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Anthropogenic Water Withdrawals Modify Freshwater Inorganic Carbon Fluxes across the United States

Elizabeth M. Flint,* Matthew J. Ascott, Daren C. Gooddy, Mason O. Stahl, and Ben W. J. Surridge

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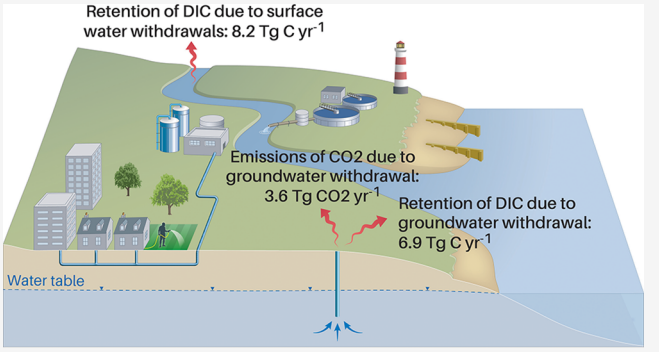
ABSTRACT: Quantifying inorganic carbon fluxes to and from freshwater environments is essential for the accurate determination of the total amount of carbon exported to both the atmosphere and oceans. However, understanding of how anthropogenic freshwater withdrawals perturb land-freshwater-ocean and freshwater-atmosphere inorganic carbon fluxes is limited. Using the United States (US) as an exemplar, we estimate that fresh surface water withdrawals across the country during the year 2015 resulted in a median gross dissolved inorganic carbon (DIC) retention flux of 8.2 (uncertainty range: 6.7−9.9) Tg C yr^{-1}, equivalent to 28.3% of the total export of DIC to the oceans from US rivers. The median gross retention flux due to fresh groundwater withdrawals was 6.9 (uncertainty range: 5.3−8.8) Tg C yr^{-1}, over eight times the magnitude of the DIC flux to the oceans by US subterranean groundwater discharge. The degassing of CO_2 supersaturated groundwater following withdrawal emitted 3.6 (uncertainty range: 2.2−5.5) Tg of CO_2 yr^{-1}, 112% larger than previous estimates. On a county level, these CO_2 emissions exceeded CO_2 emissions from major emitting facilities across 45% of US counties. Reported results and a data analysis framework have important implications for the accurate development of carbon budgets across the US and around the world.



KEYWORDS: *dissolved inorganic carbon, carbon dioxide emissions, freshwater withdrawals, biogeochemical cycling, carbon budgets*

1. INTRODUCTION

Fresh waters are critical, reactive interfaces that influence the transport and fate of carbon (C).[1] Accurately estimating fluxes of the multiple chemical and physical species of C (dissolved, particulate, inorganic, and organic) to and from freshwater environments is essential for understanding the quality of potable water, ecosystem functioning, and the role of fresh waters in the transfer of different C fractions between terrestrial, atmospheric and oceanic systems.[1−3] The delivery of both organic and inorganic C to the oceans by rivers and subterranean groundwater flow, as well as the burial of organic C within freshwater sediments and outgassing of CO_2 from fresh waters to the atmosphere, have been estimated on global[1,4−7] and continental scales.[3,8,9] However, despite growing recognition of fresh waters as critical interfaces that moderate the global C cycle,[10] many processes with the potential to perturb C fluxes remain poorly constrained, particularly those associated with groundwater and anthropogenic activities. Human activities, including climate and landscape change and the construction of reservoirs, can impact C burial, outgassing, and export.[11−13] While some research has focused on developing a more integrated understanding of freshwater C cycling,[14,15] the continued omission of these anthropogenic influences within C budgets can lead to biased estimation and associated uncertainty of other C balance components.[7,11,16−18] This may hinder the development of the robust and integrated C budgets that are necessary to inform policies that are able to respond effectively to a changing C cycle.[18]

Freshwater withdrawals are defined by the United States Geological Survey (USGS) as "the total amount of water removed from the water source for a particular use",[19] with these sources being most commonly either a groundwater well or surface water intake. Recent research has identified the anthropogenic withdrawal of fresh water as a potentially significant mechanism perturbing C cycling in fresh waters. Globally, withdrawals of groundwater were estimated to bring 19 Tg C yr^{-1} to surface water environments,[20] with 70% of this flux (13.3 Tg C yr^{-1}) being in the form of dissolved inorganic carbon (DIC). The degassing of CO_2 supersaturated groundwaters upon their equilibration with the atmosphere[21−25] and

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the treatment of organic C within withdrawn fresh water prior to distribution[26] are identified as sources of atmospheric CO_2 around the world. Reservoir drawdown areas, which are hotpots for emissions of CO_2 to the atmosphere, can also be created in part due to anthropogenic water withdrawal.[27] Freshwater withdrawals have also been found to prevent the downstream export of organic C to the oceans by rivers.[26,28] Despite these findings, an integrated understanding of the impact that both fresh groundwater and surface water withdrawals can have on C cycling, either nationally or globally, is yet to be developed. Perturbations to the C cycle continue to generate increased risks of tipping over a range of planetary boundaries.[29] Addressing this gap in understanding is therefore increasingly urgent and the focus of the research reported here.

