Increasing groundwater CO_2 in a mid-continent tallgrass prairie: Controlling factors

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Abstract. Alkalinity and groundwater CO_2 have increased linearly from 1991–2017 at the Konza Prairie Biological Station (KPBS), a tallgrass prairie research site in northeastern Kansas. The projected increase in groundwater alkalinity (as HCO_3^-) and CO_2 based on an earlier trend was confirmed in 2016, with predictions nearly equal to recent values (e.g., 408 ppm vs 410 ppm as HCO_3^-, respectively). Both the water balance and groundwater CO_2 trends within the study watershed could be impacted by long-term changes in land use and climate: 1) encroachment of woody vegetation (1983–2012) as a result of the 4-year fire return interval, 2) re-introduction of bison (phased in, 1994–2006), 3) increases in air temperature, and 4) changes in precipitation patterns. If only linear processes are driving the observed water chemistry changes, then the linear increase in air temperature (1983–2017) that stimulates soil respiration may be the most likely factor enhancing groundwater HCO_3^- and CO_2, as air temperature has risen ~1 to 1.4°C over 34 years. If groundwater chemistry is driven by more threshold behaviour, woody encroachment, which was linear but in three distinct phases, may drive groundwater chemistry. The ~2 to 3‰ decrease in the discontinuous $\delta^{13}C$ data in the groundwater-dominated stream suggests enhanced inputs of microbially-respired labile carbon, CO_2 sourced from C3 (woody vegetation), or a combination of the two.

1 Introduction

Critical zone processes involving belowground CO_2, which equilibrates with groundwater and reacts with soil and rock, are fundamental to understanding water-rock reactions and landscape evolution. Although seasonal variations in belowground CO_2 are expected in temperate climates because of seasonal changes in temperature, precipitation, and vegetation, we present here a 26.5-year trend of increasing belowground CO_2, manifested by increasing titration alkalinity along with calcium and magnesium [1, 2], in a temperate-climate, mid-continent, mesic, tallgrass prairie, the Konza Biological Station, a Prairie Long-Term Ecological Research and NEON Site (Konza). Konza occupies 35 km^2 with relief of ~70 m and is divided into 60 watersheds with different controlled-burn

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frequencies (annual, 2-, 4-, 10-, & 20-yr) and grazer pressure (bison, cattle, none). Data presented here are mostly from a 4-yr burn-frequency watershed (N04d), grazed by bison (*Bos bison*) and drained by a groundwater-dominated, intermittent, headwater stream (Fig. 1).

Increasing surface-water alkalinity, and, by extension, CO_2, is observed at many sites worldwide. The increase has been attributed to land use (increased agriculture [3], prairie reforestation [4]), precipitation chemistry (acid rain deposition [5]), and climate (belowground CO_2 increase from climate warming [6]). Although atmospheric CO_2 has increased [7], it is not considered a cause of increasing belowground CO_2 because atmosphere concentrations are typically 1-2 orders of magnitude lower than in soil and groundwater [8]. Here we discuss trends at Konza that could explain increasing groundwater alkalinity and belowground CO_2.

