

Increasing shallow groundwater CO₂ and limestone weathering, Konza Prairie, USA

G.L. Macpherson^{a,*}, J.A. Roberts^a, J.M. Blair^b, M.A. Townsend^c,
D.A. Fowle^a, K.R. Beisner^d

^a *Department of Geology, University of Kansas, 1475 Jayhawk Blvd., 120 Lindley Hall, Lawrence, KS 66045, USA*

^b *Kansas State University, Manhattan, KS, USA*

^c *Kansas Geological Survey, Lawrence, KS, USA*

^d *University of Utah, Salt Lake City, UT, USA*

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Abstract

In a mid-continental North American grassland, solute concentrations in shallow, limestone-hosted groundwater and adjacent surface water cycle annually and have increased steadily over the 15-year study period, 1991–2005, inclusive. Modeled groundwater CO₂, verified by measurements of recent samples, increased from 10^{-2.05} atm to 10^{-1.94} atm, about a 20% increase, from 1991 to 2005. The measured groundwater alkalinity and alkaline-earth element concentrations also increased over that time period. We propose that carbonate minerals dissolve in response to lowered pH that occurs during an annual carbonate-mineral saturation cycle. The cycle starts with low saturation during late summer and autumn when dissolved CO₂ is high. As dissolved CO₂ decreases in the spring and early summer, carbonates become oversaturated, but oversaturation does not exceed the threshold for precipitation. We propose that groundwater is a CO₂ sink through weathering of limestone: soil-generated CO₂ is transformed to alkalinity through dissolution of calcite or dolomite. The annual cycle and long-term increase in shallow groundwater CO₂ is similar to, but greater than, atmospheric CO₂.

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1. INTRODUCTION

The impact of contemporary atmospheric composition change and consequent climate warming on polar regions on Earth is well documented (e.g., Cook et al., 2005; Dowdeswell, 2006), but hydrogeologic response to climate change in the continental interior is less visible, slower, and more difficult to document. Recent investigations have found that elevated atmospheric CO₂ accelerates the hydrologic cycle, increasing continental river discharge, because plant water-use efficiency increases with increasing atmospheric CO₂ (Gedney et al., 2006). Hydrochemical changes may also be linked to changes in atmospheric CO₂: Raymond and Cole (2003) attribute a nearly 60% increase in

alkalinity flux in the Mississippi River over the past 47 years to the increased atmospheric CO₂, increased water flux, and changing land use. Jones et al. (2003) contradicted that finding by proposing a 22-year, 40% decline in river-dissolved CO₂ with insignificant change in alkalinity in an independent study of several North American rivers, including the Mississippi River. Although a relatively new line of inquiry, the response of continental interiors to recent climate change is important because it implies whole-earth response to change in atmospheric chemistry and because of the potential impact on water resources.

The hydrogeochemistry of most aquifers is thought to be nearly unchanging in the short term without addition of reactive contaminants or saltwater intrusion. Karst aquifers, however, have well-developed secondary porosity and are well known for fast hydrologic response to changing earth-surface conditions (e.g., White, 1988; Katz et al., 1997; Liu et al., 2007). In addition, seasonal fluctuations in

* Corresponding author. Fax: +1 785 864 5276.
E-mail address: gmac@ku.edu (G.L. Macpherson).

water chemistry have been tied to recharge dynamics (e.g., Macpherson and Sophocleous, 2004; Wilcox et al., 2005; Pfeiffer et al., 2006), suggesting a tight link between shallow, water-table aquifers and the land surface. Further, large-scale atmospheric CO₂-enrichment experiments have affected soil-water chemistry over time periods shorter than five years. In particular, during a field experiment to study ecological response to CO₂, an increase of about 50% over the present atmospheric CO₂ resulted in significant increases in soil CO₂ as well as deep-soil-water alkalinity and cations (Andrews and Schlesinger, 2001).

Hydrogeologic research at the Konza Tallgrass Prairie Long-Term Ecological Research Site (Konza Prairie) in northeastern Kansas (Fig. 1) investigates the processes of chemical weathering in thin limestone aquifers, using approximately monthly data collection from wells and stream sites, high-frequency water-level recording in two wells, and geochemical speciation modeling. The study site is a 1.2-km² research watershed that is drained by an ephemeral 4th-order stream; the watershed lies in the interior of the 35-km² Konza Prairie. The near-surface limestone aquifers at the site have a high probability of responding relatively rapidly to land surface dynamics because of secondary porosity development (solution-enlarged joints), because the nearly flat-lying beds are breached by the stream draining the watershed, and because carbonate minerals react more rapidly than silicate minerals that are typical of other aquifers. Further, the location of the site within a larger watershed restricted to use for ecological research avoids the complexities of changing land use and water management that is problematic for large-river chemistry in developed countries (e.g., Oh and Raymond, 2006), and also avoids the necessity of subtracting the direct or degraded signal from human-applied chemicals, such as road salt (e.g., Szramek and Walter, 2004) or agrichemicals (e.g., McMahon et al., 2004).

Previous work at the Konza Prairie has found dynamic stream-aquifer interactions and karst-like behavior in the 1- to 2-m thick limestone aquifers and alluvial aquifers (Macpherson, 1996; Macpherson and Sophocleous, 2004), seasonal variations in groundwater chemistry, and contributions of soil carbonate weathering as well as bedrock carbonate weathering to groundwater solutes (Wood and Macpherson, 2005). The seasonal changes in water chemistry include changing Ca:Mg ratios, alkalinity content, and concentrations of major and minor dissolved species (Macpherson, 1996; Macpherson et al., 2006), as well as a changing calcite saturation index (Macpherson, 2004). Fifteen years of observations have revealed that the seasonal cycles are superimposed on a longer-term trend of slowly increasing dissolved solids, documented here. Because alkaline-earth cations, alkalinity, and groundwater CO₂ increased over the study period, we propose the dissolved-solids increase is evidence of increasing chemical weathering of carbonate minerals related to increasing groundwater CO₂.

This study quantifies the increasing alkalinity and dissolved CO₂ that has occurred in a thin, shallow limestone aquifer in a mid-continental temperate-climate setting. The results of this study suggest that shallow groundwater,

unaffected by urbanization or other changes in land use or surface-water engineering, is undergoing an increase in net chemical weathering driven by increasing belowground CO₂.

2. STUDY AREA AND METHODS

2.1. Study area

The Konza Prairie in northeastern Kansas, USA, is a National Science Foundation Long-Term Ecological Research site and Biological Station (39°06.1'N, 96°35.7'W), located within the Flint Hills physiographic province, about 10 km south of Manhattan, Kansas (Fig. 1). It is an unglaciated remnant on the western edge of a mid-continental, mesic, tallgrass prairie. The tallgrass prairie biome once extended from southern Canada to Oklahoma, before the nutrient-rich prairie soils were converted to cropland. Continental-interior grasslands in North America have existed since the Miocene, when tectonic uplift of the present Rocky Mountains created a rain shadow, reducing the supply of moisture coming from the Pacific Ocean to the east side of the uplift. Grassland vegetation, more drought-tolerant than woody vegetation, has been replaced periodically by temperate, subtropical, or boreal forests in response to climate change over the past 30 million years. Current North American grasslands have occupied this region for at least the past 5000–8000 years (Axelrod, 1985), more recently persisting through multi-century periods of colder climate (Little Ice Age, 1450–1850 A.D.), quinquennial to decadal periods of dry climate (Dust Bowl, 1930s; 1950s; 1960s; 1970s; late 1980s—early 1990's; 2000's) (Goodin et al., 2003; U.S.G.S., 2005, 2007), and rapidly rising average annual air temperatures since about 1870 (Turekian, 1996).

Ecological research at the Konza Prairie, since about 1972, has varied grassland burning frequency and grazing animals, and has monitored climate in order understand controls on the persistence of the tallgrass prairie biome. The U.S. Geological Survey (U.S.G.S.) monitored the chemistry and flow of Kings Creek, a 5th-order stream with drainage area entirely within the Konza Prairie, from about 1980 until 1996. Streamflow measurements, only, have been recorded since 1996, through the Hydrologic Benchmark Network program; Kings Creek is site 06879650. In late 1990, intensive monitoring of the inorganic chemistry of groundwater and the south fork of Kings Creek began in the lower part of a 1.2-km² upland watershed (N04d) (Figs. 1 and 2), and some of these data are presented in this study. Kings Creek is a tributary to McDowell Creek, which empties into the Kansas River.

2.2. Geology, physiography, hydrogeology

The bedrock underlying the Konza Prairie is Early Permian-aged nearly horizontal limestone-shale couplets. Limestones form flat uplands and hillside benches, and shales form slopes with gradients of 10–25%. Topographic relief in the N04d watershed is about 60 m. This dissected-upland architecture present today may have existed

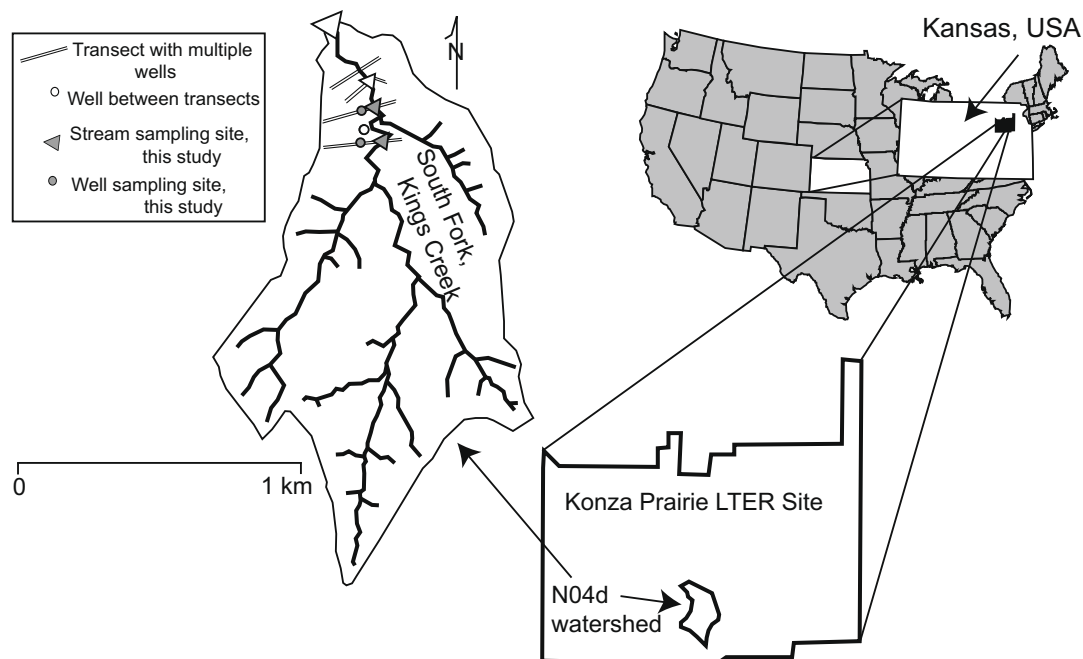


Fig. 1. The Konza Prairie LTER Site is located in northeastern Kansas, U.S.A. The study watershed, N04d, is drained by the south fork of Kings Creek; the Kings Creek watershed above the USGS gauging station is entirely contained within the LTER site. Well and stream-sampling sites for this study are located in the lower one-third of the N04d watershed.

in similar form for the past 700,000 years (Oviatt, 1998). During the Holocene Epoch, four to seven periods of erosion or stream entrenchment alternating with periods of deposition resulted in discontinuous terrace deposits in the stream valleys (Oviatt, 1998). Pleistocene loess mantles hilltops and is reworked into alluvial fill in the highest-order stream valleys.