Fluxes of total dissolved C from United States (US) fresh waters to the ocean are predominantly in the form of DIC.[30] The country has some of the highest DIC exports to the ocean of anywhere globally,[6,17] with the Mississippi River making the largest individual contribution (17.39 Tg C yr^{-1})[30] to the total amount of DIC exported by US rivers to the oceans (29 Tg C yr^{-1}).[3] The US also has some of the highest total and per capita withdrawals of fresh water in the world.[31] The removal of this water from both groundwater and surface water environments has been identified as an important inorganic nitrogen retention mechanism[32] and a nationally significant source of CO_2 emissions.[21,25] In the research reported here, the US is used as an exemplar to develop and apply a new framework in order to quantify the impacts of both groundwater and surface withdrawals on freshwater DIC fluxes. We hypothesize that

1. Surface water and groundwater withdrawals will perturb lateral dissolved inorganic carbon fluxes within freshwater environments across the United States
2. Degassing fresh groundwater withdrawals will act as locally important sources of atmospheric CO_2 that will vary spatially and by water use sector across the United States

These hypotheses are addressed using a range of publicly available data sets including freshwater withdrawal volumes and DIC concentrations. The implications of these US-based findings for global C cycling and future research needs in this area are discussed.

2. MATERIALS AND METHODS

2.1. Estimating the Gross Impact of Withdrawals of Fresh Water on the Lateral Export of DIC. The gross fluxes of DIC removed from fresh waters due to groundwater and surface water withdrawals (WD-DIC_{gw} and WD-DIC_{sw}, in Tg C yr^{-1}) were estimated for each county across the US as the product of county-level fresh groundwater and surface water withdrawal volumes for each major water use sector (WD_{gw} and WD_{sw}, in L yr^{-1}) during the year 2015,[33] and median county-level groundwater and surface water DIC concentrations (DIC_{gw} and DIC_{sw}, in Tg C L^{-1},eqs 1 and 2).

The workflow developed in this research for obtaining DIC_{gw} and DIC_{sw} concentrations is outlined in Supplementary Note 1. Concentrations of DIC are infrequently measured during water quality monitoring, and so, all water quality parameter queries were extended to be between 01.01.2010 and 31.12.2020. Data retrievals from the Water Quality Portal[34] returned no measured DIC data for groundwater sites and measured surface water DIC data for only 79 counties. Given this lack of measured DIC concentration data, THINCARB (Thermodynamic modeling of Inorganic CARBon) was used to model DIC_{gw} and DIC_{sw} concentrations.[35] Model inputs were queried using the advanced search tool within the Water Quality Portal.[34] More specifically, alkalinity (from filtered samples), pH, water temperature, altitude, and calcium concentrations were queried as characteristics (Table S1). This facilitated the return of values from both Environmental Protection Agency (EPA) and USGS databases, as well as state, federal, tribal, and local agencies. This enabled the modeling of DIC_{gw} and DIC_{sw} concentrations across 1,024 and 584 counties, respectively (Figures S1 and S2).

$$\text{WD-DIC}_{gw} = \text{WD}_{gw} \times \text{DIC}_{gw} \quad (1)$$

$$\text{WD-DIC}_{sw} = \text{WD}_{sw} \times \text{DIC}_{sw} \quad (2)$$

Where input data required for modeling DIC concentrations was not available, equilibrium equations,[36] using measured pH and the measured concentration of either carbonate or bicarbonate (CO_3^{2-} or HCO_3^-) from groundwaters and surface waters were used to calculate DIC_{gw} and DIC_{sw} concentrations for a further 463 and 188 counties, respectively (Figures S1 and S2). Measured values of pH and CO_3^{2-} and HCO_3^- concentrations were queried as characteristics using the Water Quality Portal's advanced search tool.[34] For the 1621 and 2223 counties without sufficient input data to model or calculate DIC_{gw} and DIC_{sw} values, respectively, median state-level DIC concentrations (derived from THINCARB modeling) were applied to the state's constituent county (Figures S1 and S2). It should be noted that DIC concentration data was not able to be linked to specific withdrawals from individual groundwater wells or surface water intakes, due to the fact that withdrawal data is provided on a county-level resolution.[33] The limitations associated with acquiring concentration data using these various approaches are discussed in Supplementary Note 1. County-level fluxes were aggregated to give a national-level total and lower and upper estimates for all fluxes were made by applying a ± 10% uncertainty on withdrawal volumes[37] and using 25th and 75th percentile DIC concentrations within eqs 1 and 2, respectively.[38] County-level fluxes were also normalized for land area in kg C km^{-2} yr^{-1}.

2.2. Estimating the Net Impact of Freshwater Withdrawals on the Lateral Export of DIC. Fully understanding the impact of freshwater withdrawals on C cycling requires the fate of the withdrawn DIC to be determined. The research reported here attempts to estimate net withdrawal DIC fluxes by assessing the key processes that may affect the speciation and flux of DIC returned to fresh waters following withdrawal. The sources of data and assumptions used to make initial estimates of net WD-DIC fluxes for major US water use sectors are shown in Table S2, with the methodology detailed in Supplementary Note 2. These net fluxes can be defined as the flux of DIC that is permanently prevented from downstream transport on time scales relevant to overall C budgets, due to either groundwater or surface water withdrawal, having accounted for speciation changes, return flows, and consumption. A positive net WD-DIC flux indicates DIC retention from the fresh surface water or groundwater system, whereas a negative flux denotes a net contribution of DIC to fresh water. As a hypothetical example, if DIC was removed exclusively from groundwater via

