and cover, mostly within southwestern Michigan, near the W.K. Kellogg Biological Station (KBS) of Michigan State University. Soils at the KBS site are well-drained sandy loams of

moderate fertility developed on glacial till and outwash. Mean annual temperature is 9.7°C. Annual precipitation is 930 mm, with monthly precipitation exceeding evapotranspiration from October through April; annual recharge is 280 mm. The dominant soil series are alfisols, which are typical of soils developing on uplands under forest vegetation, and include the Kalamazoo (fine-loamy, mixed, mesic Typic Hapludalfs) and Oshtemo (coarse-loamy, mixed, mesic Typic Hapludalfs) series. Clay content ranges from 13 to 30% and dominant silicate minerals include plagioclase, K-feldspar, quartz and amphibole. Carbonate minerals (dolomite and calcite) occur in the glacial drift but are leached out of the upper soil profile, as is typical of glacial soils in this region [Drees *et al.*, 2001]. Calcite and dolomite occur in roughly equal abundance by mass at depths of ~1.5–3 m (L. Jin, unpublished data, 2005), but analysis of a large set of soil cores showed that indigenous carbonate minerals are virtually absent from the upper meter of soils across the site [Kurzman, 2006]. Cation exchange capacity in the upper meter of these soils ranges from 4 to 15 cmol(+) kg⁻¹ and organic carbon content of the surface plow layer in the farmed soils is around 1%. Permeability is moderate to high, generally increasing with depth.

2.3. Soil Solution Collection and Chemical Analysis

[12] Soil solution samples were collected either with tension or gravity lysimeters. In either case such samples are subject to partial losses of dissolved CO₂ as they are removed from the soil and stored. Such losses do not directly affect our measurements of HCO₃⁻ alkalinity, however, unless carbonate minerals precipitate in the samples as a result of the loss of CO₂. Carbonate precipitation was not observed in lysimeter samples, but even if some had occurred, it would have a minor effect on the estimates of CO₂-C sink strength because formation of CaCO₃ would remove equal charge equivalents of Ca²⁺ and HCO₃⁻ ions from solution.

[13] Soil solutions in the unsaturated zone were sampled across the experimental treatments of the KBS Long-Term Ecological Research site (LTER; <http://lter.kbs.msu.edu>). These treatments include intensive row-crop systems (corn/soybean/ wheat rotations or continuous alfalfa) that receive conventional inputs of fertilizer, lime, and potash, as well as nearby unmanaged deciduous forests of early and late successional ages that provide a reference against which the effects of agriculture can be compared. Crushed dolomitic lime (molar ratio of Mg:Ca = 0.92) was added to each cropping system treatment when prescribed by soil tests and at quantities recommended by standard lime-requirement protocols. Over the period 1997–2003, dolomitic lime was added in 1997 and 1999 at 1.1–2.2 Mg ha⁻¹ to the alfalfa and corn/soybean/ wheat rotations. Soil solutions were collected biweekly over 4 years (1999–2003) during the frost-free part of the year (March–December) when there was enough water to yield a sample.

[14] Soil solutions from 1 to 1.2 m depth in the LTER experimental plots were collected under tension using samplers constructed of stainless steel, porous Teflon, and silica flour (Prenart[®]), which can sample matric water held in the soil below field capacity [Lajtha *et al.*, 1999]. These

solutions were collected from above the depth of indigenous carbonate minerals. The samplers were installed in 1995 in 10 of the LTER treatments by coring at an angle beneath an undisturbed soil profile. Each collector draws from three separate samplers spaced a few meters apart. Tension (0.5 atm) was applied to the samplers and the resulting solution was collected after 24 hours. Samples were filtered with glass fiber filters (pore size 0.45 μm) and immediately refrigerated. We analyzed a broader suite of hydrochemical variables than is reported here, including conductance, pH, and concentrations of total alkalinity, major cations and anions, dissolved organic carbon, and silica [Kurzman, 2006].

[15] Infiltrating waters (saturated flow) in the upper soil profile were collected from beneath row crops in the Living Field Lab of KBS, a set of experimental plots located just north of the LTER agricultural plots [Sánchez *et al.*, 2004]. The plots were established in 1992 and farmed in a corn/soybean/wheat rotation, with replicated treatments that received different amounts of fertilizers, composted dairy manure, and herbicides. For the present purposes, these treatments are lumped together. Zero-tension samplers to collect downward gravity flow of infiltrating waters were installed in 1992 and consisted of vertically oriented PVC pipes (60 cm long by 30 cm diameter) buried so that the tops are 25–30 cm below the surface, allowing for cultivation above them. The pipes contained intact soil cored from the site of installation. Water exiting at the base of the pipe is directed into a buried reservoir that periodically was pumped out via an access tube. These lysimeters collect water exiting the root zone but before reaching the depth at which indigenous soil carbonates occur, which was determined by coring to be between 0.8 and >2 m. Samples for the data in this paper were collected in 2003 and include two dates prior and two dates after an application of lime as marl (~97% CaCO₃), added at 3 Mg dry wt./ha on 2 June. Prior to that liming, the plots had not been limed since 1998, although annual compost additions to half of the plots may contribute cations and alkalinity because of the alkaline nature of organic inputs [Tang and Rengel, 2003] as well as small lime additions to feed and compost.

[16] Gravity drainage from the upper part of the zone of indigenous soil carbonates was collected from four 2-m-deep soil monoliths equipped with drainage lysimeters that drained continuously into a receiving vessel. These monoliths were installed in 1989 by excavating around a 1.2 × 2.2 m pedon and enclosing it within a stainless steel chamber that was subsequently replaced. Since installation the monoliths had been cultivated annually (rotations of corn/soybean/wheat) but without liming or fertilization. Soil cores taken adjacent to these monoliths established that the depth of the carbonate-leached zone is ~1.3–1.8 m here, and thus the water collected at the bottom has passed through up to ~0.2–0.7 m of carbonate-containing soil.

