

RESEARCH ARTICLE

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Groundwater Depletion: A Significant Unreported Source of Atmospheric Carbon Dioxide

Warren W. Wood¹ and David W. Hyndman¹

¹Department of Earth and Environmental Sciences, Michigan State University, East Lansing, Michigan, USA

Key Points:

- Significant and previously unidentified CO₂ source to the atmosphere

Correspondence to:

www.wood@msu.edu

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Abstract Quantifying the annual flux of CO₂ (carbon dioxide) and equivalent emissions to the atmosphere is critical for both policy decisions and modeling of future climate change. Given the importance of greenhouse gas emissions to climate change and a recognized mismatch between sources and sinks (e.g., Liu & Dreybrodt, 2015), it is important to quantify these parameters. A significant and previously unrecognized CO₂ contribution arises from groundwater depletion (net removal from storage). The average annual 1.7 MMT (million metric tons) CO₂ released in the United States from this source is greater than approximately one third of the 23 major sources reported by the US EPA (United States Environmental Protection Agency) to the IPCC (Intergovernmental Panel on Climate Change; US EPA, 2016).

Plain Language Summary We suggest that groundwater depletion adds significant and measurable CO₂ to the atmosphere and should be considered as a source in future CO₂ budgets as groundwater depletion at the same or greater rate is likely to continue

Quantifying the annual flux of CO₂ (carbon dioxide) and equivalent emissions to the atmosphere is critical for both policy decisions and modeling of future climate change. Given the importance of greenhouse gas emissions to climate change and a recognized mismatch between sources and sinks (e.g., Liu & Dreybrodt, 2015), it is important to quantify these parameters. A significant and previously unrecognized CO₂ contribution arises from groundwater depletion (net removal from storage). The average annual 1.7 MMT (million metric tons) CO₂ released in the United States from this source is greater than approximately one third of the 23 major sources reported by the US EPA (United States Environmental Protection Agency) to the IPCC (Intergovernmental Panel on Climate Change; US EPA, 2016)

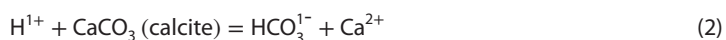
The US EPA reports to the IPCC on the annual CO₂ equivalent emissions for 23 major sources (US EPA, 2016) that ranged from less than 0.2 MMT for magnesium production and processing to 5208 MMT for fossil fuel combustion (Figure 1). Not included in these sources is the CO₂ released from groundwater depletion. If a groundwater aquifer system is in steady state, with recharge equaling discharge, there is no net CO₂ change relative to the atmosphere. However, if more groundwater is removed from storage than is recharged (depletion) there will be a net flux of CO₂ to the atmosphere.

Groundwater recharge from precipitation is in equilibrium with atmospheric CO₂. As it enters the unsaturated zone, where, owing to soil microbiological processes it encounters concentrations typically ten to one hundred times atmospheric CO₂. The recharging groundwater rapidly equilibrates to this higher concentration forming hydrogen (H¹⁺) and bicarbonate ions (HCO₃¹⁻) (equation (1));



This recharged groundwater is largely isolated from the atmosphere for hundreds to thousands of years, depending on aquifer storage volume, recharge, and discharge rates until it is discharged naturally to springs, lakes, rivers, wetlands, and oceans, or is extracted by pumping.

Many common sedimentary aquifer systems composed of sand, gravel, clay, sandstone, conglomerates, shales, and carbonates contain calcite (CaCO₃) in the skeletal mineral framework. The H¹⁺ ion reacts with the mineral framework creating bicarbonate and calcium (Ca²⁺) ions (equation (2));