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Table 1. Gross Freshwater Withdrawal Dissolved Inorganic Carbon Fluxes for Groundwater and Surface Water ($WD\text{-}DIC_{gw}$ and $WD\text{-}DIC_{sw}$), Expressed As a Percentage, Compared to Other Components of the Freshwater Carbon Cycle across the United States

flux ($Tg\ C\ yr^{-1}$)	outgassing of CO_2 by rivers and lakes (85.3)[a]	river DIC export to the ocean (29)[a]	total surface water export DIC flux (114.3)[a]	subterranean groundwater discharge DIC flux to the ocean (0.7)[b]	total DIC flux to the ocean by rivers and groundwater (29.7)
$WD\text{-}DIC_{sw}$ (6.7−9.9)	7.9−11.6	23.1−34.1	5.9−8.7		
$WD\text{-}DIC_{gw}$ (5.3−8.8)				757−1257	
$WD\text{-}DIC_{total}$ (12.0−18.7)					40.4−63.0

[a]Butman, Stackpoole, Stets, McDonald, Clow and Striegl.[3] [b]Estimated using the total subterranean groundwater discharge estimate made by Sawyer, David, and Famiglietti[41] and the median DIC concentration of groundwater determined in this study (48.2 mg C L^{-1}).

withdrawals but was then returned entirely to surface water after use via effluent discharge, this would result in a positive net $WD\text{-}DIC_{gw}$ flux and a negative net $WD\text{-}DIC_{sw}$ flux.

Data were not available for a range of additional key processes, including water consumption and key chemical processes involving DIC within the industry and the volume of irrigation and mining return flows to both surface water and groundwater. This meant that net $WD\text{-}DIC_{sw}$ flux estimates for irrigation, public supply, industrial and mining water use sectors, and net $WD\text{-}DIC_{gw}$ flux estimates for irrigation and mining water use sectors, could not be made at this time (Figure 2).

2.3. Estimating CO_2 Emissions Associated with Degassing Groundwater Withdrawals. County-level emissions of CO_2 due to the degassing of CO_2 supersaturated groundwater withdrawals ($WD\text{-}CO_{2\ gw}$, in kg CO_2 yr^{-1}) were estimated as the product of county-level fresh groundwater withdrawal volumes (WD_{gw}, in L yr^{-1}) and median county-level excess CO_2 concentrations of groundwater when in equilibrium with the atmosphere ($E[CO_{2\ gw\text{-}atm}]$; eq 3). $E[CO_{2\ gw\text{-}atm}]$ concentrations were estimated using excess CO_2 partial pressures ($EpCO_2$) modeled by THINCARB using inputs described in Section 2.1. $EpCO_2$ is the ratio of the CO_2 partial pressure in the groundwater sample ($pCO_{2\ gw}$) to the CO_2 partial pressure of the atmosphere ($pCO_{2\ atm}$), which was assumed to be 0.0003994 atm for the year 2015 (eq 4).

$$WD\text{-}CO_{2gw} = WD_{gw} \times E[CO_{2gw-atm}] \tag{3}$$

$$EpCO_2 = \frac{pCO_{2gw}}{pCO_{2atm}} \tag{4}$$

This methodology assumes the rate of CO_2 degassing from supersaturated groundwaters to be faster than the rate of groundwater's return to aquifers after use, as well as the full equilibration of groundwater with the atmosphere.[39,40] The impact of these assumptions upon $WD\text{-}CO_{2\ gw}$ fluxes is further investigated within Supplementary Note 4. $EpCO_2$ values were subsequently used to determine $E[CO_{2\ gw\text{-}atm}]$ concentrations using eqs 5−8. The use of the Van't Hoff equation allowed changes in temperature (T) to be related to changes in equilibrium constant (K_H; eq 5). $pCO_{2\ atm}$ values were then corrected using K_H to give the partial pressure of groundwater when it was in equilibrium with the atmosphere ($pCO_{2\ gw\text{-}atm}$; eq 6). $pCO_{2\ gw}$ was then estimated as the product of $EpCO_2$ and $pCO_{2\ gw\text{-}atm}$ (eq 7). Finally, excess concentrations of CO_2 in groundwater samples ($E[CO_{2\ gw\text{-}atm}]$), in mg CO_2 L^{-1}, were determined as the difference between $pCO_{2\ gw}$ and $pCO_{2\ gw\text{-}atm}$ (eq 8). Median state-level $E[CO_{2\ gw\text{-}atm}]$ concentrations were applied to the 2,084 counties without a modeled $EpCO_2$ value. See Supplementary Data 1 for full calculations.

$$K_H = 0.034e^{-(2400(\frac{1}{289}(\frac{1}{273+T})))} \tag{5}$$

$$pCO_{2gw-atm} = K_H \times pCO_{2atm} \tag{6}$$

$$pCO_{2gw} = EpCO_2 \times pCO_{2gw-atm} \tag{7}$$

$$E[CO_{2gw-atm}] = (pCO_{2gw} - pCO_{2gw-atm}) \times 1000 \times 44.01 \tag{8}$$

2.4. Contextualizing the Magnitude of Gross Freshwater Withdrawal DIC Fluxes and Groundwater Withdrawal CO_2 Emissions. The magnitude of the gross national-level $WD\text{-}DIC_{sw}$ flux was contextualized through its comparison with the national-level DIC flux from US fresh surface waters, which is the sum of lateral DIC export to the oceans and the outgassing of CO_2 from rivers and lakes.[3] The gross national-level $WD\text{-}DIC_{gw}$ flux was compared to the subterranean groundwater discharge DIC flux to the oceans (DIC_{SGD}) across the US (Table 1). The DIC_{SGD} flux (0.7 Tg C yr^{-1}) was estimated as the product of the annual US fresh subterranean groundwater discharge volume (1.5×10^{13} L yr^{-1}),[41] and the median DIC_{gw} concentration determined in this research (48.2 mg C L^{-1}). The contribution that withdrawals from each individual water use sector make to these gross withdrawal fluxes was also assessed.