Konza Prairie soils are mostly carbonate-poor, with moderately-low cation exchange capacities (mostly less than 40 meq/100 g; USDA-NRCS, 2007). The soils are developed on loess, limestone and shale, and are mostly less than 1 m thick, with thickest soils at the bases of slopes and in valleys. The highest hills have patchy areas of Dwight–Irwin Complex; other hilltops are covered by Benfield–Florence Complex. Clime–Sogn Complex soils form on slopes, and Ivan silt loam and/or Tully silty clay loam form in valley bottoms (USDA-NRCS, 2007).

Aquifers in the region are sandwich-type (White, 1969), neo-karst aquifers. The water table elevation for each limestone aquifer is usually within the limestone, so, because soils are thin, the bulk of the unsaturated zone is in bedrock. The Morrill Limestone aquifer, discussed in this paper, occurs at depths of about 6 and 13 m in the two wells used in this study. This limestone is about 1.2-m thick, and is the upper limestone member of the Beattie Formation, Council Grove Group. It is a shallow marine limestone with a sharp base and transitional top (Twiss, 1988). Below the Morrill, the Florena Shale, middle member of the Beattie Formation, is a ~3-m thick, calcareous, deep-water shale, and above the Morrill is the ~4.5-m thick Stearns Shale, a calcareous, terrigenous to marine shale (Twiss, 1988). Although not a major aquifer in the region

(Jewett, 1941), the Morrill Limestone is an important water supply locally (O'Connor, 1949). The Morrill Limestone, like other units in the region, dips ~0.1–0.2°W, with a northeast strike (Smith, 1991). It crops out within the N04d watershed as poorly-expressed topographic benches on hillsides, at an elevation of approximately 364 m above mean sea level (amsl), and as a broad nickpoint where the stream has cut below the elevation of the unit. Regionally, the Morrill Limestone is truncated on the north, east, and west of the Konza Prairie by streams and rivers (Fig. 2). The Konza Prairie, like other land in the region, is used dominantly for grazing, with parts of larger valley bottoms used to grow crops.

There is a relatively rapid communication between water on the surface and groundwater at the study site. Water level and water temperature change within a few hours after precipitation events (Fig. 3; Macpherson, 1996), and groundwater contained tritium at levels similar to meteoric precipitation at a single sampling event in 1991 (Macpherson, 1992). During extended dry periods in the growing season, water level fluctuates on a daily cycle with ~1-cm amplitude. Water level begins to decline within a few hours after sunrise, and begins to rise within a few hours after sunset (Kissing and Macpherson, 2006). The daily fluctuations are similar to daily fluctuations attributed to phreotophyte use of 1-m deep groundwater in central Kansas (Butler et al., 2007). The daily fluctuations at the Konza Prairie also corroborate the large groundwater contribution to evapotranspiration modeled by York et al. (2002) in the Mill Creek watershed, a tributary to the Kansas River the same stream-order as McDowell Creek, and located the next watershed to the east of Kings Creek.

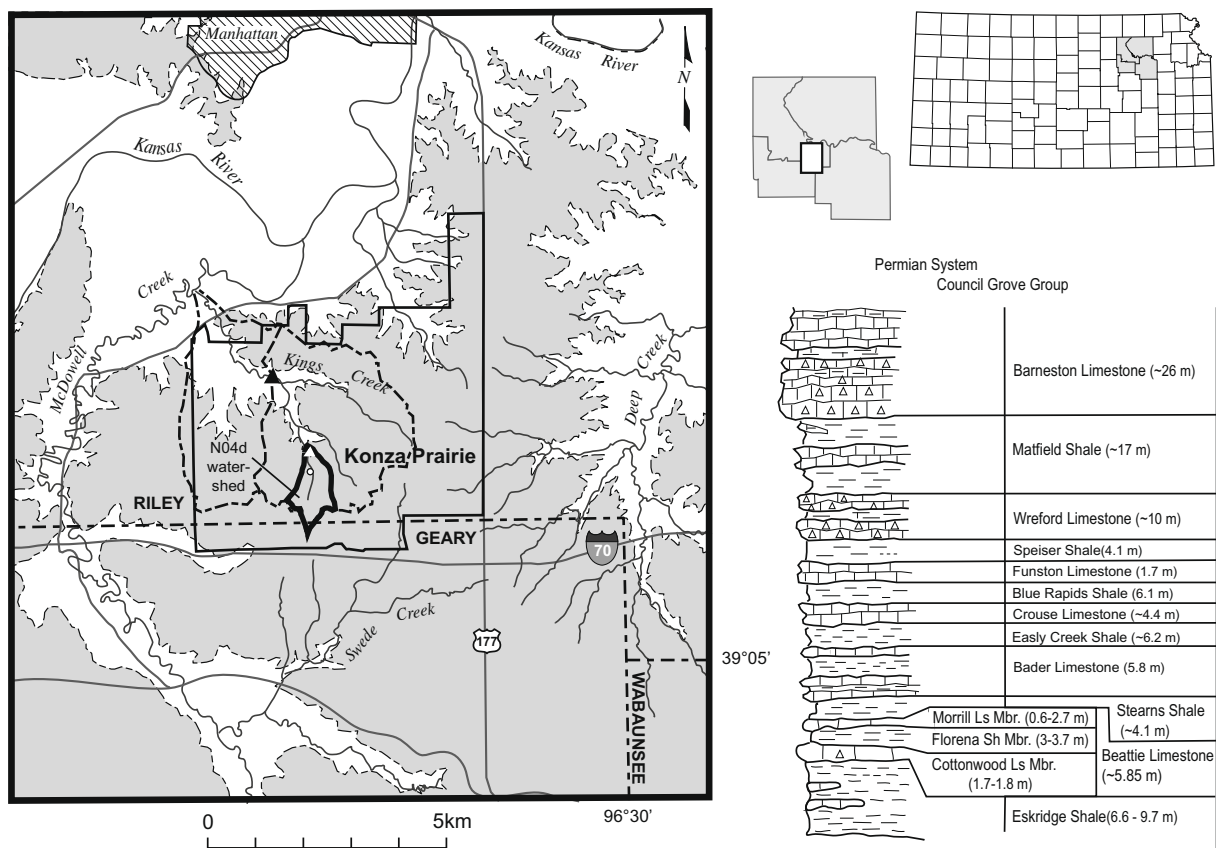


Fig. 2. The Morrill Limestone in outcrop and below ground (shaded regions) shows that the limestone has been removed in major stream valleys east, west and north of the study watershed (overlying geology is not shown). The base of the unit is at an elevation of about 363.5 ± 1 m amsl in the N04d watershed, and it is overlain by up to about 70 m of younger rocks in this area. Stratigraphic column shows that, in the limestone-shale couplets typical of the Permian in this region, shales are two to four times thicker than limestones. The Morrill Limestone is about 1.2 m thick, and so the outcrop/subcrop line shown represents both the top and bottom of the unit. The geology is well mapped within the Konza Prairie (Smith, 1991) and in Riley and Wabaunsee Counties (Kansas Geological Survey, online maps), but is less well constrained in Geary County because of multi-formation mapping units used by Jewett (1941). Entire watershed of Kings Creek is shown by dash-dot line; Kings Creek watershed above USGS gauging station (#06879650; filled triangle) is partly bounded by dashed line. White triangle shows location of flume in N04d watershed and circle shows approximate location of the two wells used in this study.

Although the study aquifer responds rapidly to precipitation and supplies water to vegetation, it is unlikely that agrichemicals affect the water chemistry, except as they affect precipitation chemistry. The 1.2 km² study watershed is isolated entirely within the 35 km² Konza Prairie, and the wells used in this study are on the west side of the stream, nearly surrounded by the aquifer outcrop or subcrop boundaries (Fig. 2). Most of the surrounding land is used as rangeland, and nearby cropland is in valley bottoms, at elevations lower than that of the aquifer.

2.3. Water sampling and analysis

Monitoring wells are constructed of 5-cm diameter PVC casing with one 61-cm PVC slotted well screen at the bottom. Steel well protectors mounted in concrete pads extend from the surface to over the tops of the wells (~0.5 m) and prevent damage from bison and from controlled burning of the grassland every four years. Wells are grouted with bentonite. We report here results from two of the 35 wells in the watershed, 4–6 Mor (12.6 m deep) and 3–5 Mor

(6.3 m deep), because they have been monitored over the entire study period. Details about well sampling and chemical analysis are given in the Appendix. A summary of the methods follows.

Water sampling for chemical analysis and water-level measurements are completed every four to six weeks. An electric sounder is used to take instantaneous measurements of depth to groundwater. Two wells, since 2004, have been instrumented with pressure transducers and data loggers recording water level, temperature, and barometric pressure every 5 min.

Wells are bailed using a pre-cleaned Teflon[®] bailer suspended on a Teflon[®]-coated wire. Bailed groundwater and grab samples of stream water are collected into pre-cleaned high-density polyethylene (HDPE) bottles, filtered in the field (0.45 μ filters), and stored in two pre-cleaned, low-density polyethylene (LDPE) bottles. In the laboratory, one bottle is acidified with reagent-grade full-strength nitric acid to 2% acid by volume.