2.4. Sampling Tile Field Drainage

[17] Tile field drainage was sampled at diverse locations from pipes that conveyed the water from adjacent tile drainage systems directly into streams. Tile drainage is not found on the KBS experimental site and therefore

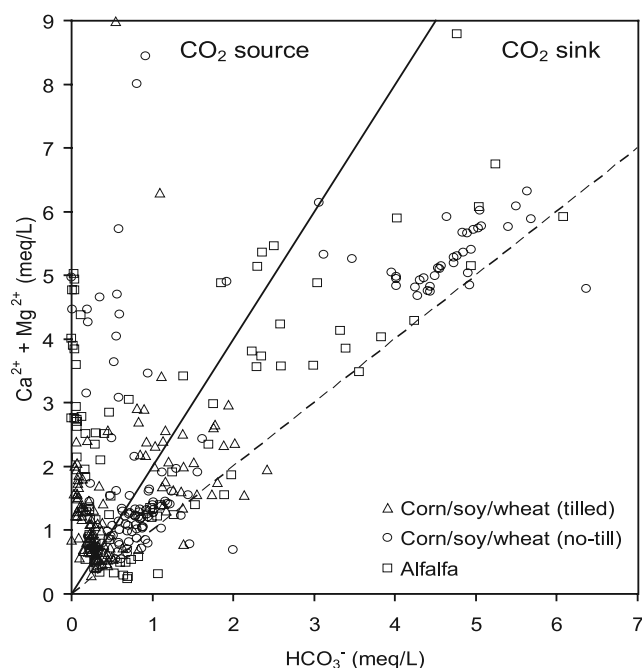


Figure 2. Evidence for carbonate mineral dissolution in soil solutions collected by tension samplers from 1 m depth in three agricultural treatments of the Long-Term Ecological Research Site at Kellogg Biological Station. All of these treatments were limed and fertilized.

samples were obtained from corn-soybean row-crop systems near Midland, Michigan, as well as from central Illinois between Peoria and the Indiana border, and north-eastern and central Iowa. Information on the liming practices of these sites was not available.

2.5. Sampling Streams and Rivers

[18] Data on the chemical composition of streams and rivers represent a combination of synoptic surveys and monitoring, mostly within the Kalamazoo River watershed, where the LTER site is located. Land cover was evaluated in a GIS using the USGS 1992 National Land Cover Data set. Most of the 85 distinct agricultural stream sites (defined as those with >70% agriculture in the watershed upstream of the sampling point) were sampled once in July 2004 and are located in the western part of the Kalamazoo River watershed. Forested streams (>70% forested watersheds) include synoptic surveys from throughout the watershed as well as certain sites that were sampled multiple times; our 212 measurements represent 28 distinct sites. An additional set of streams with mixed forest and agriculture in their watersheds included 319 measurements from 61 distinct sites. The 123 Kalamazoo River main stem samples were collected at points above and below the larger reservoirs over multiple dates. Most agricultural lands in the watersheds we sampled are farmed for corn and soybeans.

2.6. Laboratory Analyses

[19] All water samples were analyzed with the same methods. In situ pH was measured in streams and rivers

and in water residing in gravity lysimeters; in both cases electrodes were calibrated using buffers of pH 4 and 7. Water samples for analysis of solutes were filtered on the day of collection through 0.45- μ m membrane filters and refrigerated. Subsamples for dissolved Ca^{2+} and Mg^{2+} were preserved with 0.5% nitric acid. Subsamples for analysis of total alkalinity were either filtered (soil waters) or unfiltered (stream waters) and refrigerated until analysis. Tests confirmed the stability of these samples in storage, and that filtration made no difference for the alkalinity measurements in the stream samples.

[20] Total alkalinity was measured by Gran titration on unfiltered samples [Cantrell *et al.*, 1990]. Given the ion concentrations and pH range of these solutions, total alkalinity is almost entirely carbonate alkalinity in the form of HCO_3^- , so we consider total alkalinity as a measure of HCO_3^- . While gently stirring the sample, titrant (0.3 N HCl) was added to bring the pH below 4.0, then 6–8 acid additions were made to produce a titration curve in the range of pH 3.3–4.0. Total alkalinity was calculated by extrapolation of the Gran plot to the endpoint using linear regression. The normality of the titrant stock solution of HCl was verified using Na_2CO_3 . Dissolved Ca^{2+} and Mg^{2+} were analyzed by flame atomic absorption spectrophotometry (AAS) after addition of an acidic solution of lanthanum chloride to suppress interferences. Standards bracketing sample concentrations were prepared from certified stock solutions. Other analyses that were conducted on most samples but are peripheral to this paper included Na^+ and K^+ (flame AAS), Cl^- , NO_3^- , and SO_4^{2-} (ion chromatography), and silica (molybdenum blue colorimetry).

3. Results

3.1. Soil Solutions in the Unsaturated Zone

[21] The data from tension soil-solution samplers in the LTER treatments indicate the chemistry of soil solutions in the unsaturated zone beneath row crops receiving lime applications (Figure 2). Nearby deciduous forests and old fields (fallow for 15 years) serve as a reference for concentrations expected in these soils in the absence of agriculture and liming (Figure 3). These samples were collected from above the depth of indigenous soil carbonates, and because of the collection method they represent variable proportions of saturated flow and matric water [Lajtha *et al.*, 1999].

[22] The major solute chemistry of these samples was variable but on average Ca^{2+} and Mg^{2+} were the dominant cations in all cases, and HCO_3^- was the dominant anion, followed by NO_3^- in the agricultural treatments. The molar ratio of Mg^{2+} : Ca^{2+} averaged 0.27 in the agricultural treatments and 0.46 in the unmanaged forest and old-field treatments. Concentrations of NO_3^- (mean, 1.24 meq/L across the 3 treatments) tended to exceed those of SO_4^{2-} (mean, 0.16 meq/L). Details are given by Kurzman [2006].