The potential importance of the national-level $WD\text{-}CO_{2\ gw}$ flux was evaluated through its comparison with the estimated CO_2 emissions from US rivers and lakes.[3] $WD\text{-}CO_{2\ gw}$ fluxes due to irrigation and public supply water use sectors were also compared to other sector-specific CO_2 emissions, including those from agricultural liming practices[42] and the electricity generation for both the pumping of groundwater for irrigation[43] and the operation of drinking water systems.[44] Counties with significant $WD\text{-}CO_{2\ gw}$ emissions were identified through the comparison of county-level $WD\text{-}CO_{2\ gw}$ estimates to the county's total CO_2 emissions from major sources,[45] specifically, those sources obliged to report to the US EPA's Greenhouse Gas Reporting Program ($GHGRP\text{-}CO_2$). These detailed emissions data are collected from approximately 7300 greenhouse gas emitting facilities across the US that emit over 25,000 t of CO_2 yr^{-1}, either via combustion or process emissions. When combined, these emissions account for around 50% of total US greenhouse gas emissions.[46]

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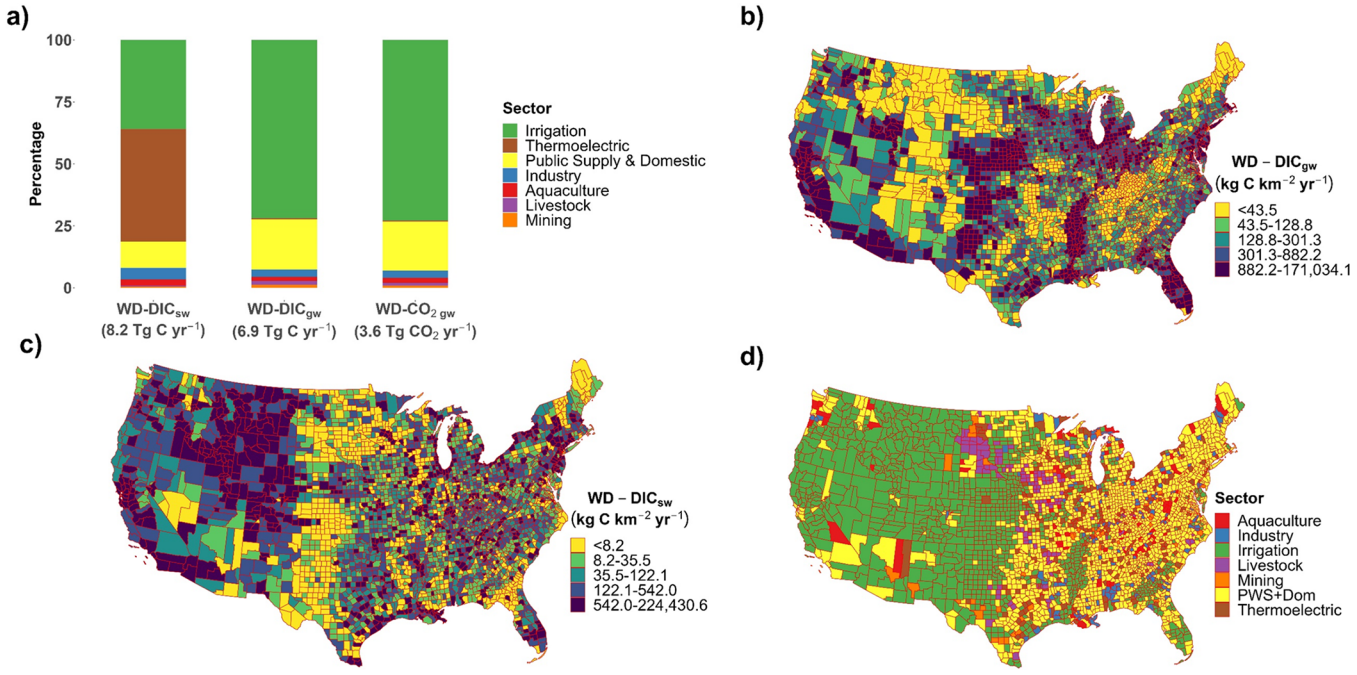

Figure 1. Freshwater withdrawal dissolved inorganic carbon flux (WD-DIC) estimates across the United States. (a) Contribution of water use sector withdrawals to gross national-level surface water and groundwater withdrawal DIC fluxes (WD-DIC$_{sw}$ and WD-DIC$_{gw}$), and the national-level emissions of CO_2 due to degassing groundwater withdrawals (WD-$CO_{2\ gw}$) across the contiguous United States. (b) Total area-normalized county-level groundwater withdrawal DIC fluxes (WD-DIC$_{gw}$) across the contiguous United States. (c) Total area-normalized county-level surface water withdrawal DIC fluxes (WD-DIC$_{sw}$) across the contiguous United States. Scales represent the quintile groups. (d) Water use sector that makes the largest contribution to the gross total withdrawal DIC flux (WD-DIC$_{total}$) for each county across the contiguous United States. Linework created using the "usmap" package in R.[48]