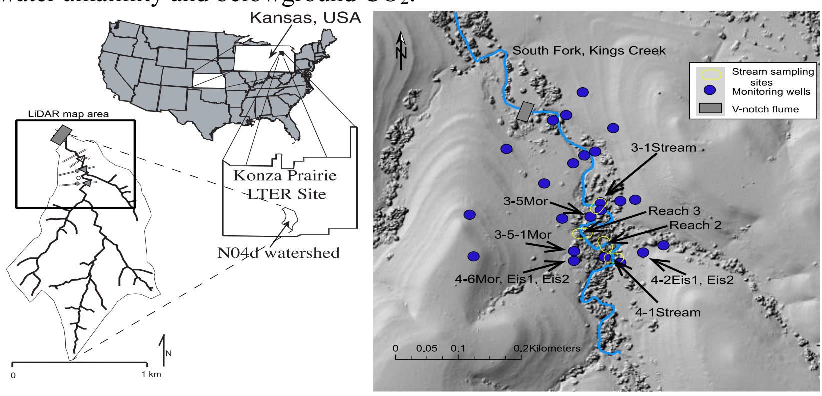

Fig. 1. Konza Prairie LTER site (Konza), Flint Hills physiographic province. Remaining tallgrass prairie is about 4% of the original prairie extent. Konza is underlain by alternating thin (~1-2 m) limestones and thicker (~2-4 m) shales of Lower Permian age that are overlain by thin (<1 m) Pleistocene loess. There are 35 monitoring wells, two regular stream-sampling sites, and other stream sites used for specific projects. This study uses seven wells and four stream-sampling sites.

2 Methods and data sources

Water was filtered in the field through 0.45µ membrane filters into LDPE bottles and chilled before laboratory determination of alkalinity (titration with ~0.02 N H_2SO_4), other anions (ion chromatography, Dionex ICS-1600), and cations (preserved with 2% v/v reagent HNO_3; ICP-OES, JY Ultima 2). Samples for C-isotope analysis of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) were collected in baked amber bottles with Teflon-lined lids and chilled until analysis with a Picarro G2201-I Isotopic CO_2/CH_4 Analyzer. Water chemistry, precipitation, stream discharge, air temperature, and bison data used in the project are from LTER (www.konza.ksu.edu) and ClimbDB/HydroDB (https://climhy.lternet.edu/). Zonal air temperature data are from NASA (https:// data.giss.nasa.gov/gistemp/; [9, 10, 11]).

3 Results and discussion

Alkalinity has risen steadily in N04d over the period of record (1991 to 2017; Fig. 2a), continuing a trend published for 1991-2005 [6]. The slope of the published trend is similar to the 1991-2017 trend (dotted versus solid line in Fig. 2a), confirming a CO_2 increase that is linear with time. Observed changes that might explain the increase are presented below.

Precipitation—Mean annual precipitation (MAP) has remained constant (~835 mm), but average annual (AA) alkalinity was antithetic to AA growing-season (GS) precipitation

(Apr – Sep) during the early part of the study period and then was coincident with GS precipitation after 2002 (Fig. 2b). Historically groundwater recharge from precipitation is greater in the Dec–Feb cold season [12] due to reduced evapotranspiration (ET), yet a shift in the delivery of GS precipitation between 1991-96 compared to 2003-16 (excluding very high MAP years of 1993, 1995, 2008, and 2016) suggests a potential increase in groundwater recharge in the GS over time. Specifically, precipitation: i) shifted from bimodal in 1991-96 (May & Jun) to unimodal (Jun) in 2003-16 for monthly maximum precipitation, ii) changed in warm-season to cold-season ratio (increasing from 2.1 to 3.0), and iii) increased in average GS amount, from 550 mm (1991-96) to 660 mm (2003-16). We propose these changes increased GS groundwater recharge, with more alkalinity coming from June soil-CO_2 chemical reactions.

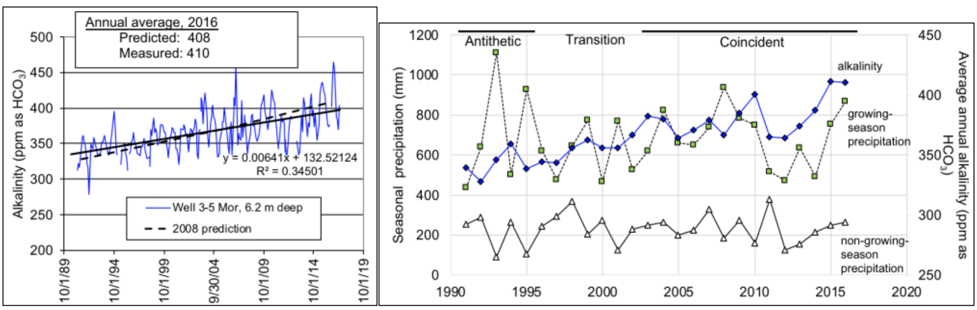

Fig. 2: (left) Titration alkalinity (4-6 week periodicity) in monitoring well 3-5Mor (6.2 m deep), January 1991 through May 2017, increased significantly (p = 3.44E-23). Prediction using trend from [6] is 0.5% lower than measured average annual (AA) 2016 alkalinity; measured 2016 AA alkalinity is 3% higher than best-fit trend (solid line) for entire 1991-2017 dataset (396 ppm as HCO_3). (right) AA alkalinity and seasonal precipitation relations through the study period.