[23] The forests and old fields usually showed $\text{Ca}^{2+} + \text{Mg}^{2+}$ of ~ 2 meq/L or less. In contrast, both Ca^{2+} and Mg^{2+} often were elevated in the limed treatments compared with the forest sites. Referring to the conceptual model in Figure 1 and considering only samples in Figure 2 with clear evidence of carbonate mineral influence (i.e., $\text{Ca}^{2+} +$

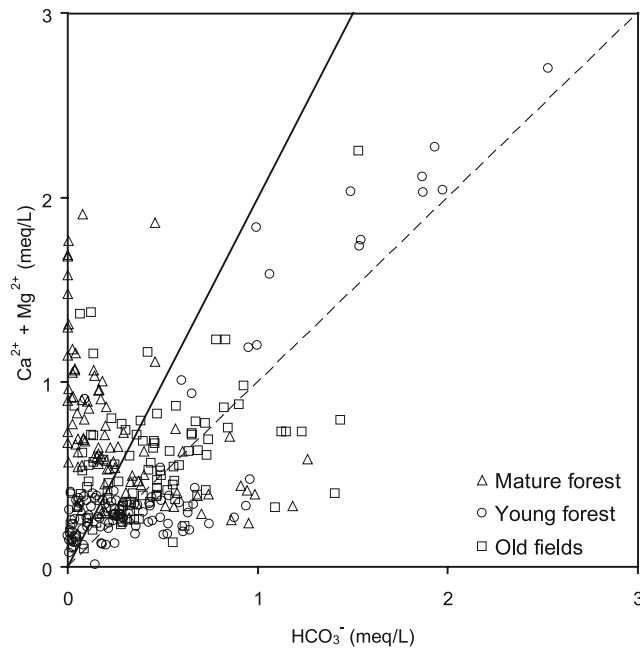


Figure 3. Evidence for carbonate mineral dissolution in soil solutions collected by tension samplers from 1-m depth in three unmanaged vegetation treatments of the Long-Term Ecological Research Site at Kellogg Biological Station. These samples show little or no carbonate mineral influence, with $\text{Ca}^{2+} + \text{Mg}^{2+}$ usually below 2 meq/L. Note that the scale is different than in Figures 1 and 2.

$\text{Mg}^{2+} > 2$ meq/L), these soil solutions span the entire range from close to the carbonate weathering line (i.e., indicating that dissolution has acted as a CO_2 sink equivalent to the C content of the lime, as would be expected for carbonic acid weathering) to points lying close to the y axis (indicating nearly complete conversion of lime C to soil CO_2). The CO_2 -C sink strength for these agricultural soil solutions, calculated using equation (3), is highly variable but suggests that, on average, liming is neither a consistent source nor a sink for CO_2 (Figure 4). The no-till treatment tended to show positive CO_2 -C sink strength in contrast to the other two, but included samples spanning the entire range.

3.2. Gravity Drainage From the Unsaturated Zone

[24] The major solute chemistry of the Living Field Lab samples was variable but on average Ca^{2+} and Mg^{2+} were the dominant cations in all cases, and HCO_3^- was the dominant anion. The molar ratio of $\text{Mg}^{2+}:\text{Ca}^{2+}$ averaged 0.29. The in situ pH and dissolved O_2 of water in the underground collection vessels was measured on one sampling date (14 May 2003; preliming); pH averaged 7.0 and all samples were close to atmospheric equilibrium for O_2 .

[25] The ionic composition of infiltrating waters (saturated flow) in the upper soil profile beneath row crops in the Living Field Lab of KBS provides evidence for carbonate mineral dissolution both before and after the experimental lime application (Figure 5). Liming increased concentrations of $\text{Ca}^{2+} + \text{Mg}^{2+}$ most markedly in the first sampling,

which represented infiltrating waters collected over the first 10 weeks after liming. However, the CO_2 -C sink strength before and after liming suggests that the tendency for sequestration of soil CO_2 by carbonate mineral dissolution increased immediately after the liming, but then returned to the preliming patterns by the end of the growing season (Figure 6). The preliming concentrations of $\text{Ca}^{2+} + \text{Mg}^{2+}$ were high compared to the unlimed forests and fields in Figure 3, likely reflecting the presence of some lime in the compost added to half of the plots (S. K. Hamilton, unpublished data, 2004) as well as the historical liming of the entire site.

[26] An indication of the source of acidity that causes lime to move from a sink to a source of soil CO_2 comes from the relationship of CO_2 -C sink strength with NO_3^- concentrations in the Living Field Lab samples (Figure 7). Liming of the Living Field Lab caused no large change in the relationship in Figure 7. Similar relationships are apparent for the soil solutions from the LTER tension lysimeters. Sulfate is also a potential source of acidity, but in most samples NO_3^- exceeded SO_4^{2-} in concentration (meq/L); SO_4^{2-} concentrations across all treatments averaged only 0.3 meq/L on each of the four sampling dates and never exceeded 0.9 meq/L. There is no apparent relationship

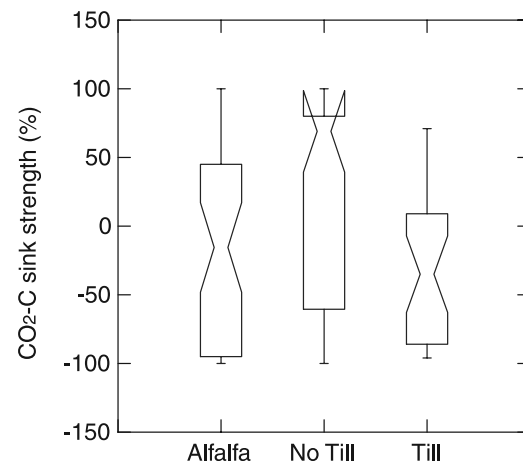


Figure 4. CO_2 -C sink strength associated with carbonate mineral dissolution in the upper meter of soils, calculated from equation (3) and the data in Figure 2, for the three agricultural treatments of the Long-Term Ecological Research Site at Kellogg Biological Station. These treatments, which were limed and fertilized, include the corn/soybean/wheat rotations with (Till) and without tillage (No-Till) as well as the alfalfa. Only samples with $\text{Ca}^{2+} + \text{Mg}^{2+} > 2$ meq/L, indicating influence of carbonate minerals, were included. CO_2 -C sink strength is negative when the carbonate minerals are a net CO_2 source and positive when they are a net CO_2 sink. The boxes show the interquartile ranges, with medians and their approximate 95% confidence intervals indicated by the notches; the medians of two distributions can be considered significantly different when the notches do not overlap [Chambers *et al.*, 1983]. In the data for No Till, the confidence interval around the median extends beyond the 75th percentile.