3. RESULTS

3.1. Impact of Withdrawals of Fresh Water on Lateral DIC Fluxes. *3.1.1. Gross DIC Carbon Fluxes Associated with Withdrawals of Fresh Water.* Median groundwater and surface water DIC concentrations (DIC$_{gw}$ and DIC$_{sw}$) across the US between 01.01.2010 and 31.12.2020 were modeled (using THINCARB) to be 48.2 and 29.7 mg C L^{-1}, respectively. County-level surface water and groundwater DIC concentrations used within flux calculations and the corresponding method of determination are reported in Supplementary Data 1 and Figure S2. Gross median national-level fresh groundwater and surface water withdrawal DIC fluxes (WD-DIC$_{gw}$ and WD-DIC$_{sw}$) across the US were 6.9 (5.3−8.8) and 8.2 (6.7−9.9) Tg C yr^{-1}, respectively (Table 1), with values in parentheses representing lower and upper estimates (Section 2.1). Irrigation and public supply withdrawals contribute 92% of the total WD-DIC$_{gw}$ flux, and irrigation and thermoelectric withdrawals contribute 81% of the national-level WD-DIC$_{sw}$ flux (Figure 1a). Counties with the largest area-normalized WD-DIC$_{gw}$ and WD-DIC$_{sw}$ fluxes were concentrated within the states of Nebraska (NE), Florida (FL), and California (CA; Figure 1b), and Montana (MT) and Wyoming (WY; Figure 1c), respectively. The water use sector making the largest contribution to total gross WD-DIC fluxes (WD-DIC$_{total}$; the sum of WD-DIC$_{gw}$ and WD-DIC$_{sw}$) for each county across the US is shown in Figure 1d, with the irrigation and public supply sectors being the largest contributors to counties across the western and eastern regions of the country, respectively.

The national-level WD-DIC$_{gw}$ flux (5.3−8.8 Tg C yr^{-1}) was estimated to be 7−12 times larger than the median estimate of the US subterranean groundwater discharge DIC flux to the ocean (Table 1). The national-level WD-DIC$_{sw}$ flux (6.7−9.9 Tg C yr^{-1}) was equivalent to 7.9−11.6% of the outgassing of CO_2 by rivers and lakes and 23.1−34.1% of the DIC exported to the oceans by rivers, making it equivalent to 5.9−8.7% of the total surface water DIC flux (Table 1). The gross national level WD-DIC$_{total}$ flux (12−18.7 Tg C yr^{-1}) was equivalent to 40.4−63.0% of the total discharge of DIC to the oceans from fresh groundwater and rivers across the US (Table 1).

3.1.2. Net Dissolved Inorganic Carbon Fluxes Associated with Withdrawals of Fresh Water. Net national-level WD-DIC fluxes that could be estimated in this research are summarized in Figure 2. It was estimated that 0.18 Tg C yr^{-1} and 0.30 Tg C yr^{-1} of the irrigation WD-DIC$_{sw}$ and WD-DIC$_{gw}$ fluxes could be returned to groundwater via leakage during irrigation conveyance, respectively. Determining the fate of DIC once both surface waters and groundwaters are used for irrigation is beyond the scope of this study (Section 3.2). Thermoelectric plants utilizing water-recirculating technologies result in net WD-DIC$_{gw}$ and WD-DIC$_{sw}$ fluxes of 0.024 Tg C yr^{-1} and 0.17 Tg C yr^{-1}, respectively. The return of withdrawals from once-through cooling plants to surface water environments via effluents was estimated to cause net WD-DIC$_{gw}$ and WD-DIC$_{sw}$ fluxes of 0.008 and −0.008 Tg C yr^{-1}, respectively. The reduced solubility of CO_2 within once-through cooling plant effluents due to their elevated temperatures was estimated to cause the degassing of 0.35 Tg of CO_2 yr^{-1} (Supplementary Note 3).

The return of WD-DIC$_{sw}$ to groundwater due to leakage from public supply distribution pipes and outdoor water use at domestic residences resulted in a net public supply WD-DIC$_{sw}$ flux of 0.43 Tg C yr^{-1}. Approximately 95% of the remaining

