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Climate controls on soil respired CO_2 in the United States: Implications for 21st century chemical weathering rates in temperate and arid ecosystems

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ABSTRACT

The most recent IPCC (2007) report predicts that regional-scale precipitation patterns will change significantly in the 21st century as a result of increasing atmospheric CO_2. The amount of respired CO_2 stored in the soil atmosphere is heavily influenced by climate, and the concentration of CO_2 in soils controls the concentration of dissolved CO_2 ($[CO_{2aq}]$) in pore water involved in chemical weathering. Therefore, we can expect changes to chemical weathering rates as a result of climate change, which can influence the global carbon cycle through the consumption of CO_2 during continental silicate weathering. These changes may even be important on human timescales. To predict changes to the $[CO_{2aq}]$ of soil water, we have produced an extensive literature review of soil respired CO_2 measurements to study the spatial variability of soil respired CO_2. We show that respired CO_2 concentrations and $[CO_{2aq}]$ vary with precipitation. This study focuses on the western United States, where we find a strong relationship between summer average soil-respired CO_2 and mean annual precipitation for soils forming in or below 900 mm yr^{-1} precipitation ($R^2 = 0.91$). The correlation breaks down when higher mean annual precipitation rates are considered, restricting the use of this relationship to arid to subhumid precipitation regimes.

We estimate the response of $[CO_{2aq}]$ in soil pore water in the western United States to projected anthropogenic CO_2 emissions using this new relationship and projected changes in precipitation simulated by the North American Regional Climate Change Assessment Program for the decade 2051–2060. According to our model, $[CO_{2aq}]$ in soil pore water is expected to decrease by up to 50% in the southwestern United States and to increase by up to 50% in areas of the Northern and Central Great Plains. These results have important implications for CO_2 consumption and changes to terrestrial carbon cycling in the next century.

1. Introduction

As anthropogenic emissions of CO_2 to the atmosphere continue to increase (IPCC, 2007), it is important to study how the biosphere reacts to perturbations in the carbon cycle so that future sources and sinks of carbon can be identified. While roughly half of the annual anthropogenic CO_2 emissions are taken up by the biosphere and oceans in various carbon sinks (Schimel et al., 2001; Ballantyne et al., 2012; Graven et al., 2013), it is currently unclear whether these sinks will continue to buffer CO_2 emissions at the same rate as the previous two decades (Ballantyne et al., 2012). Terrestrial silicate weathering, which is influenced by ecosystem productivity, is one process that may respond to increasing atmospheric CO_2 concentrations, as silicate weathering drives carbon sequestration by converting atmospheric CO_2 to $CO_3^{=}$ and moving it to terrestrial and oceanic reservoirs. While originally only thought to influence the carbon cycle on geologic time scales (Berner, 1992; Berner and Kothavala, 2001), recent studies have shown that chemical weathering rates can increase in response to changes in temperature and precipitation by up to 50% in a matter of years (Gislason et al., 2009; Beaulieu et al., 2012). Such changes in chemical weathering may alter atmospheric CO_2 consumption, and Beaulieu et al. (2012) suggest that increases in chemical weathering could account for nearly 40% of the 1.4 GT increase in biosphere consumption of atmospheric CO_2 observed between 1750 and the present (IPCC, 2007). Thus, identifying regions of change in the rate of chemical weathering may help to pinpoint new sinks and sources of CO_2 in the global carbon cycle.

Previous studies (e.g., Moosdorf et al., 2011) have modeled broad-scale modern chemical weathering and CO_2 consumption for North America by calculating CO_2 consumption based on measured dissolved bicarbonate concentrations from watersheds across the continent and interpolating these concentrations between hydrochemical monitoring stations. While this method works well for modern estimations of weathering rates, it is not easily adapted for predicting changes to

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weathering rates in the future. Runoff is dependent on many factors, including precipitation timing, intensity and land use changes, that are not well constrained by models of future climate. We address these issues by modeling future changes in the concentration of soil CO_2 derived from respiration (called *S(z)* herein) and dissolved CO_2 in soil pore water ($[CO_{2aq}]$) directly from climate variables that are predicted by climate models. These results are used to estimate future sources and sinks of carbon from terrestrial weathering.

Though large amounts of CO_2 flux data are available through Ameriflux and the global FluxNet network (http://fluxnet.ornl.gov/), these fluxes do not necessarily correlate to concentration of CO_2 within the soil because of differences in soil porosity and tortuosity, and are often influenced by atmospheric transport (Keppel-Aleks et al., 2011, 2012). Instead we compile previously published measurements of the concentration of CO_2 within soils to determine how $[CO_{2aq}]$ changes with climate. Brook et al. (1983) compiled mean growing season soil CO_2 concentrations from 19 soils worldwide and found relationships with climatic variables such as mean annual temperature (MAT), mean annual precipitation (MAP), potential evapotranspiration (PET), and actual evapotranspiration (AET). Using the relationship between growing season soil CO_2 and AET, Kessler and Harvey (2001) produced a global map for the flux of CO_2 into soil water. Here, we follow similar methods as Kessler and Harvey (2001) to model *S(z)* using its relationship to MAP, but because the previous relationships were based on only 19 soils worldwide, it is necessary to test the strength of these relationships with the inclusion of more data.