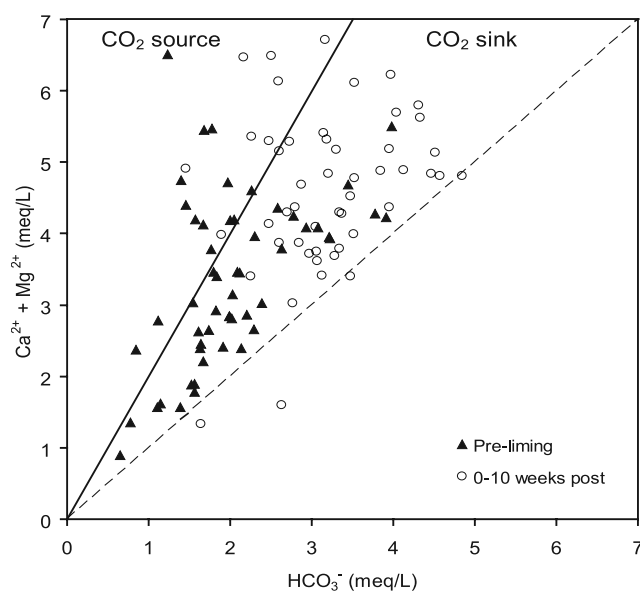


Figure 5. Evidence for carbonate mineral dissolution in gravity drainage from the upper 55–60 cm of the soil profile beneath agricultural treatments of the Living Field Lab at Kellogg Biological Station. Samples were collected prior to (24 March 2003) and during the first 10 weeks after adding lime (as CaCO_3) on 2 June 2003. The 24 March sampling represented infiltration over the preceding winter.

between CO_2 -C sink strength and SO_4^{2-} concentrations in the LFL or LTER soil solutions.

[27] Gravity drainage from the upper part of the zone of indigenous soil carbonates in the unlimed soil monoliths showed a markedly different pattern, with the data plotting much closer to the carbonic acid weathering line (Figure 8). These data show how passage of the infiltrating soil water through only ~ 0.5 m of soil containing indigenous carbonate minerals is sufficient to bring the Ca^{2+} , Mg^{2+} , and HCO_3^- alkalinity concentrations close to equilibrium with calcite and dolomite. Fertilizer was not used on these plots, and compared to the fertilized treatments discussed above, soil solutions showed much lower concentrations of NO_3^- (mean, 0.3 meq/L), closer to those of SO_4^{2-} (mean, 0.2 meq/L).

3.3. Tile Field Drainage

[28] Tile field drainage from three disparate locations across the midwest United States showed patterns of carbonate mineral influence that are consistent with those observed in infiltrating waters at the Living Field Lab (Figure 9). The major solute chemistry of the tile drainage samples was variable but in all cases Ca^{2+} and Mg^{2+} were the dominant cations and HCO_3^- was the dominant anion. The molar ratio of $\text{Mg}^{2+}:\text{Ca}^{2+}$ averaged 0.50. NO_3^- and SO_4^{2-} were similar in concentration (means, 1.40 and 1.15 meq/L, respectively).

3.4. Streams and Rivers

[29] The major solute chemistry of the stream and river samples showed that Ca^{2+} and Mg^{2+} were the dominant

cations, and HCO_3^- was the dominant anion. The molar ratio of $\text{Mg}^{2+}:\text{Ca}^{2+}$ averaged 0.60 in the agricultural streams and 0.45 in the forested ones. Sulfate tended to be more abundant than NO_3^- in stream waters, and averaged 3.5-fold higher in concentration in streams draining agriculture (mean, 1.56 meq/L) than in those draining forest (mean, 0.47 meq/L). The in situ pH averaged 7.89 in the forested streams and 7.81 in the mixed streams (pH was not measured in the agricultural stream survey). The mean in situ pH in the Kalamazoo River was 8.17, tending to be higher below the two largest reservoirs.

[30] The streams and rivers we sampled were strongly influenced by carbonate mineral dissolution (Figure 10). Streams draining largely forested watersheds plot close to the carbonic acid weathering line, as has been observed in many larger rivers throughout the world [Stumm and Morgan, 1996]. In contrast, streams draining largely agricultural watersheds carry higher ratios of $\text{Ca}^{2+} + \text{Mg}^{2+}$ to HCO_3^- alkalinity, and a number of them carry high concentrations of $\text{Ca}^{2+} + \text{Mg}^{2+}$ but lack the corresponding HCO_3^- alkalinity, indicating that carbonate mineral dissolution has acted as a net CO_2 source.

[31] Compared with forested watersheds, estimates of CO_2 -C sink strength in streams draining agricultural watersheds were markedly lower but mostly still indicative of

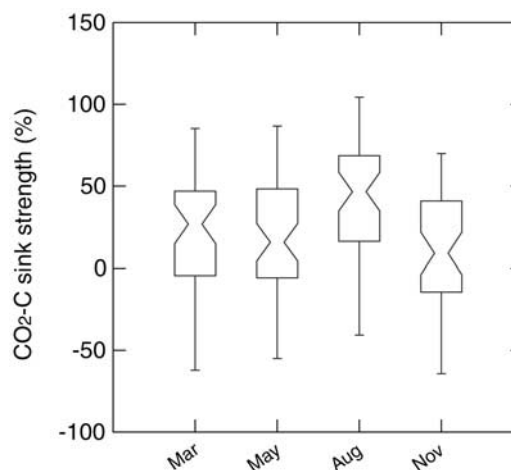


Figure 6. CO_2 -C sink strength associated with carbonate mineral dissolution in samples of gravity drainage from the upper soil profile in the Living Field Lab, calculated from equation (3) and the data in Figure 5 as well as data from two additional sampling dates. These treatments were limed on 2 June and regularly received either inorganic fertilizers or composted manure. The August and November samplings represented 0–10 and 10–22 weeks post-liming, respectively. CO_2 -C sink strength is negative when the carbonate minerals are a net CO_2 source and positive when they are a net CO_2 sink. The boxes show the interquartile ranges, with medians and their approximate 95% confidence intervals indicated by the notches. Only samples with $\text{Ca}^{2+} + \text{Mg}^{2+}$ exceeding 2 meq/L, indicating influence of carbonate minerals, were included.