Alkalinity was determined by titration with ~0.02 N H₂SO₄. Cl, SO₄, and NO₃-N were determined by sup-

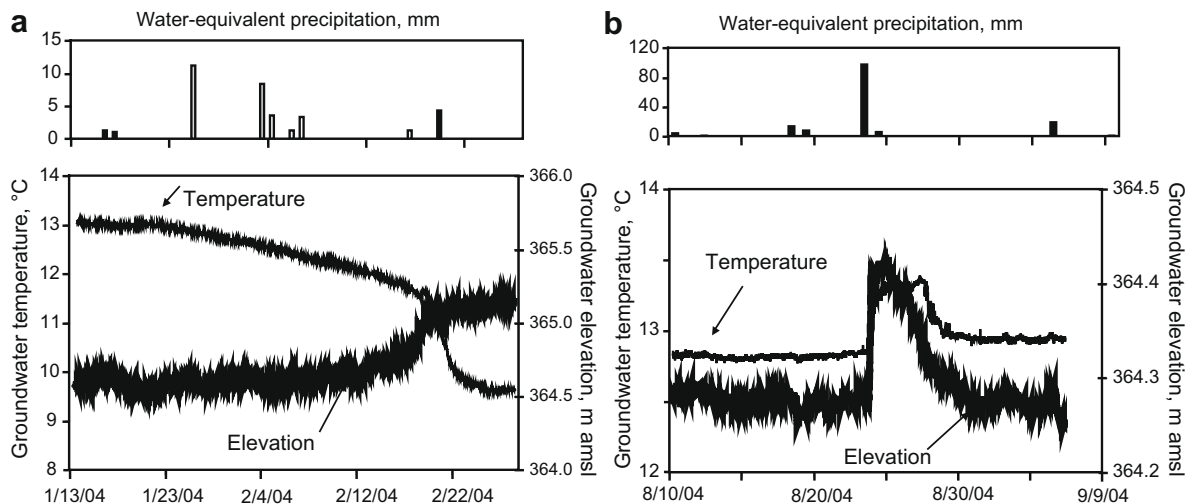


Fig. 3. Change in water-level elevation in well 4–6 Mor occurs within a few hours of precipitation and water temperature changes in response to recharge both during winter recharge events (a) and summer recharge events (b). Unfilled precipitation bars indicate snow; grey-filled bars are mixtures of rain and snow; filled bars are rain. Note different scales of precipitation, temperature, and water-level elevation for the two time periods.

pressed ion chromatography (IC). Cations were determined by atomic absorption spectrophotometry (AAS), IC, or inductively-coupled plasma-optical emission spectroscopy. Quality control samples were checked with each sample set analyzed. Charge balances on the analyses, by the method of Fritz (1994), were always within 5% and usually less than 2%. Selected samples in 2006 were collected for headspace CO₂ by gas chromatography.

During a previous study, pH was determined using the deliberate-degassing bottle technique (DDB pH; Macpherson, 2004; described in more detail in the Appendix) on samples from four wells at the Konza Prairie, 4–12.6 m deep, including the two wells used in this study. DDB pH determinations were made on samples collected between June, 1998, and February, 2000.

3. RESULTS AND DISCUSSION

3.1. Annual cycles in measured parameters

In the upland watershed at the Konza Prairie, titration alkalinity (dominantly HCO₃⁻), calcium, and magnesium together make up 82–94% (by weight) of the total dissolved solids in groundwater and stream water. The chemistry of water in the Morrill Limestone aquifer (Morrill) and the south branch of Kings Creek, which is the 4th-order stream with which the Morrill is hydraulically linked, oscillates annually with a range of approximately 0.7 pH units, up to 1 mmol L⁻¹ alkalinity, 0.15 mmol L⁻¹ calcium, and 0.1 mmol L⁻¹ magnesium (Figs. 4 and 5). The pH is out of phase with the other dissolved species listed above.

3.2. Geochemical speciation modeling

Measured pH, alkalinity, and other dissolved species constrain the saturation states of carbonate minerals and other dissolved inorganic carbon (DIC) species distribu-

tion. Alkalinity, a conservative species except when carbon-containing solids precipitate or dissolve (Stumm and Morgan, 1996), is easily determined by titration. Other dissolved species are also easily determined with modern instrumentation. However, the limestone aquifers at the Konza Prairie are relatively low-yield, neo-karst aquifers for which groundwater pH measurement is difficult (Macpherson, 2004). Accurate pH measurements are critical for determining carbonate system equilibria (Langmuir, 1971) and pH errors can skew modeling results. For this reason, we used the DDB pH (Macpherson, 2004; see also Section 2.3 and the Appendix) in geochemical speciation modeling of groundwater chemistry with the PHREEQC computer model (Parkhurst and Appelo, 1999) and the PHREEQC thermodynamic database. The full chemical analysis and DDB pH were used to calculate the partial pressure of CO₂ (P-CO₂) and calcite and dolomite saturation states in the groundwater; results from the two wells used in this study are shown in Fig. 5. Calculated P-CO₂ reflects the theoretical partial pressure of CO₂ that would be in equilibrium with the DIC, rather than an actual gas phase in the saturated zone of the aquifer.

Carbonate-mineral saturation states and DIC species distribution are somewhat sensitive to water temperature. Because the low-yield wells used in this study are bailed, the groundwater temperature at time of sampling was not well known. For the past two years, we recorded water temperatures every 5 min in conjunction with a pressure-transducer and data-logger. The extreme temperatures from this data set, 9 °C (typical January–February groundwater temperature) to 14 °C (typical September–November temperature), are similar to extreme temperatures recorded every 3–14 days on a downhole maximum/minimum-recording thermometer in 1992. Geochemical speciation model results at these extreme temperatures were close to those run at 13 °C, the mean annual air temperature (Fig. 5a). For all results presented here, the mean annual air temperature was

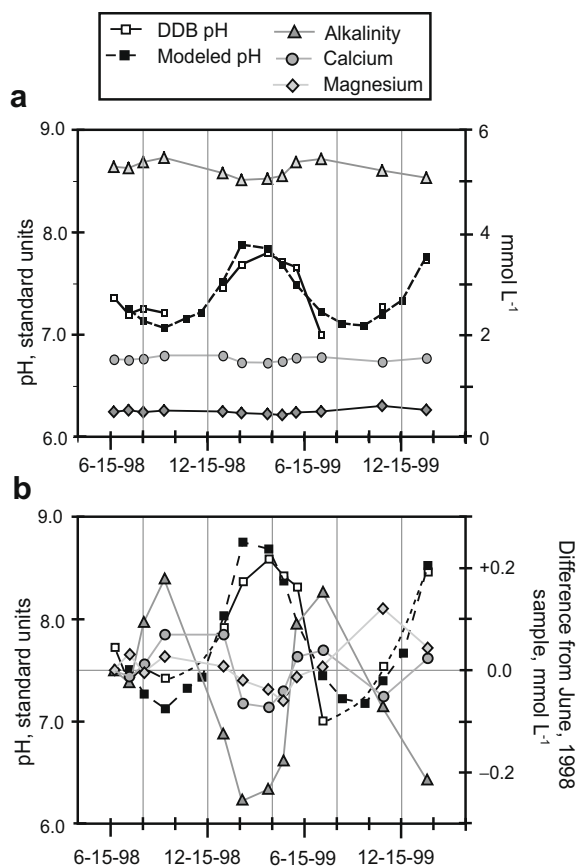


Fig. 4. Dissolved species oscillate annually in the shallow limestone aquifer (Morrill Limestone, 12.6 m deep in the well depicted here) at the Konza Prairie. Two pH plots are shown: deliberate-degassing bottle method pH (Macpherson, 2004) and pH modeled using PHREEQC (see text). (a) Annual cycle of dissolved species typically has a range of approximately 0.7 pH units, 0.4 mmol alkalinity, 0.15 mmol calcium, and 0.1 mmol magnesium, and the pH cycle is out of phase with carbonate-related dissolved species. (b) Because of the large differences in absolute concentrations, the difference between an initial value from June, 1998, and subsequent values shows the inverse relationship more clearly.

used as the groundwater temperature in the geochemical speciation model calculations.

Geochemical modeling of the measured-pH data subset shows annual oscillations in saturation state ($\log SI = \log_{10} IAP - \log_{10} K$; Fig. 5a) of calcite, dolomite, and P-CO₂ (Fig. 5b). These oscillations are smoother than the dissolved-species oscillations, suggesting a dominant carbonate-mineral control on pH, alkalinity, dissolved CO₂, and alkaline-earth element species. Both calcite and dolomite follow an annual saturation cycle, and both phases show dissolution features under SEM (Fig. 6), although bulk rock analysis (Runnels and Schleicher, 1956) and laser-ablation microprobe ICP-MS spot analysis (Wood, 2001) of the Morrill Limestone have found only 1.5–3 mol% MgCO₃. Calcite is undersaturated for a shorter time during the cycle than dolomite, but this may be because we used pure-mineral phase equilibrium constants and did not consider the possible enhanced solubility of small grains, com-

mon in the core (Fig. 6). These issues may result in an apparent oversaturation (Langmuir, 1997) and we suggest that the calcite (and dolomite) saturation state trends are correct, even if the saturation values are too high. The value of the equilibrium constant for dolomite is less certain than that of calcite (Sherman and Barak, 2000; Busenberg and Plummer, 1982), and there is low abundance of dolomite relative to calcite. For these reasons, we chose calcite to represent the annual saturation cycle, and to predict patterns in dissolved CO₂ and pH. Implications to the CO₂ and pH annual cycles are the same, whether calcite or dolomite saturation is used to develop a function representing the annual pattern. The coefficients for best-fit curves to the annual cycle of calcite saturation state for each of two wells are shown in Table 1. These coefficients were adjusted slightly (Table 1) so that the beginning and end of the year had the same saturation state (Fig. 5a).

The annual calcite saturation cycle, based on the samples with measured water chemistry collected from 1998–2000, constrains the PHREEQC-modeled P-CO₂ and pH for the entire database presented here, that is, for samples collected from 1991 through 2005. We recognize that there is uncertainty in geochemical modeling (Criscenti et al., 1996). To test the validity of using a repetitive annual cycle of calcite saturation state to represent 15 years of aquifer chemistry, we collected samples for headspace CO₂ and field pH determination in 2005. These results correspond well with modeled P-CO₂ (Fig. 7) and pH.

3.3. Long-term trends

Non-parametric statistical tests were applied to the alkaline-earth metals, alkalinity and P-CO₂ data to evaluate temporal trends. We used SPlus (ver.7) and SAS (ver. 9) for the PC, applying the Shapiro–Wilk test for normality of the data, the Kruskal–Wallis equivalent of a one-way ANOVA parametric test to determine if observed differences between sampling periods were statistically significant, the Kendall Seasonal test for trend, and calculated the Kendall tau (τ) to determine the strength of a monotonic trend relation for the variables with time. The Kendall–Theil robust line represents the straight-line slope of the trend based on the Kendall τ (Lurry and Dunn, 1997). The slope of the Kendall–Theil line is calculated as the median of all possible pairs of slopes between points. The intercept is calculated so that the line will run through the median of the data used (Granato, 2006). The Kendall–Theil line is not affected by outliers and therefore is a good representation of monotonic trend if it exists. All trend lines shown on time-series plots are Kendall–Theil lines.

The comparison level for the probability of statistical significance was set to $\alpha = 0.10$. This value of α is applicable because of the uncertainty related to collection of geologic data and the spatial variation that is often observed among geologic sampling points (Davis, 1986).

