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Increasing shallow groundwater CO_2 and limestone weathering, Konza Prairie, 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 CO_2, 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 CO_2 is high. As dissolved CO_2 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 CO_2 sink through weathering of limestone: soil-generated CO_2 is transformed to alkalinity through dissolution of calcite or dolomite. The annual cycle and long-term increase in shallow groundwater CO_2 is similar to, but greater than, atmospheric CO_2.

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 CO_2 accelerates the hydrologic cycle, increasing continental river discharge, because plant water-use efficiency increases with increasing atmospheric CO_2 (Gedney et al., 2006). Hydrochemical changes may also be linked to changes in atmospheric CO_2: 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 CO_2, increased water flux, and changing land use. Jones et al. (2003) contradicted that finding by proposing a 22-year, 40% decline in river-dissolved CO_2 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

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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 CO_2-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 CO_2, an increase of about 50% over the present atmospheric CO_2 resulted in significant increases in soil CO_2 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-km^2 research watershed that is drained by an ephemeral 4th-order stream; the watershed lies in the interior of the 35-km^2 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 CO_2 increased over the study period, we propose the dissolved-solids increase is evidence of increasing chemical weathering of carbonate minerals related to increasing groundwater CO_2.

This study quantifies the increasing alkalinity and dissolved CO_2 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 CO_2.

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 unplowed 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–km^2 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