Woody-encroachment—Woody (C3) vegetation (sumac, *Rhus glabra*, and roughleaf dogwood, *Cornus drummondii*) has increased from ~1 to 25% at Konza over a 39-year period (1983–2012; Fig. 3a). Shrub cover exhibits threshold behaviour around the year 2000, with trend steepness increasing with decreasing frequency of prescribed burns (Fig. 3a; [13]). The groundwater-elevation decrease around year 2000 (Fig. 3a, b) could be attributed to increased water demand by woody vegetation except the water trend after 2000 is flat while the woody vegetation trend continues to increase. Potential alternate explanations are deeper rooting depth of C3 than C4 vegetation or C3 using deeper water than C4 vegetation [14]. In a semi-arid region [15], areas invaded by phreatophyte shrubs had greater increases in ET in excess of precipitation and net ecosystem exchange (i.e., CO_2) than less-invaded areas with the hypothesis that ET was groundwater. At Konza, shrubs are not phreatophytes and eddy covariance (EC) measurements showed consistently higher C sequestration in a 4-year burn watershed (woody-encroached) than in an annual-burn watershed (grass), potentially because C3 woody vegetation has greater access to deeper water than C4 grasses [16]. EC data also showed annual ET fluxes in the woody-encroached site were only greater than the grassland site when GS precipitation inputs were low and woody species had a competitive advantage for accessing deeper water.

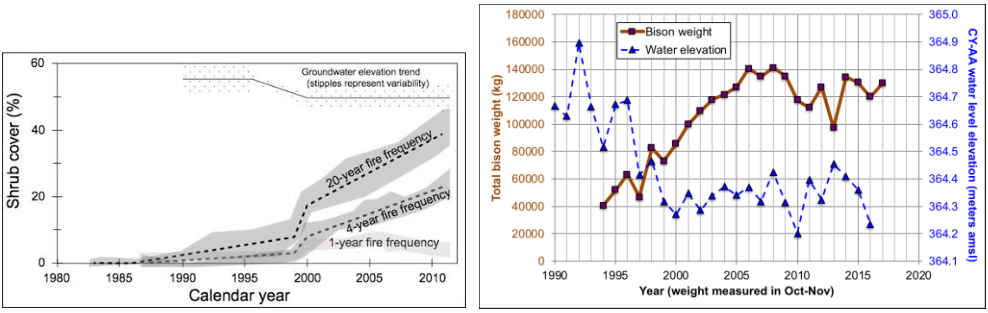

Fig. 3. (left) Increasing shrub cover in watersheds with different prescribed-burn frequencies (1983–2012). Shaded areas encompass the data spread; dashed lines are linear trends fitted to data segments. (Modified from [13]). (right) Average annual (calendar year, CY) groundwater elevation (monitoring well 4-6Mor, 12.2 m deep), 1990–2016, and bison population weight, 1994–2017.

Bison–The bison herd increased from 1994–2006 (Fig. 3b). This could have increased pressure on the groundwater resource, reducing recharge, increasing unsaturated zone thickness, and changing CO_2 delivery to groundwater. However, the groundwater elevation decrease occurs from 1996 to 2000, so the timing differs from the bison build-up.

Air temperature—Temporal air-temperature trends are positive and linear (fig. 4), as is zonal air temperature trend (1980–2017; N 35° to 40°, W 95° to 100°), which is significant ($p = 0.01$) with temperature change of +0.7°C at Konza (N 39.1° and W 96.6°). Warming climate could stimulate soil respiration [17], increasing soil CO_2 that moves downward into groundwater. Although a change in net primary productivity (NPP) has not been statistically proven at Konza, the data are noisy [6].