Results of the statistical tests are shown in Table 2. The Shapiro–Wilk tests showed that the P-CO₂, log P-CO₂ and Ca data are not normally distributed (p values are <0.10), so the non-parametric approach is appropriate. The alkalinity and Mg data are normally distributed (p values

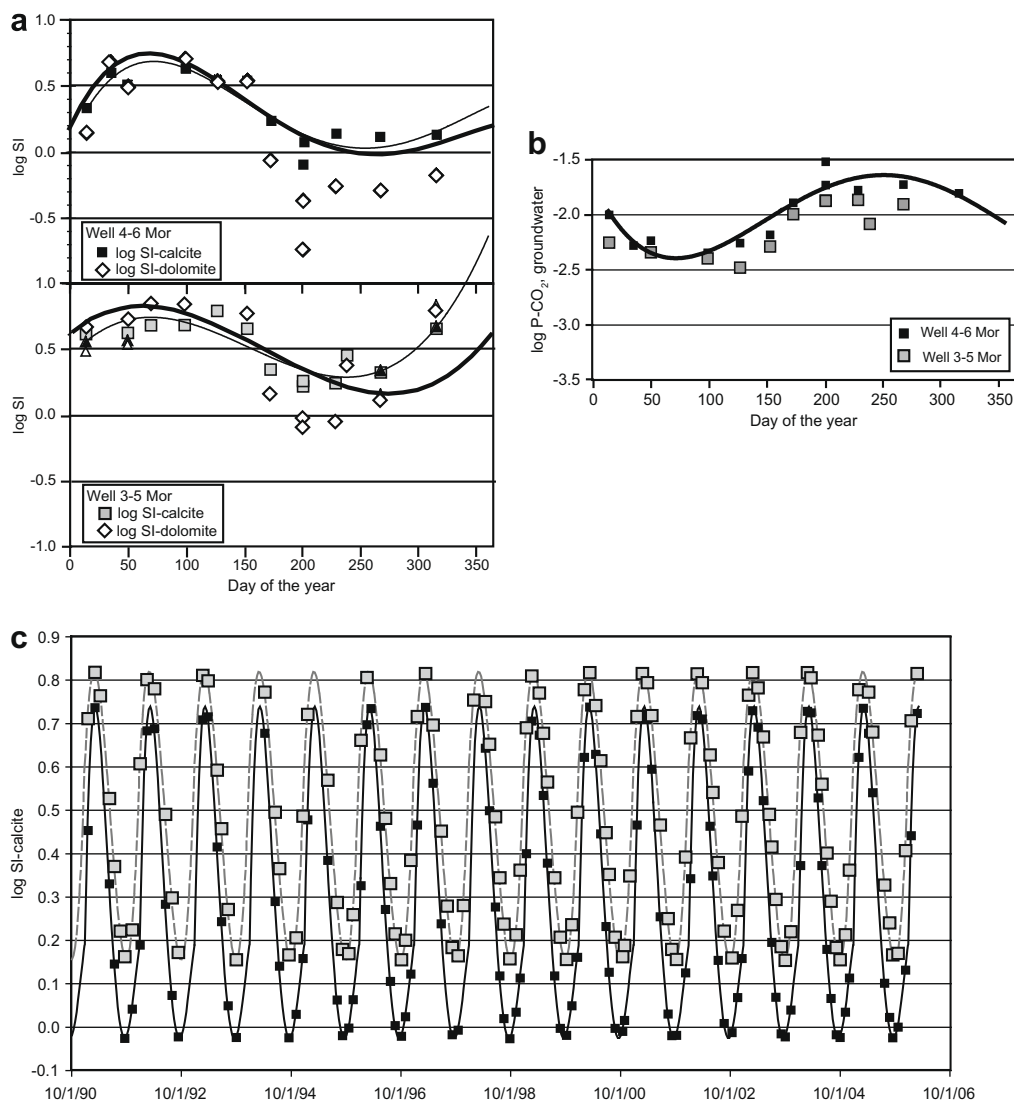


Fig. 5. (a) Calcite and dolomite saturation indices (log SI) in the two wells modeled for this study oscillate on an annual cycle. Samples were collected between 1998 and 2000 and plotted on the day of the year they were collected, without separation by year. Log SI-calcite (small, filled squares, well 4–6 Mor; large grey squares, well 3–5 Mor) and log SI-dolomite (unfilled diamonds). Light solid line is best-fit curve to annual pattern of calcite saturation; heavy solid line is adjusted fit to annual SI cycle (see text). Triangles (well 3–5 Mor) show that results are relatively insensitive to the measured water temperature extremes (see text). All other modeled results here and in other figures are calculated at 13 °C, the mean annual air temperature for the area. (b) Annual cycle of log P-CO₂ for 4–6 Mor (small, filled squares and solid line) and 3–5 Mor (large, grey squares) are similar. (c) Annual calcite saturation cycle is used with measured alkalinity to calculate pH (not shown) and P-CO₂ for wells without field pH measurements. Well 4–6 Mor: small filled squares, solid line; well 3–5 Mor: large grey squares, grey dashed line. Sampling dates may not fall on days with maximum or minimum saturation index.

>0.10), but the non-parametric tests were used to facilitate comparison of the results with the CO₂ results. The Kruskal–Wallis tests showed a high probability of differences between sampling periods by year and month for alkalinity, Ca and Mg data in both wells, but only by month for P-CO₂. The Kendall or Kendall Seasonal tests-for-trend showed a high probability of a positive trend for all parameters in both wells.

The Kendall–Theil line for alkalinity (Fig. 8) shows that, over the 15-year study period, alkalinity has increased by 0.6 and 0.8 mmol L⁻¹ in the two wells, about a 13% increase above 1991 values. Over the same time period, Ca in-

creased about 5% (about 0.1 mmol; Fig. 8) and Mg increased by about 29% (about 0.2 mmol; Fig. 8). P-CO₂ (Fig. 7) has increased by about 2100–2400 ppmv in the wells, an increase of about 18–36% above 1991 levels. The P-CO₂ increases in groundwater are higher than in atmospheric CO₂, which was about 7% higher (about 23 ppmv increase) in 2005 than in 1991.

3.4. Dissolved CO₂ annual cycle

Data and modeling show that the annual chemical cycle is nearly symmetric: dissolved solids and P-CO₂ are lowest

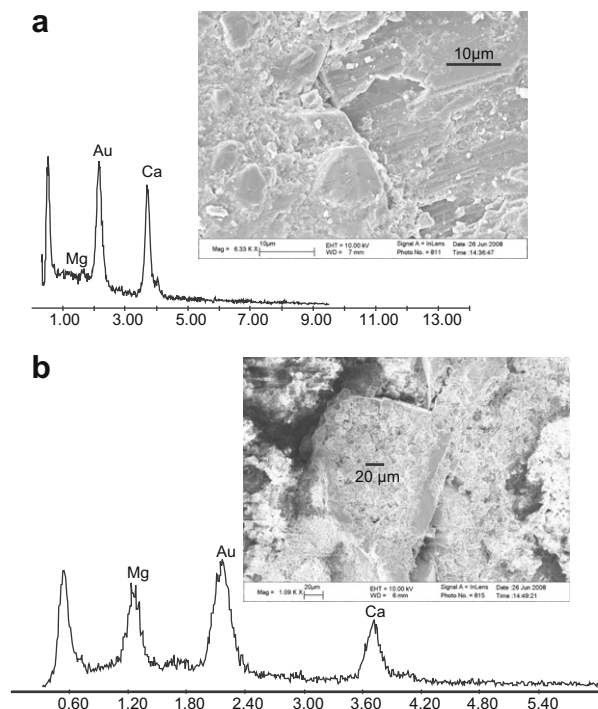


Fig. 6. SEM images of a piece of a core from the research site showing evidence for dissolution of calcite (a) and dolomite (b). Scale bar locations correspond to locations near EDS scans.

Table 1
Coefficients for equations of lines relating day of the year to calcite saturation index

Terms	Well 4–6 Mor		Well 3–5 Mor	
	log ₁₀ SI-calcite, fitted	log ₁₀ SI-calcite, adjusted	log ₁₀ SI-calcite, fitted	log ₁₀ SI-calcite, adjusted
x ⁴	-6.48E-10	-6.60E-10	0	0
x ³	6.39E-07	6.43E-07	1.902E-07	1.400E-07
x ²	-0.0001984	-0.000199	-8.810E-05	-7.130E-05
x	0.019589	0.01912	0.00956	0.0074
Constant	0.0811	0.1700	0.4369	0.6000

“Fitted” coefficients: best-fit lines using Microsoft Excel. “Adjusted” coefficients: lines adjusted so that calcite saturation is the same at the beginning (day 1) and end (day 365 or 366) of the year. See the text for the test of the validity of this approach.

between February and April and highest between September and November (Fig. 5b). There is a 7-month period to transition from the minimum to the maximum dissolved solids and P-CO₂ that occurs in a year, followed by about 5 months to transition back to the minimum annual dissolved solids and P-CO₂. Log SI_{cal}, log SI_{dolomite}, and pH cycle inversely to dissolved solids and P-CO₂.

P-CO₂ in the groundwater is at a maximum during the late fall to early winter, timing that is typical of shallow aquifers. Shallow soil P-CO₂ peaks during the summer (Hendry et al., 1999), CO₂ content increases with soil depth, and there is increasingly greater lag time to maximum CO₂

with increasing soil depth (Hendry et al., 1999; Cannovo et al., 2006; Bernhardt et al., 2006; Oh et al., 2007). At our site, the slight asymmetry in the P-CO₂ annual cycle suggests that CO₂ build-up in the shallow aquifer is slower than CO₂ decline. The decline also corresponds approximately to the annual water-level recovery in the aquifer. Although it is possible that recharge water during the winter months may deliver recently recharged low-CO₂ water into the aquifer, the P-CO₂ and water-level trends are not consistently out of phase, and episodic recharge in the summertime, when soil P-CO₂ is high, is not reflected in the P-CO₂ plot (Fig. 9). Therefore, although both recharge and groundwater P-CO₂ respond to seasonal factors, it is unlikely there is a closely-coupled causal relation between them at this site.

3.5. Implications to mineral weathering

The 15-year increase in DIC and alkaline-earth elements, signifies increased chemical weathering. Increase in Mg²⁺ is greater than Ca²⁺, suggesting dedolomitization. Increase in alkalinity and CO₂ is greater than increase in the sum of alkaline-earth elements, suggesting increasing groundwater CO₂ not neutralized by reaction with carbonate minerals. Possible explanations are (1) longer groundwater residence time increases the chemical weathering by increasing the contact time between water and rock, (2) increased atmospheric nitrogen loading increases rates of soil organic matter breakdown, thereby increasing the soil CO₂ that drives increased weathering, or (3) increased soil CO₂ for other reasons. These are addressed below.

3.5.1. Groundwater residence time

Increasing groundwater residence time, allowing more reaction time between water and limestone, could produce increasing DIC, so long as certain conditions are met. First, the aquifer water must begin as undersaturated with respect to calcite or dolomite. Second, the calcite precipitation threshold cannot be not exceeded, because calcite precipitation will remove DIC from water. Residence time could increase because drought reduces recharge and recharge-event-forced discharge, or because a shift in precipitation timing reduces recharge. These possibilities are addressed below.

Drought is defined as lower than normal meteoric precipitation (MP-drought), reduced soil moisture and/or surface-water (SW-drought) or reduced groundwater inventory (GW-drought). The average annual meteoric precipitation over the past 111-years in Manhattan, KS was 837 mm (Konza Prairie data set APT02). At the Konza Prairie, the shorter-term average from the National Atmospheric Deposition Program (NADP site KS 31; Konza Prairie data set ANA01) and Konza Prairie (data set APT01) was 839 mm for 1991–2005. The shorter-term average, then, is nearly identical to the longer-term average, notwithstanding the fact that variability in annual precipitation amount is high (130–160% relative standard deviation, RSD; Hayden, 1998). We propose that a 15-year-long MP-drought that could increase groundwater residence time is not supported by available data.