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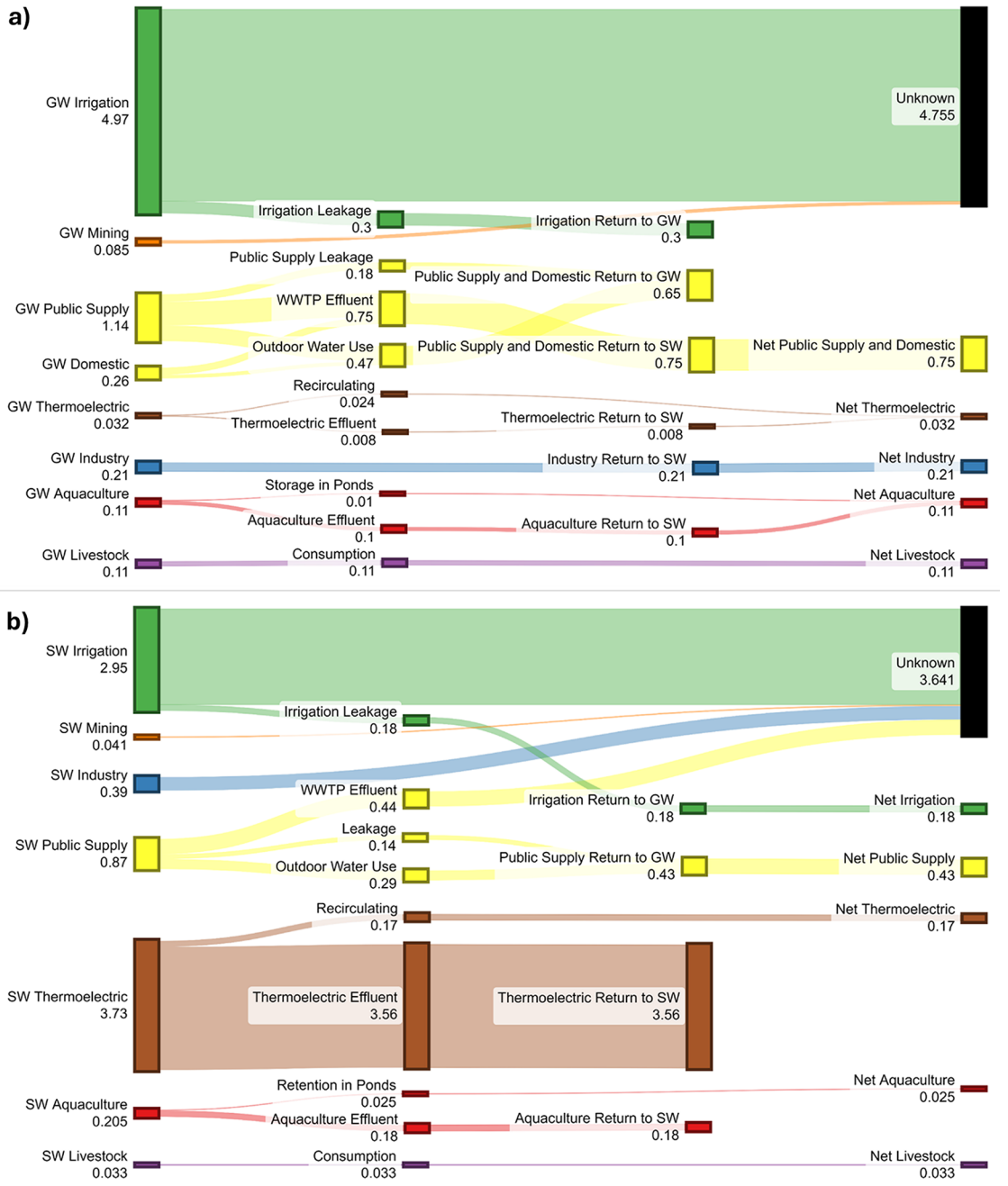

Figure 2. Median gross and net freshwater withdrawal DIC fluxes for each major water use sector across the United States. (a) Sankey diagram showing median gross and net freshwater withdrawal DIC fluxes for each major water use sector across the United States due to groundwater withdrawals. (b) Sankey diagram showing median gross and net freshwater withdrawal DIC fluxes for each major water use sector across the United States due to surface water withdrawals.

public supply and domestic WD-DIC_{gw} and WD-DIC_{sw} fluxes will be returned to wastewater treatment plants and subsequently be released into a surface water environment,[47] resulting in a combined net public supply and domestic WD-DIC_{gw} flux of 0.75 Tg C yr^{-1}.

The return of groundwater used within the industrial sector to surface water environments results in a net industry WD-DIC_{gw} flux of 0.21 Tg C yr^{-1}. The consumption of water for livestock results in net WD-DIC_{sw} and WD-DIC_{gw} fluxes of 0.033 and 0.11 Tg C yr^{-1}, respectively. The storage of fresh water within aquaculture ponds was estimated to temporarily retain 0.010 and 0.025 Tg C yr^{-1} from groundwater and surface waters, respectively. In addition to the storage of DIC in ponds, the return of water exclusively to surface water environments after aquacultural use results in a total net aquaculture WD-DIC_{gw} flux of 0.11 Tg C yr^{-1}.

3.2. Degassing Groundwater Withdrawal CO_2 Emissions. Through the use of the THINCARB model, the median excess CO_2 partial pressure of groundwater ($EpCO_2$) across the US was estimated to be 29.2 (unitless), with 97% of samples being supersaturated relative to the atmosphere ($EpCO_2 > 1$). The median national-level excess CO_2 concentration of groundwater ($E[CO_{2\ gw\text{-}atm}]$) was estimated to be 13.7 mg of CO_2 L^{-1}. Modeled $EpCO_2$ values and calculated $E[CO_{2\ gw\text{-}atm}]$ concentrations for all groundwater sites are reported in Supplementary Data 1. The national-level

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Table 2. National-Level CO_2 Emissions Associated with the Degassing of Withdrawn Groundwaters (WD-CO_{2gw}), Expressed As a Percentage, Compared to Other Major National-Level CO_2 Sources across the United States

flux (Tg CO_2 yr^{-1})	outgassing by rivers and lakes (313)[a]	facility emissions (GHGRP-CO_2) (2640)[b]	liming practices (3.8)[c]	electricity use for pumping irrigation groundwater (10.7)[d]	degassing of CO_2 from groundwater irrigation withdrawals (1.43)[e]	electricity generation for drinking water system operation (26.5)[f]
national-level total						
WD-CO_{2gw} (2.2−5.5)	0.7−1.8	0.08−0.2				
national-level irrigation						
WD-CO_{2gw} (1.6−3.9)			42.1−102.6	14.9−36.4	112−273	
national-level public supply & domestic						
WD-CO_{2gw} (0.5−1.1)						1.8−4.1

[a]Butman, Stackpoole, Stets, McDonald, Clow and Striegl.[3] [b]USEPA.[45] [c]USEPA.[42] [d]Driscoll, Conant, Marston, Choi, and Mueller.[43] [e]Qin, Duan, Zou, Chen, Huang, and Rosa.[25] [f]Zib, Byrne, Marston, and Chini.[44]

emission of CO_2 due to the degassing of CO_2 supersaturated groundwater withdrawals (WD-$CO_{2\,gw}$) across the US was estimated to be 3.6 (2.2−5.5) Tg CO_2 yr^{-1} (Table 2), with irrigation and public supply withdrawals contributing 93% of this total (Figure 1a). Counties with the largest area-normalized WD-$CO_{2\,gw}$ fluxes were generally concentrated within the states of Nebraska (NE) and North Carolina (NC; Figure 3a).