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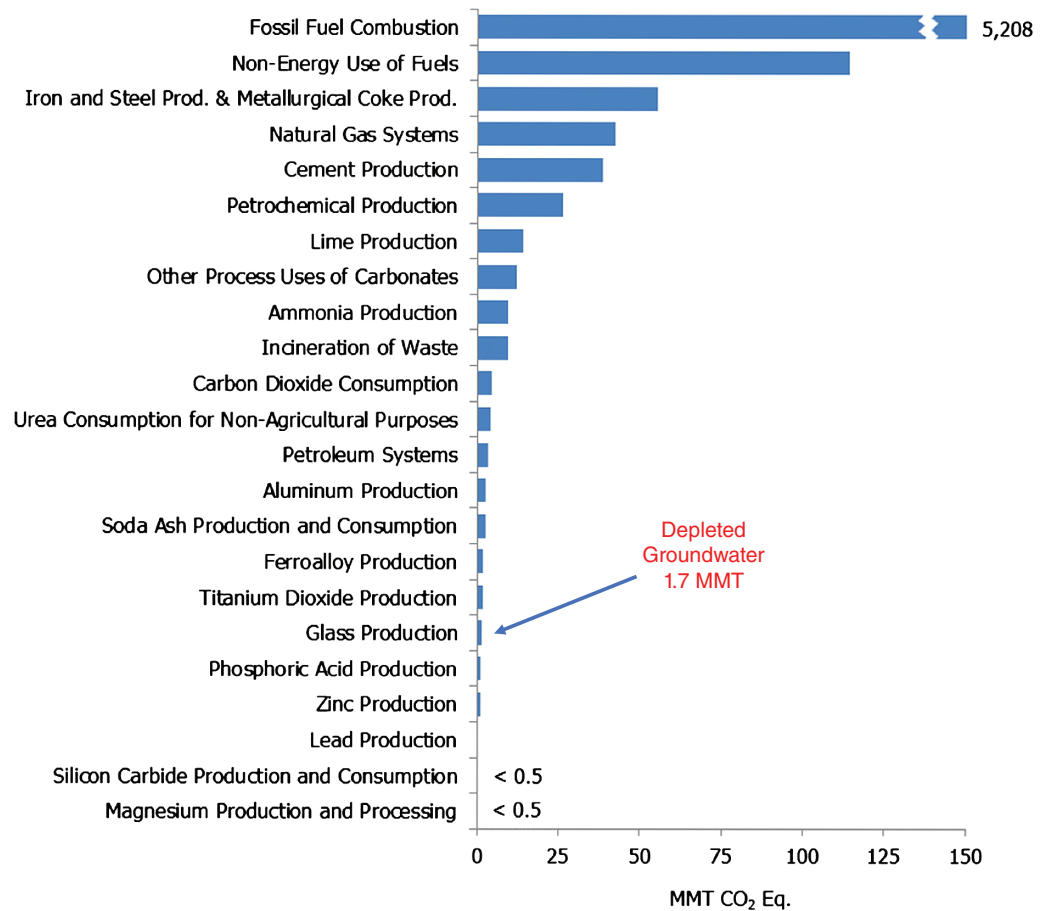
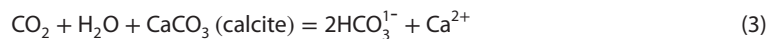


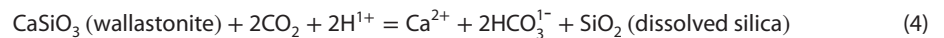
Figure 1. 2014 United States annual emission equivalent CO₂ for 23 sectors, the previously unidentified depleted groundwater of approximately 1.7 MMT (modified from US EPA, 2016) is greater than approximately one third of the 23 sources.

The combination of equations (1) and (2) yields (equation (3));



Thus, half the mass of carbon in bicarbonate ions originates from atmospheric and soil gas (CO₂), and the other half originates from the solid aquifer framework (CaCO₃).

In the less quantitatively important igneous and metamorphic aquifer environments, the skeletal mineral framework is composed largely of silicate minerals (such as CaSiO₃, wallastonite). The CO₂ reaction for this condition can be generalized and written as (equation (4));



In the case of silicate mineral weathering, the entire mass of carbon in bicarbonate in groundwater is a product of atmospheric and soil gases.