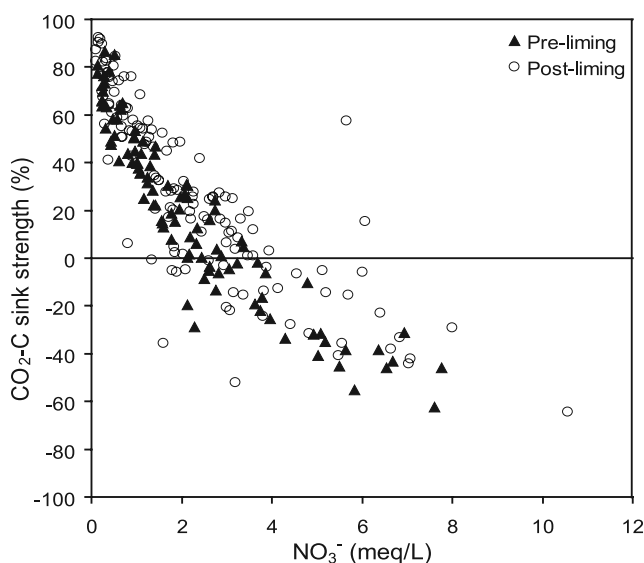


Figure 7. Relationship between NO_3^- concentrations and the $\text{CO}_2\text{-C}$ sink strength associated with carbonate mineral dissolution in infiltrating waters from the upper soil profile in the Living Field Lab, calculated from equation (3). Data include two sampling dates prior to liming with CaCO_3 and three sampling dates within the following year after liming. Only samples with $\text{Ca}^{2+} + \text{Mg}^{2+}$ exceeding 2 meq/L, indicating influence of carbonate minerals, were included. These treatments regularly received either inorganic fertilizers or composted manure.

carbonate dissolution as a CO_2 sink (Figure 11). Streams draining mixtures of forest and agriculture, including the Kalamazoo River, showed intermediate $\text{CO}_2\text{-C}$ sink strength. Streams draining forested watersheds showed $\text{CO}_2\text{-C}$ sink strength resembling that of the gravity drainage from the carbonate-containing soil layer in the monolith lysimeters (Figure 8), although they often had higher concentrations of Ca^{2+} , Mg^{2+} , and HCO_3^- alkalinity.

4. Discussion

4.1. Sources of Ca^{2+} , Mg^{2+} , and HCO_3^- in Soil Solutions

[32] Agricultural liming was the most likely source of elevated Ca^{2+} , Mg^{2+} , and HCO_3^- alkalinity in soil solutions from the upper meter of soils around the KBS LTER site (Figure 2). In the absence of liming (or indirect inputs of lime via compost), soil solutions in the upper meter of soils around the KBS LTER usually have concentrations of $\text{Ca}^{2+} + \text{Mg}^{2+}$ below 1 meq/L, and carbonate mineral dissolution is evidently not the predominant source of these ions (Figure 3). Carbonate minerals are abundant in the underlying glacial drift, however, and at KBS they abruptly increase in abundance between soil depths of 1.5–2 m. Upon reaching the depth of indigenous carbonates, infiltrating soil solutions are rapidly and strongly influenced by carbonate mineral dissolution (e.g., Figure 8). In the relatively permeable, sandy loam soils that are common in

southwestern Michigan, most water infiltrates the soils rather than running off over the surface, and most infiltration would reach the depth of carbonate minerals. Thus the chemistry of groundwater-fed surface waters, such as the forested streams we sampled, reflects the fact that groundwater exists in equilibrium with abundant solid-phase dolomite and calcite in the glacial drift, and that it acquires its Ca^{2+} , Mg^{2+} , and HCO_3^- alkalinity largely by carbonic acid dissolution.

4.2. Liming as a Source or Sink for Atmospheric CO_2

[33] Our results suggest that liming is likely to act as a net sink for atmospheric CO_2 via the generation of dissolved HCO_3^- alkalinity and its transport to groundwater and fluvial systems. Although soil solutions sampled under tension from beneath limed crops often showed considerable enrichment of $\text{Ca}^{2+} + \text{Mg}^{2+}$ relative to HCO_3^- alkalinity, indicating that the lime acted as a net CO_2 source (i.e., a negative $\text{CO}_2\text{-C}$ sink strength: Figures 2 and 4), samples of infiltrating waters from comparable soils tended to show net CO_2 uptake (Figures 5 and 6). Tile drainage was not unlike infiltrating waters from surface soils, with most samples showing lime dissolution as a net CO_2 sink (Figure 9). Water remaining in the soil matrix after saturated flow ceases may be more susceptible to eventual reaction with strong acids, whereas infiltrating waters may tend to bypass sites of reaction, and/or they may tend to pass through soils during cooler times of the year when there is lower microbial activity that generates strong acidity (see below).

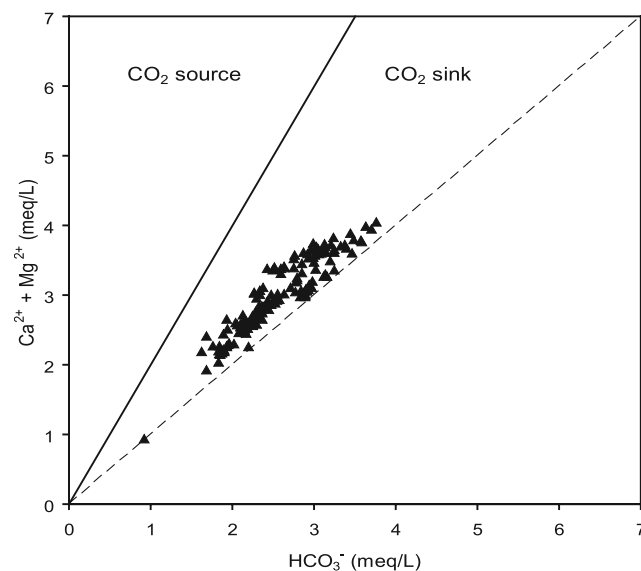


Figure 8. Evidence for carbonate mineral dissolution in infiltrating waters from the upper 200 cm of the soil profile beneath agricultural treatments of the experimental monoliths at Kellogg Biological Station. These corn/soybean/wheat treatments were neither limed nor fertilized. Indigenous carbonate minerals occur in the lower ~ 0.5 m of the profile. The 165 samples show a $\text{CO}_2\text{-C}$ sink strength of $+72 \pm 17\%$ (mean \pm s.d.).