The national-level WD-$CO_{2\,gw}$ flux (2.5−5.5 Tg CO_2 yr^{-1}) was estimated to be equivalent to between 0.7 and 1.8% of the CO_2 outgassed by rivers and lakes and 0.08−0.2% of total CO_2 emissions from major directly emitting facilities required to report to the US EPA's Greenhouse Gas Reporting Program (GHGRP-CO_2; Table 2). The national-level WD-$CO_{2\,gw}$ flux due to irrigation withdrawals (1.6−3.9 Tg CO_2 yr^{-1}) was equivalent to 42.1−102.6% of the CO_2 emissions associated with the country's liming practices and between 14.9 and 36.4% of the CO_2 emissions associated with electricity generation for pumping groundwater for irrigation use. The national-level WD-$CO_{2\,gw}$ flux due to public supply and self-supplied domestic withdrawals (0.5−1.1 Tg CO_2 yr^{-1}) was equivalent to between 1.8 and 4.1% of the CO_2 emissions associated with electricity generation for the operation of US drinking water systems (Table 2). Approximately 45% of all US counties (1,401) were estimated to have median WD-$CO_{2\,gw}$ fluxes that exceeded county-level GHGRP-CO_2 emissions, with these counties concentrated in the states of Montana, South Dakota (SD), Nebraska, and Idaho (Figure 3b).

4. DISCUSSION

4.1. Anthropogenic Withdrawals of Fresh Water Perturb the Lateral Transport of DIC. This research provides the first insights into how anthropogenic withdrawals of fresh water across the US may act as an important DIC retention mechanism, delaying the delivery of DIC to the ocean via fresh subterranean groundwater discharge and surface water export. The magnitude of the country's gross surface water and groundwater withdrawal DIC fluxes (WD-DIC_{sw} and WD-DIC_{gw}), in comparison to other DIC fluxes to the oceans, suggests that withdrawals may cause important perturbations to overall national-level DIC cycling (Table 1). Many overall C budgets are determined using a mass balance approach. These findings therefore emphasize the importance of incorporating WD-DIC fluxes into national-scale C cycling budgets as a way of more accurately determining other budget components.[3,11,16,18] Uncertainties associated with gross WD-DIC fluxes, largely due to the scarcity of measured DIC concentration data (Supplementary Note 1), should be reduced as more temporally and spatially resolved water use and DIC concentration data become available.[49]

4.2. Sector Dependent Controls on Net DIC Fluxes. It is important to note that estimating gross WD-DIC fluxes provides a necessary first step in understanding the net impact of freshwater withdrawals upon DIC cycling across the US. Subsequent to freshwater withdrawal, a vast range of interlinked hydrological, biological, and chemical processes will modify the amount of DIC that is either retained or returned to fresh waters. This means that gross WD-DIC flux estimates often exceed those of their net WD-DIC flux counterparts. Comparing gross WD-DIC fluxes with other major DIC fluxes is intended to assess the potential maximum magnitude and importance of WD-DIC fluxes in the broader context of freshwater DIC cycling.

The retention of DIC through the consumption and storage of water varies across the country and between different water use sectors.[50] The capacity for recirculating thermoelectric plants to temporarily store DIC is small compared to those of other naturally occurring mechanisms that remove DIC from fresh waters, such as riverine export of DIC to the oceans (Figure 2; Table 1). However, this capacity may increase in the future given the predicted transition to recirculating technologies across the US.[51] The temporary storage of water within thermoelectric plants, aquaculture ponds, and both irrigation and municipal water towers may impact both DIC burial and CO_2 emissions.[12] The storage and consumption of water within industrial and mining water use sectors are largely unknown and complex to estimate,[52−54] contributing to unresolved net WD-DIC flux estimates for these sectors.

Return flows of withdrawn water can also redistribute water and associated DIC between groundwater and surface water environments.[55,56] Industrial, thermoelectric, public supply, and aquaculture sectors return both groundwater and surface water almost exclusively to surface water environments via effluents, resulting in the net removal of DIC from ground-