On exposure to the atmosphere, the groundwater will reequilibrate with the atmosphere releasing CO₂ and precipitating calcite (the reverse of equation (3)). Equation (4) is irreversible at ambient surface temperatures but does release CO₂ and precipitate calcite due to reequilibrium of CO₂ (equation (5));



It is assumed that discharged groundwater eventually reenters the hydrologic cycle as a vapor leaving solutes and solids at the surface. The CO₂ released from groundwater is typically isotopically lighter than

atmospheric CO₂ by between 2 and 12 per million depending on pH, temperature and whether the plants in the recharge area are of the C3, C4, or CAM photosynthetic cycle. Equations (1)–(5) are generalized reactions, but they are believed adequate for this proof of concept.

In a robust analysis of aquifers in the United States, Konikow (2013) estimated the total depletion of approximately 1000 km³ between 1900 and 2008. The median bicarbonate concentration of aquifer systems in the United States is approximately 190 mg/L based on 2003 representative samples from eight aquifer types of 30 U.S. Geological Survey, National Water Quality Assessment aquifer study units (Desimone, 2009). Using a conservative assumption that upon reentry of the groundwater to the surface, half of the bicarbonate (95 mg/L) in groundwater is converted to CO₂. This mass is equivalent to 68 mg/L CO₂, or 68 MMT CO₂ released to the atmosphere from approximately 1000 km³ of depletion. The current annual depletion in the United States is 25 km³ thus, per equation (6), the average annual current contribution of CO₂ to the atmosphere from US groundwater depletion is approximately 1.7 MMT per year.

$$\text{Atmospheric CO}_2\text{ contribution} = (\text{GW depletion}) * (\text{CO}_2\text{Equiv. Concentration in GW}) \quad (6)$$

The variability of the U.S. depletion estimate is not well constrained since different methods have been utilized for the estimate, however, the solute variability is estimated from a large and consistent database (Desimone, 2009). The HCO₃⁻ concentration of the 25 percentile of the 2003 groundwater samples is 95 mg/L and the 75 percentile is 293 mg/L (Desimone, 2009), providing a range of between 0.9 and 2.6 MMT/yr. CO₂ emission with a mean of 1.7 MMT/yr. This estimate of CO₂ release from groundwater depletion in the United States is equal to or greater than approximately one third of the 23 major sources (Figure 1).

The total amount of groundwater depletion on Earth is not well constrained but is estimated to be between 145 km³/yr. (Konikow, 2011) and 189 km³/yr. (Wada, 2016, mean of estimates from literature) based on volumetric estimates, models, GRACE satellite data, and limited water level monitoring. The average bicarbonate content of groundwater on Earth is likely similar to that measured in the United States and if we assume 20% variability in this groundwater depletion rate, then the global CO₂ flux from this source is likely between 8 and 17 MMT/yr. Although estimates of global groundwater depletions are less well constrained than in the United States, many large aquifers have experienced large water level declines (Konikow, 2011; Wada, 2016) and thus are significant contributors to the net global CO₂ flux; estimated annual global CO₂ emissions due to groundwater depletion are thus approximately 9.7 and 13.5 MMT based on US average solute analyses and groundwater depletion estimates of Konikow and Wada, respectively.

Although the range of variation in bicarbonate concentration and groundwater depletion are not well constrained, we believe that they are adequately represented for this proof of concept analysis. Thus, we suggest that groundwater depletion adds significant and measurable CO₂ to the atmosphere and should be considered as an important source in future CO₂ budgets since groundwater depletion is likely to continue at the same or greater rate in the future (Konikow, 2011, 2013; Wada, 2016). Given the importance of this greenhouse gas source, we encourage additional data synthesis and analysis to better estimate global groundwater depletion rates and bicarbonate concentrations.

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