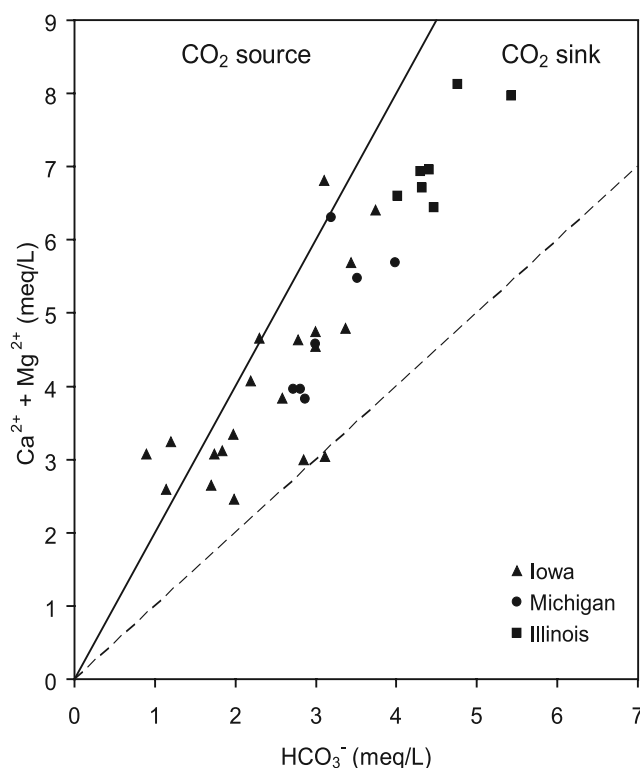


Figure 9. Evidence for carbonate mineral dissolution in tile field drainage from agricultural fields across the corn belt of the midwest United States. The 34 samples show a CO_2 -C sink strength of $+25 \pm 28\%$ (mean \pm s.d.).

[34] The apparent impact of liming on soil solution chemistry extends to tile drainage and to streams draining agricultural landscapes (Figures 10 and 11), in spite of the presence of indigenous carbonate minerals in deeper soils in this region. Shallow subsurface flow paths to streams, perhaps aided by widespread tile drainage, can explain how soil waters supplying streamflow may circumvent contact with carbonate-rich underlying soils that would otherwise bring their chemistry into line with the groundwater-fed forested streams in Figure 10.

[35] It is difficult to derive average values of the CO_2 -C sink strength associated with agricultural liming from the limited types of crops and soils studied here, but overall our results suggest that liming produces a net CO_2 -C sink strength of approximately +25 to +50%, and therefore over the timescale from its initial dissolution to transport and residence of dissolution products in groundwater, lime dissolution acts as a sink rather than a source of CO_2 . Thus ~ 12 –25% of applied lime ultimately dissolves by reaction with strong acids. This range concurs with two estimates derived from analysis of river water chemistry: 12–26% for agricultural watersheds in France [Semhi et al., 2000] and 14% for two agricultural watersheds in the Ohio River watershed of the United States [Oh and Raymond, 2006]. Thus our study together with the aforementioned ones refute the currently used IPCC assumption that the CO_2 -C sink strength from lime is -100% (i.e., that all of the

lime C becomes CO_2) [Intergovernmental Panel on Climate Change, 1997].

[36] West and McBride [2005] concluded that liming results in a net CO_2 source equivalent to 49% of the C in the lime (i.e., CO_2 -C sink strength of -49%). West and McBride arrived at this estimate by building a budget for lime dissolution products that extended from lime applications through leaching from soils, riverine transport to the marine environment, and marine CaCO_3 precipitation and dissolution, not accounting for time lags in the transport of solutes across landscapes. Although West and McBride noted that they lacked detailed information on the relative importance of the two alternative pathways for lime dissolution in soils, they effectively assumed that the CO_2 -C sink strength at the point of leaching from soils was +24%, on the basis of unpublished data for the Mississippi River. The present study suggests that this figure may be too low, since the CO_2 -C sink strength ascertained from our sampling of stream and river waters ranges from approximately +25 to +50%. If we use our CO_2 -C sink strength estimate of +50% in place of the +24% in West and McBride's budget and leave all other assumptions unchanged, the overall net CO_2 emissions from lime change only modestly, from 0.059 to 0.046 Mg C per Mg CaCO_3 .

[37] West and McBride [2005] noted that there were major uncertainties in some of their assumptions, however, including the proportion of dissolved HCO_3^- alkalinity produced by lime dissolution that may be retained in soils in

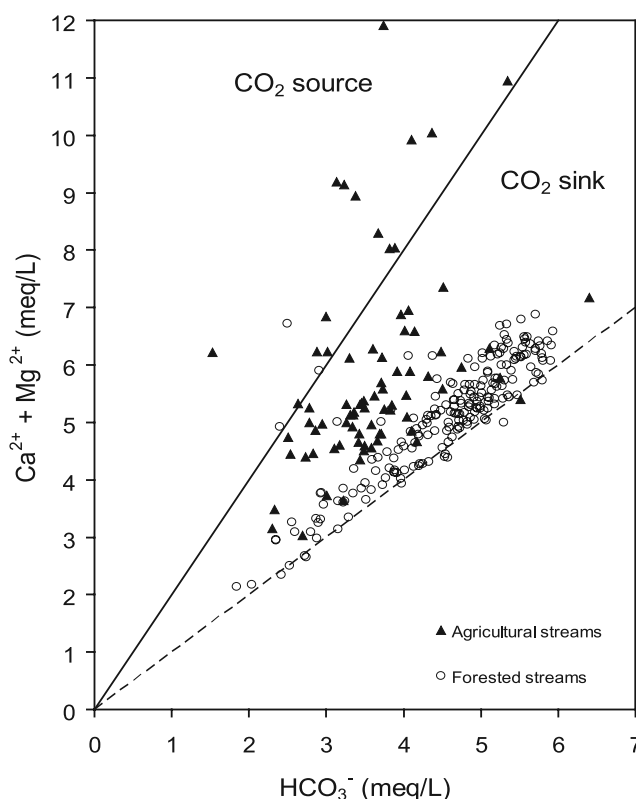


Figure 10. Evidence for carbonate mineral dissolution in streams draining primarily agricultural or forested watersheds in southwestern Michigan.