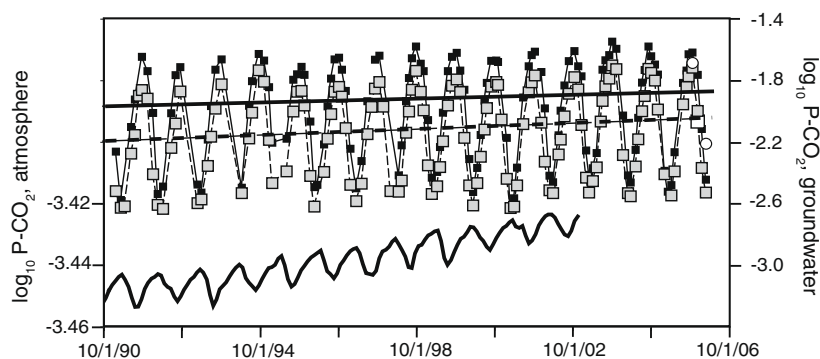


Fig. 7. P-CO₂ cycles annually and has been rising in Konza Prairie groundwater. Speciation modeling of groundwater from two wells, 3–5 Mor, 6.3 m deep (shaded squares) and 4–6 Mor, 12.6 m deep (filled squares), shows that log P-CO₂ cycles annually; points are connected with lines, without smoothing. Kendal Theil lines (see text) are shown for time series for both wells (dashed line, well 3–5 Mor; solid line, well 4–6 Mor). The increase is highly probable ($p \ll 0.1$) and tau values are positive for both trends (see Table 2). In any year, highest P-CO₂ occurs in September to November and lowest P-CO₂ occurs in February to April. Large white symbols in 2005 are measured dissolved CO₂ in the two wells (circles, 3–5 Mor; squares, 4–6 Mor); the measured values correspond well with model-predicted results. Atmospheric P-CO₂ (mixing ratio) from Niwot Ridge is shown as a heavy line.

Timing of precipitation is at least as critical to recharge as amount of precipitation. Even if average annual precipitation rate is normal, groundwater recharge could be less if precipitation is of high magnitude and short duration, so that it exceeds infiltration capacity and becomes surface runoff; or if more than the usual amount of precipitation occurs during the growing season when vegetation intercepts it. A cursory comparison of meteoric precipitation monthly totals shows that only the month of September shows a change from the long-term average. September precipitation occurs near the end of the growing season and was a little over 11% of the 111-year average annual total. Over the 15-year study period, September precipitation was 7% of the total. However, the sum of the August and September meteoric precipitation was nearly the same for the short and long periods of record, being 23% of the total for the 111-year record and 21% of the total for the 15-year record. Therefore, it does not appear that a shift in timing of MP is supported by the precipitation record. We propose that an increase in groundwater residence time is unlikely because of a MP-timing shift.

Stream discharge is another indicator of drought and an indirect indicator of increased groundwater residence time. If short flow-path groundwater cycling is slowed or halted, then streams receiving discharge from those flow-paths exhibit lower flow rates. At the study site, the South Fork of Kings Creek, which drains the study watershed, and Kings Creek, the main stream draining the Konza Prairie, have been dry during some periods of every year except 1985 since records have been kept (data sets ASD02 and ASD01, Konza Prairie LTER Program). Both are fast-response streams with sharp-fronted and rapid-recession hydrographs. Although MP-drought reduces streamflow during a drought year, there has been no long-term change in annual stream discharge that can be identified in the highly variable annual discharge record of Kings Creek and its tributaries (Gray et al., 1998). For this reason, SW-drought identified by decreased surface-water flow is not a supportable conclusion.

Groundwater supplies the base flow to streams as well as receiving recharge from them during periods of high flow, and provides a more continuous record. Within the study watershed, the average annual water level measured in the Morrill aquifer decreased until 2000, and then stabilized (Fig. 10). This suggests a possible GW-drought until 2000, and lack of complete recovery from that drought since then. This pattern of initial decline and then stasis differs from the steady increase in alkalinity and groundwater CO₂ at the study site over the entire study period. If the steady increase in groundwater DIC implies steadily increasing residence time caused by steadily decreasing aquifer water level, then the Konza Prairie water-level data do not directly support the residence-time increase hypothesis. However, the water-level pattern is not an unambiguous indicator of groundwater residence time.

A water budget, various physical or chemical tracer methods, or various physical measurement techniques have all been used to assess groundwater recharge (Scanlon et al., 2002), which relates to water residence time in aquifers. Each technique presents different challenges, and location and available data dictate the appropriate choice of method. At this study site, the best choice is a conservative chemical species that is found mainly in meteoric precipitation. At the Konza Prairie, Cl⁻ is sourced dominantly from meteoric precipitation, because road salt is never used at the site and halide minerals are not reported in this part of the stratigraphic section. In the groundwater, measured Cl⁻ was relatively steady until about 1998 and has been increasing since then (Fig. 11). The Cl increase in groundwater, a potential indicator of longer residence time of water in the soil where evapoconcentration increases MP-sourced Cl, coincides only very approximately with the annual water level decline stabilization period (from 2000 to the 2005). The groundwater Cl increase also coincides with soil-moisture drought, as indicated by the Palmer Drought Severity Index (PDI). The PDI showed normal to moderately severe drought conditions from 1999 to 2004, with only short periods with above-normal moisture. However, the increase in

Table 2
Results of statistical tests for probability level (α) of 0.10

	Calcium	Magnesium	Alkalinity	P-CO ₂	log ₁₀ P-CO ₂
<i>Well 4–6 Mor (n = 123)</i>					
Shapiro–Wilk test for normality	W = 0.967 <i>p</i> = 0.005	W = 0.993 <i>p</i> = 0.836	W = 0.984 <i>p</i> = 0.149	W = 0.898 <i>p</i> = 0.0001	W = 0.914 <i>p</i> < 0.0001
Kruskal–Wallis (by year)	<i>p</i> = 0.026	<i>p</i> < 0.0001	<i>p</i> < 0.0001	<i>p</i> = 0.98	<i>p</i> = 0.98
Kruskal–Wallis (by month)	<i>p</i> = 0.0032	<i>p</i> = 0.0844	<i>p</i> < 0.0001	<i>p</i> < 0.0001	<i>p</i> < 0.0001
<i>Well 3–5 Mor (n = 129)</i>					
Shapiro–Wilk test for normality	W = 0.963 <i>p</i> < 0.0001	W = 0.992 <i>p</i> = 0.751	W = 0.989 <i>p</i> = 0.458	W = 0.910 <i>p</i> < 0.0001	W = 0.919 <i>p</i> < 0.0001
Kruskal–Wallis (by year)	<i>p</i> = 0.049	<i>p</i> < 0.0001	<i>p</i> < 0.0001	<i>p</i> = 0.864	<i>p</i> = 0.893
Kruskal–Wallis (by month)	<i>p</i> = 0.002	<i>p</i> = 0.002	<i>p</i> = 0.042	<i>p</i> < 0.0001	<i>p</i> < 0.0001
<i>Well 4–6 Mor (n = 123)</i>					
Kendall	τ = 0.121 <i>p</i> = 0.0526	τ = 0.376 <i>p</i> < 0.0001	τ = 0.413 <i>p</i> < 0.0001	τ = 0.071 <i>p</i> = 0.2439	τ = 0.080 <i>p</i> = 0.191
Kendall Seasonal	τ = 0.131 <i>p</i> = 0.077	τ = 0.3806 <i>p</i> < 0.0001	τ = 0.549 <i>p</i> < 0.0001	τ = 0.230 <i>p</i> = 0.0014	τ = 0.230 <i>p</i> = 0.0014
<i>Well 3–5 Mor (n = 129)</i>					
Kendall	τ = 0.139 <i>p</i> = 0.0224	τ = 0.398 <i>p</i> < 0.0001	τ = 0.422 <i>p</i> < 0.0001	τ = 0.119 <i>p</i> = 0.0455	τ = 0.119 <i>p</i> = 0.0455
Kendall Seasonal	τ = 0.113 <i>p</i> = 0.114	τ = 0.401 <i>p</i> < 0.0001	τ = 0.549 <i>p</i> < 0.0001	τ = 0.458 <i>p</i> < 0.0001	τ = 0.455 <i>p</i> < 0.0001

Boldface type indicates $p < 0.10$.

Cl⁻ in the last 7 years of the study is not proportional to the increase in alkalinity, and the soil-moisture drought did not persist over the entire study period, as has the increase in carbonate-mineral-sourced solutes.

In summary, none of the lines of evidence that might indicate drought-related increase in groundwater residence time, including decrease in annual meteoric precipitation, stream flow, or aquifer water level, or increase in precipitation-sourced conservative dissolved species in groundwater, show the steady pattern of change evident in groundwater DIC. Increased carbonate-mineral weathering that adds alkalinity and alkaline-earth elements to groundwater will not also increase P-CO₂, unless there is a mechanism to decrease pH. Increased groundwater residence time (and increased water–rock interaction), then, is an unlikely sole explanation for the observed steady increase groundwater DIC and CO₂.

3.5.2. Nitrogen fertilization

Dissolved inorganic nitrogen (DIN), including ammonium (NH₄⁺) and nitrate (NO₃⁻), in meteoric precipitation increased significantly in the midwestern USA between 1985 and 2002 (Lehmann et al., 2005). At the Konza Prairie site, NO₃⁻ did not change significantly, but NH₄⁺ concentration increased about 46% (Lehmann et al., 2005); NH₄⁺ is about half the DIN in meteoric precipitation (NADP, 2007; NADP Site 31 monthly precipitation chemistry). Arithmetic average of DIN in meteoric precipitation, 1991–2004, was 0.63 g N m⁻² yr⁻¹, so the increase was about 0.15 g N m⁻² yr⁻¹ over the study period. Other typical sources of N, such as fertilizer, are unlikely to affect the Konza Prairie groundwater because the closest acreage under tillage in the area is at lower elevation and more than 2 km away from the study watershed.

Nitrogen fertilization increase can alter ecosystems in a variety of ways (Wedin and Tilman, 1996; Fisher et al., 2007), some of which increase soil CO₂, potentially accelerating chemical weathering. In one experiment, after 12 years of monitoring, C4 grasses retained N applied at the lowest rate tested, 1–2 g N m⁻² yr⁻¹, and carbon stores increased (Wedin and Tilman, 1996). This rate of N fertilization may, then, stimulate vegetation but not necessarily organic carbon oxidizers, although the latter was not tested in that study. The increase in DIN in meteoric precipitation at the Konza Prairie (Lehmann et al., 2005) is on the order of one-tenth of the lowest N addition rate in Wedin and Tilman (1996), and it is not known whether a small increase in NH₄⁺ in meteoric precipitation would produce a measurable vegetation response. Further, Zeglin et al. (2007), contrasting three grasslands including the Konza Prairie, found that rates of enzymatic breakdown of soil organic matter were not responsive to N addition (application rates of about 10 g N m⁻² yr⁻¹), and Henry et al. (2005) also found that a California grassland showed oxidative enzyme activities were unresponsive to N additions.