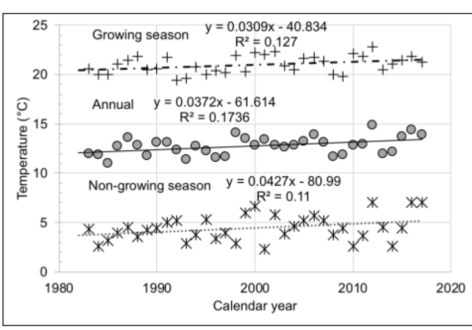

Fig. 4. Study site air temperature, 1983–2017. Trends are significant, with p values and average temperature changes of 0.013 and 1.26 °C, 0.036 and 1.05 °C, and 0.052 and 1.45 °C, respectively, for annual, GS, and non-GS.

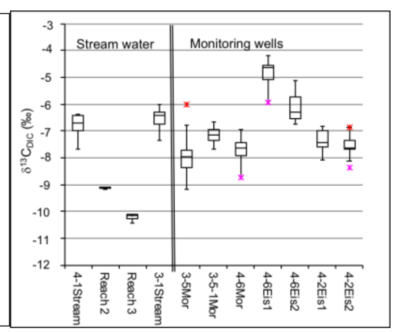

Fig. 5. Values of $\delta^{13}C$ in water DIC. All but "Reach" samples are from 2008–2009; stream samples "Reach 2" and "Reach 3" are from 2015. Upstream to downstream is left to right. "Mor" wells are deepest; "Eis2" wells are shallowest.

Stable C isotopes—Dissolved inorganic carbon ($\delta^{13}C_{DIC}$) in ground- and stream water in 2008–09 ranged from –9.2 to –4.2‰ (n=53) and –7.6 to –6.0‰ (n=15), respectively, while stream water during 2015 was –10.4 to –9.1‰ (n=6). Although the data set is small for 2015, the possible shift to lower $\delta^{13}C_{DIC}$ supports a shift either to microbial breakdown of more labile (summer) than refractory (winter) organic matter, or from a CO_2 source from C4 grasses to C3 shrubs. Soil organic matter $\delta^{13}C$ ranges in a sinusoidal pattern from –18‰ at the surface to a maximum of –16‰ at ~0.24m and a minimum of –25‰ at ~1.25-1.5m depth, so resident organic matter likely available for microbial breakdown (close to the land surface) reflects the pre-woody-invasion C4 vegetation [18], and not the observed C-isotope shift.

4 Conclusions

The linear alkalinity increase observed over ~26.5-years at the Konza Prairie LTER site corresponds to a linear increase in air temperature, a non-linear increase in woody vegetation, a shift to more warm-season precipitation, and a possible shift to more negative $\delta^{13}C_{DIC}$. The decrease in groundwater-level elevation may be attributed in part to introduction of bison into the study area, but is more likely the result of a cool-season to warm-season change for a portion of the recharge, which, if true, should affect the entire region. These trends suggest the increasing CO_2 may be caused by a combination of climate-warming-increase in microbial activity, a shift in organic matter available to microbes from C4 to C3, and an increase in delivery of warm-season soil-CO_2-charged water to groundwater.

Acknowledgements. Climate and Hydrology Database Projects, a partnership between the National Science Foundation Long-Term Ecological Research (NSF-LTER) program and the USDA Forest Service (USDA-FS) Pacific Northwest Research Station, Corvallis, Oregon provided data. Significant funding for these data was provided by the NSF-LTER program and the USDA-FS. Datasets AGW01, APT01, ASD01, AWE01, and CBH01 were supported by the NSF-LTER program (DEB 1440484) at the KPBS. We thank the 48 undergraduates and 10 graduate students who contributed to this project, the anonymous reviewers and R. Harmon who improved this manuscript.

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