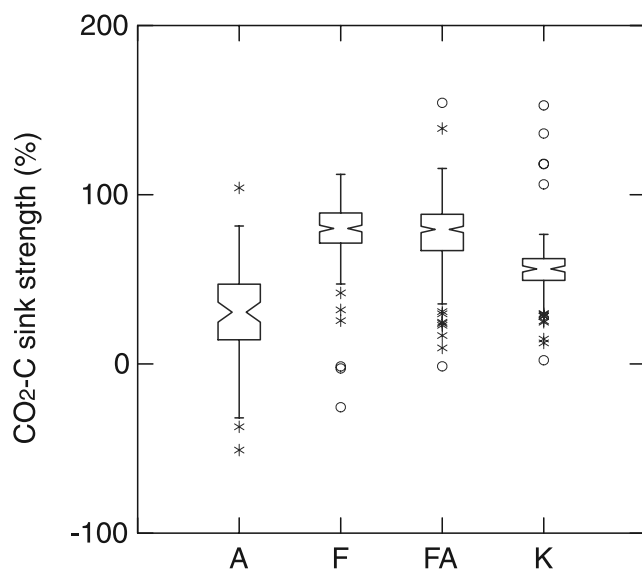


Figure 11. CO₂-C sink strength associated with carbonate mineral dissolution in streams draining primarily agricultural (A), forested (F), or mixed (FA) land cover within the Kalamazoo River watershed of southwestern Michigan, as well as data for the larger Kalamazoo River (K). CO₂-C sink strength is negative when the carbonate minerals are a net CO₂ source and positive when they are a net CO₂ sink. The boxes show the interquartile ranges, with medians and their approximate 95% confidence intervals indicated by the notches (asterisks and circles indicate more outlying data points). All of these samples had Ca²⁺ + Mg²⁺ exceeding 2 meq/L, indicating influence of carbonate minerals. For Michigan data, fluxes were calculated from equation (3) and the data in Figure 2 as well as additional data on streams draining mixed forest/agricultural watersheds (N = 319 samples) and the Kalamazoo River (~60% of its watershed is agricultural; N = 123 samples).

association with sorbed Ca²⁺ and Mg²⁺, and thus subject to eventual reaction with strong acids. An important assumption of that study, based on short-term experiments in the literature, is that half of the dissolved HCO₃⁻ alkalinity produced from lime ultimately is consumed by strong acidity in the soils rather than transported out via infiltrating water [see also Oh and Raymond, 2006]. Verification of this assumption requires further study over time periods that encompass at least one complete interval between lime applications.

[38] Mass balance experiments to account for the fate of carbon in lime applied to agricultural soils with a history of liming would help resolve this uncertainty, and could be designed to show the impacts of alternative management options. The timescales and ultimate fate of alkalinity transport to groundwater and river systems under diverse geologic and climatic settings need greater consideration. Further research also is required to demonstrate whether our findings apply to other kinds of managed ecosystems that receive lime amendments. Despite these uncertainties, the work reported here suggests that current estimates of the

GWP impact due to liming [West and Marland, 2002] require revision.

4.3. Acidifying Reactions That Control the CO₂-C Sink Strength

[39] Strong acid sources in soils include various reactions mediated by microbes, such as ammonium oxidation (nitrification) and iron sulfide oxidation [Schnoor and Stumm, 1985]. The inverse relationship of CO₂-C sink strength with NO₃⁻ concentrations in infiltrating soil solutions (e.g., Figure 7), as well as the lack of a relationship with the generally lower SO₄²⁻ concentrations, suggests that nitrification and subsequent leaching of NO₃⁻ may be the predominant acidifying process that controls the source-sink relationship in the agricultural soils we studied. Nitrification produces 2 moles of H⁺ for every mole of NH₄⁺ oxidized, and is known to be a major source of soil acidity in agricultural ecosystems [Fisher et al., 2003]. High concentrations of NO₃⁻ are typical of agricultural drainage [Böhlke, 2002] and are associated with high rates of nitrogen fertilization or cultivation of nitrogen fixing crops [Tang and Rengel, 2003], both of which stimulate nitrification by increasing soil NH₄⁺ availability. Studies of soils [Helyar and Porter, 1989], groundwater [Böhlke and Denver, 1995], and rivers [Semhi et al., 2000; Oh and Raymond, 2006] in agricultural regions support our contention that nitrification may be a primary source of strong acidity that affects the CO₂-C sink strength associated with carbonate mineral dissolution, although Oh and Raymond [2006] also considered sulfuric acid loading to be important. The high concentrations of Ca²⁺ + Mg²⁺ relative to HCO₃⁻ alkalinity that we observed in some samples of tile field drainage and agricultural streams (Figures 9 and 10) also have been observed in other studies of agricultural drainage waters, and have been attributed to reaction of carbonate minerals with nitric acid [Böhlke, 2002].

[40] The maximum potential of nitrification to consume alkalinity derived from lime is readily calculated: suppose that either anhydrous ammonia or urea, the two most common N fertilizers in use today, is applied to a maize cropping system at 100 kg N ha⁻¹ yr⁻¹. Eventual nitrification of the resultant NH₄⁺ [Robertson, 1997] would yield up to 14 kmol of H⁺. This acidity is capable of consuming alkalinity equivalent to 1.3 Mg ha⁻¹ of dolomite, which is close to typical liming rates for intensive row crop systems in the midwest United States.