The Konza Prairie and surrounding grassland is, in general, N-limited (e.g., Risser et al., 1981; Wedin and Tilman, 1996; Blair et al., 1998), but the burn history, accumulation of N in the soil, and the soil-moisture history can create a non-N-limited system for periods of time (Knapp et al., 1998). At the Konza Prairie, DIN in meteoric precipitation is efficiently transformed in the vegetation canopy to dissolved organic nitrogen (Seastedt and Ramundo, 1990). A small amount of additional DIN from meteoric precipitation would probably also undergo this transformation before being transformed again and used by vegetation, stored in the soil, or volatilized. Konza Prairie above-ground net primary productivity (NPP) shows no statisti-

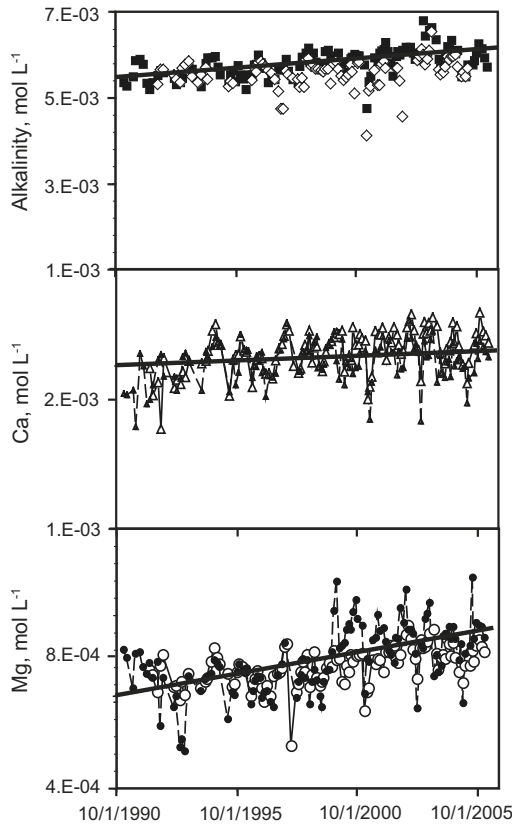


Fig. 8. Carbonate-sourced solutes have increased during the monitoring period. Top: Alkalinity. Well 4–6 Mor: filled squares. Nearby stream: white diamonds. (Well 3–5 Mor well, not shown, is similar.) Anomalous low alkalinity data correspond to stream-flooding events. Middle: Ca²⁺. Well 4–6 Mor: small, filled triangles. Well 3–5 Mor: large, unfilled triangles. Bottom: Mg²⁺. Well 4–6 Mor: small, filled circles. Well 3–5 Mor: large, unfilled circles. Lines are Kendall-Thiel trend lines for the 12.6 m-deep 4–6 Mor well. Well 3–5 Mor trend lines (not shown) are very similar. Analytical error bars are slightly larger than symbols.

cally defensible directional change (Fig. 12), although aboveground NPP rates are highly variable (Briggs and Knapp, 1995). The high NPP variability suggests that a longer record is required before directional changes due to climate change are discernable (Knapp and Smith, 2001).

NH₄⁺ from meteoric precipitation, if it passes into the soil, could also effect base-cation exchange directly or through acid produced during nitrification. However, the small documented NH₄⁺ increase in meteoric precipitation suggests that the effects on weathering will be small, also.

In summary, nitrogen fertilization has the potential to stimulate NPP, and, if accompanied by stimulation of organic carbon oxidizers, could increase soil and groundwater CO₂ and rock weathering. Addition of NH₄⁺ could have additional effects on weathering, through cation exchange or release of acid during nitrification. At the Konza Prairie, the N fertilization is exclusively from an increase in meteoric precipitation NH₄⁺, and this increase is on the order of one-tenth of the amount added in experiments that demonstrated an N-fertilization effect on NPP (Wedin and Tilman, 1996). Field experiments at another grassland site (Wedin and Tilman, 1996) showed that, among other results, low N fertilization (at levels still an order of magnitude higher than DIN increase in meteoric precipitation at our study site) increased C stores in the soil, and the effect was vegetation-type dependent, with C4 grasses having the higher increase. Transformation of soil C stores to CO₂ is strongly temperature dependent (e. g., Trumbore, 1997), and only some fractions of the soil organic C are responsive to increasing temperature (Davidson and Janssens, 2006). Therefore, the relation between N fertilization and soil and groundwater CO₂ is not clearly supported at the Konza Prairie site, but cannot be completely excluded at this time. We suggest, tentatively, that the large increase in DIC in Konza Prairie groundwater is not due to the small amount of N fertilization from meteoric precipitation.

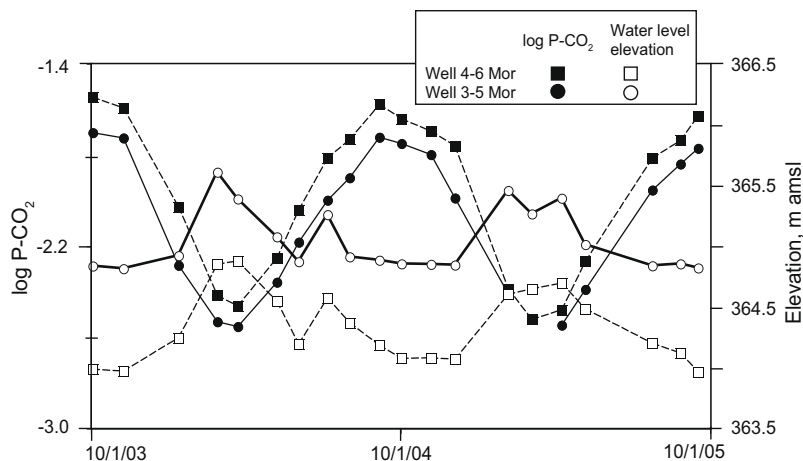


Fig. 9. Measured water-level elevation in two wells is only approximately out-of-phase with modeled groundwater CO₂. The rapid up-and-down water-level elevation pattern (well 3–5 Mor, unfilled circles; well 4–6 Mor, unfilled squares) is not evident in groundwater CO₂ trend (well 3–5 Mor, filled circles; well 4–6 Mor, filled squares). In addition, during times of nearly constant water level elevation (ca. 10/2004), groundwater CO₂ continues to change.

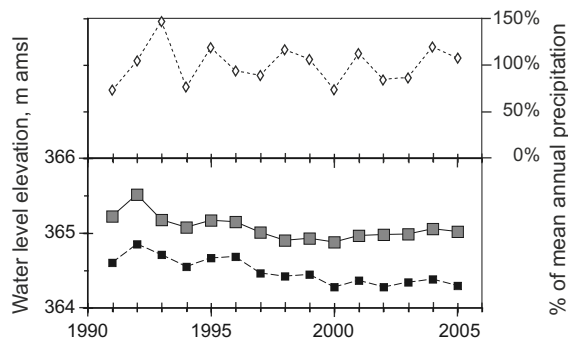


Fig. 10. Average annual water-level elevation in the Morrill Limestone (3–5 Mor, large grey squares; 4–6 Mor, small filled squares) and percent of mean annual precipitation (unfilled diamonds) over the study period are not clearly related. Meteoric precipitation did not deviate much from the long-term meteoric precipitation average over the study period, but water-level elevation dropped from the start of the study until about 2000, after which it was relatively steady (4–6 Mor) or increased slightly (3–5 Mor).

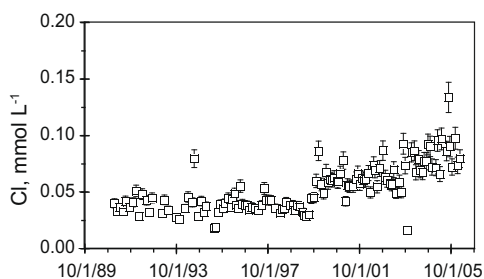


Fig. 11. Cl in the deeper well at the Konza Prairie (4–6 Mor) was nearly constant from 1991 to 1997, and then increased beginning about water-year 1998. Data from shallower well (3–5 Mor, not shown) shows a similar pattern. The Cl increase is about a three-fold increase ($0.03\text{--}0.09\text{ mmol L}^{-1}$), which is a much greater increase than the DIC increase, and change in Cl concentration occurs over about half of the study period, instead of over the entire study period.

3.5.3. Dissolved organic carbon

Although groundwater can, in some circumstances, acquire aquatic humic and fulvic acids through mineralization of sedimentary organic carbon (Buckau et al., 2000), dissolved organic carbon (DOC) at this site is sourced in the soils, and both grass vegetation and woody vegetation contribute (Pomes, 1995). DOC in soil water under areas dominated by grasses is generally less than 10 mg C L^{-1} in the A soil horizon and less than 5 mg C L^{-1} in the C soil horizon (Pomes, 1995). Groundwater DOC content was generally less than about 1 mg C L^{-1} in 1991 (Pomes, 1995) and in 2003. These limited data suggest that, if there is increased primary productivity contributing to groundwater CO_2 , it has not resulted in increased groundwater DOC.

3.5.4. CO_2

Soil P-CO_2 is typically one to two orders of magnitude higher than atmospheric P-CO_2 , so the rising atmospheric

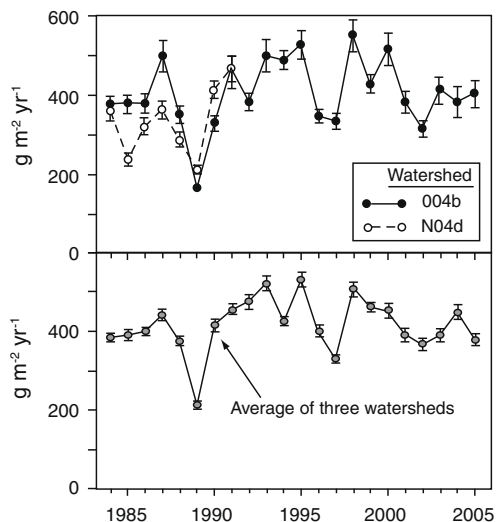


Fig. 12. Aboveground NPP from 1984 to 2005 shows high variability and no statistically defensible trend. Study watershed (N04d), record discontinued in 1991, is similar to a watershed with continuous record (004b), and these are both similar to an average of three watersheds with different fire histories.

CO_2 levels should not have a direct effect on belowground CO_2 . However, the belowground CO_2 time series from this study oscillates on an annual cycle, similar to atmospheric CO_2 , and is approximately six months out-of phase with the atmospheric CO_2 trend (Fig. 7). Earth-atmosphere CO_2 content at Niwot Ridge, Colorado, USA, closest long-term atmospheric monitoring site to the Konza Prairie, increased by about 7% ($\sim 23\text{ ppm}$) over 1991 levels by the end of 2005, atmospheric CO_2 data (based on extrapolation of the published data from January 1990 to November 2002; Tans and Conway, 2005). Groundwater CO_2 at the Konza Prairie has increased by about 20% ($\sim 2100\text{ ppm}$) over 1991 levels, and the annual change in groundwater CO_2 per change in atmospheric CO_2 ($dP_{\text{gw}}/dP_{\text{atm}}$) is about 92.