Given that a large proportion of chemical weathering occurs during the reaction of carbonic acid with silicate minerals in soils (West, 2012), we have produced an extensive literature review of soil respired CO_2 concentration measurements in order to study the spatial variability of gaseous and dissolved CO_2 concentrations within the soil atmosphere and pore water. The highest density of soil respired CO_2 concentration measurements are from the United States. In the western United States, the relationship between *S(z)* and mean annual precipitation (MAP) is strong where precipitation rates are 900 mm yr^{-1} or less. This relationship is then combined with model results from the North American Regional Climate Change Assessment Program (NARCCAP) for the decade of 2051–2060 to predict future changes to *S(z)* and $[CO_{2aq}]$. Understanding dissolved CO_2 trends makes it possible to identify potential sources and sinks of atmospheric CO_2 due to changes in weathering driven by anthropogenic climate change.

2. Background

Chemical weathering is an important component of the global carbon cycle, and influences the fluxes of carbon pools on multiple time scales. The primary driver of chemical weathering is carbonic acid, which is formed from the dissolution of CO_2 into water by the following reactions:

$$CO_{2(g)} + H_2O_{(l)} \leftrightarrow H_2CO_{3(aq)} \quad (1)$$

$$H_2CO_{3(aq)} \leftrightarrow H^+_{(aq)} + HCO^-_{3(aq)} \leftrightarrow H^+_{(aq)} + CO^-_{3(aq)}. \quad (2)$$

Because concentrations of CO_2 are much greater in soils than the atmosphere (up to hundreds of times atmospheric levels, de Jong and Schappert, 1972; Rightmire, 1978; Brook et al., 1983, carbonic acid formed in soils is the major source of acid for chemical weathering, and a large proportion of chemical weathering occurs within soils (West, 2012). The concentration of dissolved CO_2 ($[CO_{2aq}]$) in the soil water is controlled by Henry's law for the dissolution of gases into a liquid, which is influenced by the concentration of CO_2 in the soil atmosphere as well as the temperature of the soil water. Increasing the concentration of CO_2 in the soil atmosphere will increase $[CO_{2aq}]$, while increasing soil temperatures will decrease $[CO_{2aq}]$ because gases have lower solubility at higher temperatures. However, it is important to note that productivity also tends to increase with temperature (Raich and Schlesinger, 1992), which counteracts the effect of decreased gas solubility. The concentration of CO_2 in a soil is an important factor in chemical weathering rates (Amundson and Davidson, 1990; Oh and Richter, 2004). Over short time periods, weathering drives pedogenesis as well as the release of nutrients to plants for photosynthesis (Chadwick et al., 1994). These processes are important to the global carbon cycle on short time scales because soils store three times as much carbon as terrestrial vegetation (Schlesinger, 1977), and twice as much as the carbon stored in the surface ocean (Sigman and Boyle, 2000), so soil carbon pools have the potential to become important sinks and sources of atmospheric carbon (Trumbore et al., 1996; Knorr et al., 2005). Weathering also consumes CO_2 and removes it from the atmosphere through the formation of HCO_3^-, which is eventually transported to the oceans to be stored as $CaCO_3$ according to the following simplified equation:

$$CaSiO_3 + H_2CO_3 \rightarrow CaCO_3 + SiO_2 + H_2O \quad (3)$$

where one mole of CO_2 is consumed for every mole of silicate mineral that is weathered (Berner, 1992). While this process has been recognized as the long-term control on the concentration of atmospheric CO_2 for many years (Ebelmen, 1845; Berner et al., 1983), silicate weathering may also play an important role in the global carbon cycle on human timescales. The largest drawdown of carbon on human timescales is photosynthesis, but it is countered by a release of carbon through respiration of the same magnitude and does not represent a net flux of CO_2 from the atmosphere to land (Schlesinger, 1997). The global consumption of carbon through terrestrial weathering is estimated to be ~0.4 Gt $year^{-1}$ (Sarmiento and Gruber, 2006), which is not an insignificant number in comparison to the anthropogenic ~8 Gt $year^{-1}$ release of carbon. Increases to this weathering flux could partially offset increasing CO_2 emissions. Recent studies have observed increases in chemical weathering rates in arctic regions corresponding to increases in CO_2 consumption of up to 50% for particular watersheds, showing that the carbon fluxes can change significantly in a matter of decades (Gislason et al., 2009; Beaulieu et al., 2012).

In soils, CO_2 is formed through the respiration of plant roots, through the microbial oxidation of organic material (Witkamp, 1966; Brook et al., 1983; Kuzyakov, 2006), and also enters the soil through the diffusion of atmospheric CO_2 (Amundson and Davidson, 1990; Cerling, 1991; Sheldon and Tabor, 2013). The concentration of CO_2 in a soil is dependent primarily on the CO_2 production rate (Brook et al., 1983), but also on soil properties such as porosity and tortuosity (Raich and Schlesinger, 1992; Royer et al., 2001), the gradient of CO_2 between the soil and the atmosphere, and soil hydrology (Howard and Howard, 1993; Greenway et al., 2006; Gulbranson et al., 2011; Mintz et al., 2011). The production rate of soil CO_2 is a function of primary productivity (Wanner, 1970; Raich and Schlesinger, 1992). Primary productivity is controlled by climatic factors such as temperature, precipitation and nutrient availability (Rosenzweig, 1968; Lieth, 1975; Raich and Schlesinger, 1992; Raich and Potter, 1995; Ryan et al., 1996; Hu et al., 2001). With climate change, one would also expect to observe changes in soil CO_2 concentrations and chemical weathering rates and here we investigate the effects of changing climate on future soil CO_2 and dissolved CO_2 concentrations.

3. Methods

3.1. Modern soil CO_2 spatial variability

Measurements of summer total soil CO_2 concentrations from soils worldwide were compiled from the literature (see *Supplemental Table 1* for locations), representing all USDA soil orders except Vertisols and Histosols (Soil Survey Staff, 2010). In order to constrain