[41] Other potential acidifying processes include atmospheric deposition, sulfur-based fertilizers, and crop harvest. Inputs of strong acids from atmospheric deposition cannot explain the high rates of lime consumption in agricultural soils, nor can atmospheric deposition explain differences across closely situated experimental treatments. Assume, for example, a mean annual precipitation rate of 930 mm and a volume-weighted mean pH of 4.45 for precipitation at KBS (National Atmospheric Deposition Program (NRSP-3)/National Trends Network means of annual volume-weighted means for 1979–96 from the KBS station (MI26), downloaded 2 December 1997, <http://nadp.sws.uiuc.edu/>). Four moles of H⁺ are required to dissolve one mole of CaMg(CO₃)₂, which means that acid deposition is capable

of reacting with only $21 \text{ kg ha}^{-1} \text{ yr}^{-1}$ of dolomite, less than 5% of typical application rates. The role of sulfur-based fertilizers is minor at our LTER study site but could be more important elsewhere. Biological uptake of cations by the crops and export via harvest is likely a significant but not major part of the acid-base budgets in fertilized agricultural soils with high nitrification rates [Fisher *et al.*, 2003; Oh and Raymond, 2006].

4.4. Applicability of This Approach for Other Regions

[42] Riverine export of inorganic carbon may be enhanced at continental scales by widespread liming. Raymond and Cole [2003] reported that the export of dissolved inorganic carbon as carbonate alkalinity by the Mississippi River has increased considerably in the past 50 years, and that agricultural subwatersheds have some of the highest areal rates of export. Their analysis suggested that the export of alkalinity via the Mississippi River may have been twofold to threefold lower prior to the advent of intensive agriculture. The concentration of alkalinity had remained approximately constant over a period of increasing discharge, which is what would be expected if an excess of solid-phase carbonate minerals was being maintained by soil liming in the most agricultural subwatersheds. Further work by Oh and Raymond [2006] analyzed stream chemistry together with data on crops and lime use in agricultural and forested watersheds within the Ohio River watershed (tributary to the Mississippi River), and concluded that liming has increased alkalinity export by rivers, with known applications of lime explaining up to $\sim 30\%$ of the observed increase in alkalinity export from agricultural watersheds.

[43] In other regions, there may be other significant sources of elevated Ca^{2+} , Mg^{2+} , and HCO_3^- alkalinity in soil solutions besides liming and indigenous carbonate minerals. In particular, Ca-bearing minerals such as calcium sulfates can be abundant in some soils, and also are sometimes used as soil amendments in agriculture [Böhlke, 2002]. Ca^{2+} also may originate from deicing salts in urban areas [Szramek and Walter, 2004], and could potentially be affected by municipal and industrial wastewater discharges. Thus our approach should be applied with caution in other areas, and we cannot be certain that our samples of tile field drainage from other regions are free of these influences. Our approach is likely to be most applicable in humid climates with intensive row-crop agriculture. If other sources of these ions are thought to be significant, they can be accounted for by geochemical models that consider the full suite of solutes in the water [e.g., Gaillardet *et al.*, 1999; Semhi *et al.*, 2000].

4.5. Implications for Mitigating the GWP Impact of Agriculture

[44] Assumptions regarding the fate of carbon in lime are important for the overall greenhouse gas accounting for agriculture, and for particular row-crop systems alternative assumptions can change the overall net radiative forcing between warming and cooling (e.g., Table 1). Our results show that the $\text{CO}_2\text{-C}$ sink strength is somewhere in between the two extreme assumptions of Table 1, but that liming is more likely to sequester CO_2 than to act as a net source. As

discussed above, even if this carbonate mineral dissolution were ultimately balanced by new carbonate mineral precipitation in marine environments, the long time required for hydrological transport from land surfaces to the oceans effectively sequesters carbon for decades to centuries. Moreover, there is evidence that the oceans are not in steady state with respect to carbonate in part because of increasing atmospheric CO_2 partial pressures [Milliman, 1993; Andersson and Mackenzie, 2004], and that biogenic precipitation of carbonate minerals by marine organisms removes less alkalinity per unit Ca than the converse reaction of dissolution in freshwaters (reviewed by West and McBride [2005]).

[45] A reduction in the rate of acidifying processes and/or an increase in the availability of lime in the soil will shift the net carbon balance associated with liming from a CO_2 source to a CO_2 sink. More efficient use of N fertilizers would reduce the acidifying effect of nitrification, as would the development of crops that utilize NO_3^- rather than NH_4^+ , and such measures would bring other economic and environmental benefits as well. Yet if these and other measures to increase the efficiency of N use prove inadequate or impractical, manipulating liming could represent an additional strategy for mitigation of greenhouse gas emissions by intensive agriculture. Liming at a greater frequency or to a higher soil pH than is often practiced may enhance the role of lime as a sink for CO_2 while remaining within the bounds for desirable agronomic yields. Agricultural soils would thus be maintained under conditions that favor the carbonic acid weathering pathway, effectively employing lime as a vehicle to sequester soil $\text{CO}_2\text{-C}$ in a form that will be transported into groundwater and stream systems. For example, suppose that lime were added at $1 \text{ Mg ha}^{-1} \text{ yr}^{-1}$ ($12 \text{ g C m}^{-2} \text{ yr}^{-1}$) and dissolved with a $\text{CO}_2\text{-C}$ sink strength of 80%. The resultant sequestration of soil CO_2 as HCO_3^- alkalinity transported to the underlying groundwater is equivalent to $22 \text{ g C m}^{-2} \text{ yr}^{-1}$. While lower than rates of C sequestered as soil organic matter by conversion to no-till cropping systems ($\sim 30\text{--}60 \text{ g C m}^{-2} \text{ yr}^{-1}$) [Davidson and Ackerman, 1993; Franzluebbers and Steiner, 2002; West and Post, 2002], soil organic matter sequestration will saturate within a couple of decades whereas the export of dissolved inorganic C can potentially be sustained indefinitely. The CO_2 cost of mining and distributing lime [West and Marland, 2002] would likely make this practice most useful where agriculture exists in proximity to limestone sources.

[46] The possibility of manipulating lime inputs to mitigate greenhouse-gas emissions from agricultural soils deserves additional consideration as we evaluate the contribution of intensive agriculture to global climate change. Programs to stimulate changes in agronomic management via incentives such as carbon credits, which are presently focused solely on management to enhance soil carbon reserves, need to incorporate liming as another one of the agricultural activities that influences net GWP impact. The results presented here suggest that liming sequesters carbon, in contrast to the heretofore prevailing view that liming is a source of CO_2 emissions.

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