Field and microcosm experiments testing the effect of elevated atmospheric P-CO_2 on forests and grasslands have shown a variety of plant and microbial responses (e.g., Jones and Donnelly, 2004; King et al., 2004; Heath et al., 2005; Jastrow et al., 2005; Lichter et al., 2005). These experiments create CO_2 partial pressures that are on the order of 150% of the present atmospheric CO_2 or higher (Table 3) and impose constant levels of CO_2 rather than mimic the ambient annual cycle, and so test CO_2 conditions much higher than have yet been achieved in the recent Earth's atmosphere and do not reproduce the vegetation-driven annual oscillation. Even so, documented response to elevated CO_2 in grassland-imitating microcosms or mesocosms includes increased NPP (Konza Prairie, Williams et al., 2004; Owensby et al., 1999), increased NPP only in the absence of other factors (Shaw et al., 2002), and suppressed NPP in combination with temperature, precipitation, and nitrogen (Shaw et al., 2002); responses in forests are mostly increased NPP (see Oh et al., 2007, for summary). As discussed above, the Konza Prairie aboveground NPP over the past 30 years under ambient conditions has shown no

Table 3
Compilation of results from selected CO₂-enrichment experiment results and comparison with this study

§	Location	Atmospheric CO ₂ concentration	Length of experiment	Dominant vegetation
1	Konza LTER site, KS	Ambient	15 yr	C4 grass
2	FACE, Duke Forest, NC	575 µL/L	3 yr	<i>Pinus taeda</i> L. plantation
3	FACE, Rhinelander, WI	542 ± 81 µL/L	138 days	<i>Populus tremuloides</i> , <i>Betula papyrifera</i> , <i>Acer saccharum</i>
4	FACE, Duke Forest, NC	Ambient + 200 ppm = ~550 ppm	8 yr	<i>Pinus taeda</i> L. plantation
5	FACE, Jasper Ridge, CA	750 ppm	2 yr	C3 grass in C4 soil
6	Synthesis paper, four forest FACE sites	Average = ambient + 168 µL/L	6 yr	<i>Pinus taeda</i> plantation, <i>Liquidambar styraciflua</i> plantation, <i>Populus sp.</i> re-establishment
7	FACE, Jasper Ridge, CA	680 ppm	3 yr	“annual” grassland
8	Field experiment, Konza LTER site, KS	Two times ambient CO ₂	7 mo	C4 grass
8	Lab experiment, Konza LTER site, KS	410–490 µL CO ₂ /L	455 days	C4 grass
9	Global Change Field Research Facility, Oak Ridge, TN	696 ± 10 ppm CO ₂ (300 ppm over ambient)	19 mo	“old-field community” (C3 and C4 grasses, C3 forbs, C3 shrub)
§	Total change in atmospheric P-CO ₂ ^a	Total change in soil or groundwater CO ₂ , atm ^b	Change in alkalinity or DIC per year, mmol ^c	dP _{gw} /dP _{atm} , ^d
1	23.3 ppmv	2.15 E-03	3.76 E-02	92
2	200 ppmv	5.09 E-03	0.35	25
3	182 µL L ⁻¹	1.30 E-03	1.59 E-04	7

§ Reference:

- 1 This work, based on observation well 4-6Mor, using statistically derived trend lines to calculate parameters at beginning and end of study period
- 2 Andrews and Schlesinger (2001)
- 3 Karberg et al. (2005)
- 4 Bernhardt et al. (2006)
- 5 Cardon et al. (2001)
- 6 King et al. (2004)
- 7 Shaw et al. (2002)
- 8 Williams et al. (2004)
- 9 Wan et al. (2007)

^a Atmospheric CO₂ increase over entire study period (ambient CO₂ study) or atmospheric CO₂ increase over ambient imposed during experiments.

^b Soil or groundwater P-CO₂ (average of two wells) at end of study—P-CO₂ at start of study.

^c (Alkalinity or DIC at end of study—alkalinity or DIC at start of study)/length of experiment or study.

^d Groundwater P-CO₂ increase per atmospheric CO₂ increase, entire experiment.

statistically significant change (Fig. 12), although NPP trends are difficult to identify (Tate and Ross, 1997) over the rapid response of vegetation to meteoric precipitation amount and timing. Grasslands belowground biomass is higher than aboveground biomass, and grasslands allocate more productivity below ground than above ground, compared to forests, but belowground NPP is difficult to measure and is usually characterized as proportional to aboveground NPP. Changes in the soil carbon stores are small compared to the amount of soil carbon, making soil-carbon responses to elevated atmospheric CO₂ within experimental errors and so difficult to detect (Hungate et al., 1996). Nevertheless, a recent compilation of many carbon-nitrogen manipulation studies concluded that vegetation responds to elevated CO₂ by storing more carbon and nitrogen (Luo et al., 2006). Elevated CO₂ may increase decomposition of newer organic material associated with increased root biomass, and decrease decomposition of old-

er soil organic carbon (Cardon et al., 2001), making determination of changes in soil C complicated.

Soil respiration in a mixed C3–C4 oldfield -type (mixed C3–C4) grassland increased by almost 36% in response to elevated CO₂ (Wan et al., 2007). In a loblolly pine forest, soil respiration rates (Bernhardt et al., 2006) in elevated CO₂ plots were higher than in ambient-CO₂ plots for at least seven years, although the differences in soil respiration rates decreased after the first two years of the experiment. These experiments show that, ignoring the details of the many parts of the C cycle, NPP and soil respiration (*R*) are likely to increase under increased atmospheric CO₂; if the increase in *R* is greater than the increase NPP, then gross primary production (GPP) will have increased, and the increase in *R* could supply more CO₂ to belowground reservoirs such as groundwater.

Few enhanced-CO₂ experiments have also examined the soil-water or shallow groundwater and none have been re-

ported for grassland settings. Two elevated CO_2 field experiments in forests reported elevated soil-water DIC and/or soil-gas P-CO_2 (Andrews and Schlesinger, 2001; Karberg et al., 2005; Bernhardt et al., 2006; Taneva et al., 2006). The annual $\text{dP}_{\text{gw}}/\text{dP}_{\text{atm}}$, 25 and 7, in the Duke FACE (loblolly pine forest, southeastern USA; Andrews and Schlesinger, 2001) and Rhinelander FACE (aspen-birch-maple forest, north-central USA; Karberg et al., 2005), respectively, in these field experiments was less than we are reporting at the Konza Prairie ($\text{dP}_{\text{gw}}/\text{dP}_{\text{atm}} = 92$) under ambient conditions (Table 3). The increased DIC, alkalinity and other solutes for the elevated CO_2 experiments in the forest setting were attributed to biogenic CO_2 or silicate weathering. More recent interpretations point out the difficulty in interpreting water chemistry changes in the inherently heterogeneous vadose zone, finding that, although increased soil CO_2 is statistically defensible at the Duke FACE site, increased weathering of mineral components of soil derived from the mafic to felsic bedrock is not (Oh et al., 2007). These results serve to emphasize the fact that silicate minerals weather slowly, and so may not be the best medium for observing short-term response to increased CO_2 .

The pioneering large-scale CO_2 -enrichment experiments in eastern-USA forests have demystified C-cycle processes in forest vegetation and soil. However, assumptions continue to be made (Palmroth et al., 2006) that export of C out of the soil other than efflux to the atmosphere is negligible, based on the first three years of the experiments (Schlesinger and Lichten, 2001). Further, soil respiration, with elegant statistical treatment to transform monthly instantaneous daily maximum measurements into mean annual rates adjusted for temperature and soil moisture effects, is calculated using CO_2 efflux to the atmosphere (Bernhardt et al., 2006), without consideration of downward flux and potential export to groundwater (Reardon and Allison, 1979; Wood and Petraitis, 1984; Walvoord et al., 2005).

We suggest that there is an as yet un-examined link between the atmospheric CO_2 cycle and shallow groundwater that has become evident because of the easily weathered

carbonate minerals in the soil and bedrock of our study area. The soil zone must be the transfer layer, where CO_2 is generated. At the Konza Prairie, carbonate mineral weathering results from CO_2 moving downward from the CO_2 -generating soil zone to the groundwater. The groundwater calcite and dolomite saturation indices oscillate seasonally (Fig. 5) as a result of the changing CO_2 and pH, and range from slightly undersaturated to oversaturated. Notwithstanding the errors inherent in geochemical speciation calculations, the degree of oversaturation is small, as much as about 5.5 (4–6 Mor, deeper well) to 6.6 (3–5 Mor, shallower well) times calcite saturation. Calcite precipitation probably requires on the order of five to 10 times oversaturation (Herman and Lorah, 1987), so we suggest that there is net carbonate-mineral dissolution occurring at the Konza Prairie. CO_2 -controlled carbonate-mineral saturation is supported by relatively small variation in the $(\text{Ca} + \text{Mg})/\text{alkalinity}$ ratio (Fig. 13). We propose that increased belowground CO_2 effects mineral dissolution. Dolomite precipitation is usually kinetically inhibited, but at this site extensive calcite precipitation is also kinetically inhibited even as belowground CO_2 decreases, pH increases, and calcite saturation index increases during part of the annual cycle. The data cannot exclude the possibility that some precipitation occurs at the highest saturation states, but the net result is increasing groundwater DIC that results from carbonate-mineral weathering during the high- CO_2 part of the annual cycle, and relatively little mineral precipitation during the low groundwater CO_2 part of the annual cycle. The increasing DIC in this small watershed corroborates increasing alkalinity in the Mississippi River (Raymond and Cole, 2003), but the increase is independent of human-driven land-use change.

The cause of the enhanced groundwater CO_2 is beyond the scope of this study, but some observations are possible. First, we stress that, at the Konza Prairie, carbonate-mineral weathering dominates with minimal silicate weathering (Wood and Macpherson, 2005), and the setting is mid-continental, mesic grassland instead of eastern temperate forest. The belowground C-cycle may not be directly

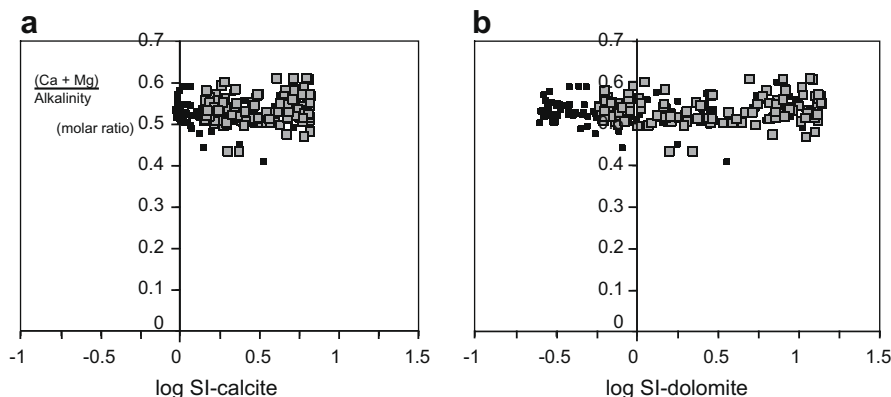


Fig. 13. Molar ratio of alkaline-earth elements to alkalinity shows some variability, but has a dominantly horizontal trend with calcite (a) and dolomite (b) saturation indices. A horizontal trend is strong evidence for saturation-index control by CO_2 ; a dominantly vertical trend would result from carbonate-mineral precipitation or dissolution independent of changes in CO_2 (after Szramek and Walter, 2004). Well 4–6 Mor: small, filled squares; well 3–5 Mor: large, shaded squares.

comparable in these two settings, and further characterization in grassland settings is requisite. Nevertheless, some generalities probably apply. Increasing soil respiration and NPP were discussed above. Increasing mean average air temperature due to a CO₂-induced greenhouse effect could stimulate organic matter decomposition in the soil (Davidson and Janssens, 2006), increasing soil CO₂ directly or interactively with CO₂ (Wan et al., 2007). Soil-temperature and soil-CO₂ monitoring has not been done at the Konza Prairie to confirm whether soil temperature is increasing. However, current Konza groundwater temperatures are similar to 1992 measurements, so increased temperature, if it has occurred, has not reached the shallow groundwater realm. In addition, because calcite exhibits retrograde solubility, an increase in belowground temperature should decrease net chemical weathering of limestone rather than increase it.

Changing climate can change plant community composition in a landscape. In grasslands, invasion of shrubs (C3 woody plants) is an important vegetation change that occurs with decreased fire frequency or increased water availability. At the Konza Prairie, a study of the effect of shrubs on grass macronutrients showed that there was decreased surface CO₂ flux without measurable change in soil C stores or N mineralization rates in small "islands" of monoculture shrubs (McCarron et al., 2003). The decreased CO₂ flux was linked to increased soil moisture and temperature in the shrub-dominated areas. Whether that decreased CO₂ flux resulted from decreased CO₂ production, transient storage of C in the woody vegetation, or increased downward CO₂ flux is not known.

In summary, carbonate-mineral weathering, as evidenced by increasing DIC and alkaline-earth cations in shallow groundwater, has increased over the past 15 years at the Konza Prairie. The annual cycle of groundwater CO₂ results in mineral dissolution when groundwater CO₂ is high. Mineral precipitation apparently does not occur, or does not completely remove the dissolved species from the groundwater, when groundwater CO₂ is low and water becomes oversaturated with respect to calcite. This lack of precipitation contrasts with some forested watersheds (Szramek and Walter, 2004), where back precipitation with release of CO₂ may be significant. The increase in groundwater CO₂ at the Konza Prairie is greater than the increase in atmospheric CO₂, but the annual cycle of groundwater CO₂ suggests an indirect link to the atmospheric CO₂ annual cycle. Elevated-atmospheric CO₂ experiments in forests may have documented increased weathering in the soil zone, but as yet there have not been measurements in similar experiments in grassland settings to characterize the soil or shallow groundwater response.

4. SUMMARY

An annual cycle of belowground CO₂ and rapid water throughput in the thin, neo-karst limestone aquifer at the Konza Prairie drives chemical weathering. Carbonate-mineral dissolution occurs when groundwater CO₂ is higher, which is during and just after the growing season. During the non-growing season, moderate levels of calcite and

dolomite oversaturation (5–7 times saturation) occur as groundwater CO₂ decreases and pH increases, even as recharge dilutes the groundwater and water levels rise. Calcite saturation state remains below the threshold for precipitation, or at least precipitation does not completely remove carbonate minerals dissolved during the high-groundwater CO₂ part of the cycle. The alkalinity and associated cations from mineral dissolution at the Konza Prairie persist in groundwater, which is discharged to streams and to deeper aquifers.

Groundwater CO₂ has increased about 20% over the past 15 years at this site, which is greater than the 7% increase in atmospheric CO₂ over the same time period. The forcing mechanism for increasing belowground CO₂ is not clear, but the mechanism is unrelated to increased groundwater residence time because of drought, or stimulation of the vegetation-controlled carbon cycle because of increased N in meteoric precipitation. Soil CO₂, from microbial breakdown of vegetation and root respiration, may be synergistically enhanced, in an as yet unidentified way, to increasing atmospheric CO₂ and perhaps atmospheric temperature.

The increase in atmospheric CO₂ has already decreased ocean pH and alkalinity (Orr et al., 2005; Feely et al., 2004). We suggest, based on our observations in the undisturbed grassland setting of the Konza Prairie, that there may be an as yet unidentified link between rising atmospheric CO₂ and groundwater CO₂. At the Konza Prairie, increasing groundwater CO₂ is partially accommodated by net weathering of limestone on an annual cycle, confirming a similar, experimentally-induced but smaller response in the soil zone of a forest ecosystem. How the atmosphere and shallow groundwater CO₂ systems are linked is not clear, but the annual cycle in groundwater CO₂ suggests that shallow groundwater is acting as a sink for CO₂.

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APPENDIX. SAMPLING AND ANALYTICAL METHODS

A.1. Water-Level Measurement and Water Sampling

Water sampling and water-level measurements are completed every four to six weeks. Depth to groundwater is measured with an electric sounder. Since 2004, a high-fre-

quency record of water level and water temperature has been kept of two wells (one of which is considered in more depth in this study) using pressure transducers and data loggers. Barometric pressure is recorded at the time and time interval as water level and temperature.

Before sampling for water chemistry, wells are bailed using a Teflon[®] bailer suspended on a Teflon[®]-coated wire. A volume equivalent to at least twice the volume of water within the casing and gravel pack is discarded before sample collection. Between sampling trips, the bailer is soaked in 5% HCl for at least 24 h, rinsed five times with distilled water followed by three times with distilled-deionized water, and dried in a Class 100 laminar flow work station. During a sampling day, the bailer is rinsed three times with distilled water between wells. Bailed stream water or groundwater is stored briefly in pre-washed, dedicated, one-half gallon (1.9 L) high-density polyethylene (HDPE) bottles until it is filtered. Samples are filtered in the field through 0.45- μm membrane or cartridge filters directly into two previously acid-cleaned 250-mL low-density polyethylene (LDPE) bottles. One bottle is filled so there is no headspace; a second bottle, pre-weighed, is filled with approximately 250 mL of water. Bottle lids are sealed with Parafilm[®] and stored in a cold environment (ice chest in the field; non-frost-free refrigerator in the lab) until water is analyzed. In the laboratory, the second bottle is weighed, acidified with reagent-grade full-strength nitric acid to 2% acid by volume, and reweighed within a day of sample collection.

A.2. Chemical analysis of water and gas

Alkalinity was determined by titration with $\sim 0.02\text{ N}$ H_2SO_4 in the field or within two days of collection at the University of Kansas; tests on 80 samples collected in 1991–1993 and 2004 show that alkalinity is stable for at least 10 days after collection at this site (data not shown).

Other anions of significance to the bulk water chemistry (Cl, SO_4 , $\text{NO}_3\text{-N}$) were determined by suppressed ion chromatography (IC) with a Dionex 4000i (AG4A-SC and AS4A-SC columns, and micro-membrane suppressor or anion self-regenerating suppressor) on the filtered, non-acidified aliquot.

Cations (Na, K, Mg, Ca as well as others not discussed here) were determined on acidified filtered aliquots. Analysis was accomplished using atomic absorption spectrophotometry, AAS, with a Perkin-Elmer 2380 AAS from 1990 to 1994, IC using CG-12A and CS-12A columns with cation micromembrane suppression from 1994 to 1999, and inductively-coupled plasma-optical emission spectroscopy using a JY 138 Ultracore ICP-AES from 1997 through the present. Calibration standards were made, by weight, from purchased, certified stock solutions; density corrections were applied if certified concentrations were given as mass/volume. Quality control samples were checked with each sample set analyzed. Charge balances on the analyses, by the method of Fritz (1994), were always within 5% and usually less than 2%.

Selected samples in 2006 were collected for headspace CO_2 by gas chromatography. Glass serum vials (70 mL;

Wheaton) were filled with a nitrogen atmosphere, and sealed with a crimp top before autoclaving and weighing. In the field a syringe was used to pull a vacuum on the bottles, which were then backfilled with a flowing stream of groundwater until atmospheric pressure was reached. Samples were stored on ice for transport to the laboratory, where they were weighed and then stored in a non-frost-free refrigerator at $\sim 7^\circ\text{C}$ for two–five days before analysis. Samples were analyzed at room temperature. Headspace analysis was performed using thermal couple detection gas chromatography on an Agilent 6890 gas chromatograph equipped with a Haysept Q packed column using He as the carrier gas. Gas concentration was calculated using Henry's Law, accounting for the volume of groundwater, volume of headspace, and assuming 25°C and atmospheric pressure in the bottle.

During a previous study, pH was determined using the deliberate-degassing bottle technique (DDB pH; Macpherson, 2004), on samples from four wells at the Konza Prairie, 4–12.6 m deep, including the two wells used in this study. DDB pH determinations were made on samples collected between June, 1998, and February, 2000. The DDB technique employs known-volume, pre-weighed, inert-gas-filled 125-mL glass bottles with Teflon-lined caps. These were filled with groundwater directly from the bottom of a one-liter bailer into the bottom of the bottle, to approximately 50% full. The sealed bottles were stored in a cold environment for one week to allow degassing of CO_2 into the headspace. The pH of the water was then measured by sealing the pH probe in the bottle, insulated against temperature change, and then recording pH and temperature measurements every 10–30 s until the pH and temperature stabilized. The pH (corrected to aquifer temperature) and alkalinity determined earlier were used to calculate total DIC and P- CO_2 in the bottle, the headspace volume was used to calculate the amount of CO_2 that had degassed, and that amount of inorganic carbon was added to the total DIC. The pH before degassing of CO_2 was determined by iteration, until calculated and measured alkalinity differed by less than 10^{-5} molal. The pH probe calibration was verified before measurements began and after the final measurement was taken for each sample. Water and headspace measurements were made both by volume and by mass, taking into account temperature effects on volume measurements and sediment in the bottle (if present), and the average volumes used. The percent relative standard deviation on the headspace volume by the different methods was always less than 1%, and typically less than 0.5%.

A.3. Scanning electron microscopy

A piece of core sampling the Morrill Limestone from a well in the N04d watershed drilled in 1999 was examined using at the University of Kansas Microscopy and Electronic Imaging Laboratory, using a 1550 LEO Field Emission scanning electron microscope, equipped back scattered electron detector and EDAX electron backscattering spectroscopy, energy dispersive system. The sample was mounted on a stub, gold-sputtered coated for about 1 min, and analyzed at 10 KV.

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