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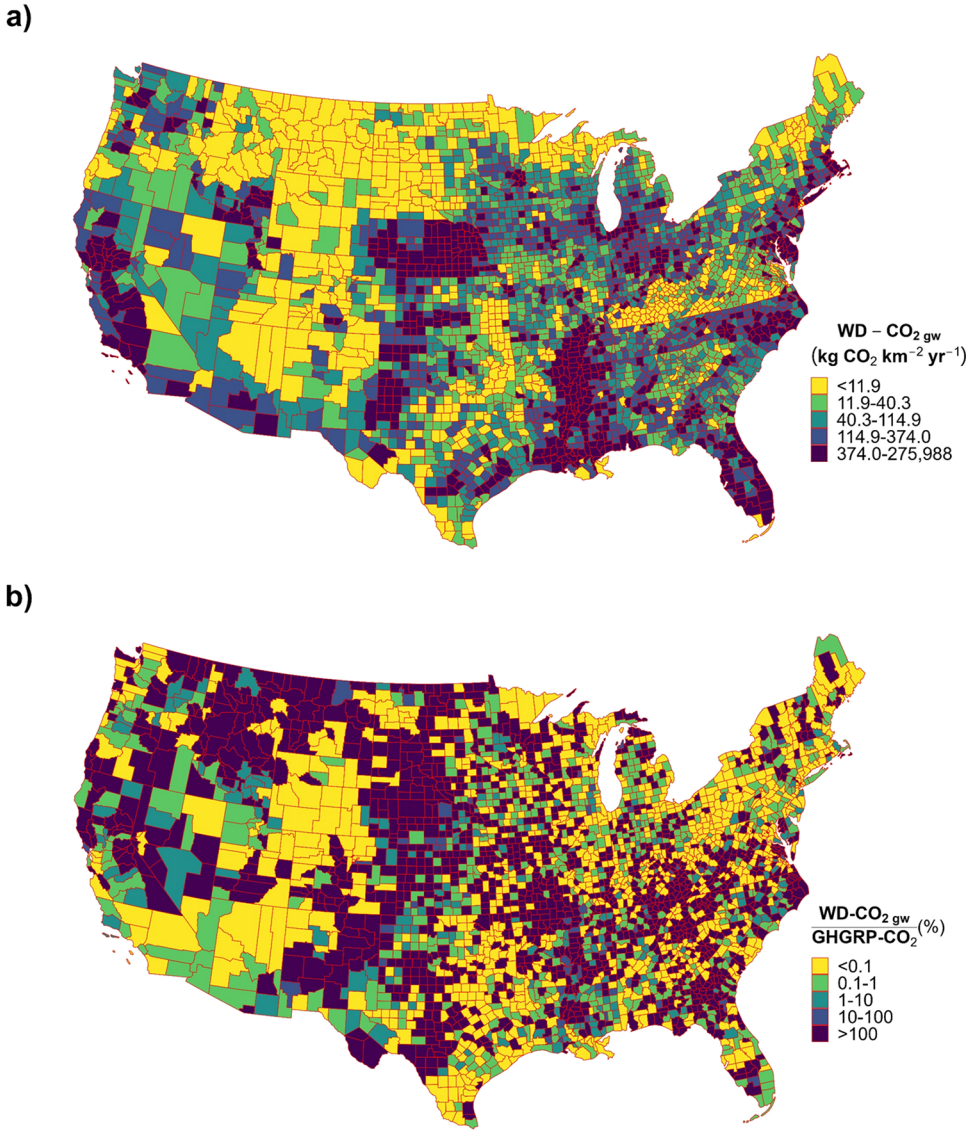

Figure 3. Emissions of carbon dioxide from degassing groundwater withdrawals across the United States. (a) Total area-normalized county-level emission of carbon dioxide due to groundwater withdrawals (WD-$CO_{2\ gw}$) across each county of the contiguous United States. (b) Percentage equivalence of carbon dioxide emissions due to degassing groundwater withdrawals (WD-$CO_{2\ gw}$), to the carbon dioxide emissions from the facilities required to report to the Greenhouse Gas Reporting Program (GHGRP-CO_2), for each county across the contiguous United States. GHGRP-CO_2 data was sourced from the USEPA.[45] Linework created using the "usmap" package in R.[48]

water (Figure 2a). Conversely, the leakage of water from main distribution pipes and return of water during outdoor water use can return biologically important nutrients to subsurface environments,[32,57] thus resulting in the net removal of DIC from surface waters (Figure 2b). The use of water for irrigation and mining will also result in the complex and localized movement of water and associated DIC between groundwater, surface water, and atmospheric environments.[55,58−61] However, there are no comprehensive national-level data sets disclosing the volume of water that is retained and returned to each environment. For example, the consumptive use of surface water for irrigation across the US was modeled to decrease fresh surface water discharge to the ocean by 4.2%.[59] A lack of data relating to whether this consumption was due to evaporative loss or reallocation to groundwater, as well as any associated C speciation changes, hinders the determination of net irrigation WD-DIC_{sw} flux. Despite this, the (4.2%) decrease in surface water export can be used as a means of validating the magnitude of our irrigation WD-DIC_{sw} flux. Applying a proportional decrease in the reported river DIC export flux (29 Tg C yr^{-1})[3] would result in a retention flux of 1.3 Tg C yr^{-1} due to fresh surface water withdrawals for irrigation, which is around 44% of our gross WD-DIC_{sw} flux estimate (2.95 Tg C yr^{-1}).

The use of water for irrigation, mining, industrial, and public supply sectors will also lead to changes in DIC speciation and concentration. For example, freshwater withdrawals can cause increased evaporation,[59] which in turn may increase DIC concentrations within the remaining water. However, this may also occur in tandem with the precipitation of carbonate minerals within soils, CO_2 emissions, and the utilization of DIC for primary production, which can act to decrease DIC concentrations and the amount of DIC that can be leached to groundwaters or transported in runoff to surface waters.[62] However, data relating to mechanisms controlling these speciation and concentration changes remain spatially limited,

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and alongside the lack of comprehensive data regarding the impact of freshwater withdrawals upon the US water balance, net national-level WD-DIC_{gw} fluxes for irrigation and mining sectors (Figure 2a), and net WD-DIC_{sw} fluxes for irrigation, industrial, mining and public supply sectors remain unknown (Figure 2b). Research priorities and data needed to resolve these issues are highlighted in Section 4.4.

Our research has also estimated the impact of increased thermoelectric plant effluent temperatures on national-level CO_2 emissions to the atmosphere (Supporting Information Note 3). More localized assessments could also be conducted to identify hotspots of these emissions, particularly across eastern regions of the country, where once-through technologies responsible for thermal pollution are more common.[63] Estimating CO_2 emissions across heavily thermally polluted river systems worldwide will be necessary to understand the impact of thermal pollution upon global CO_2 degassing.[64]

4.3. Degassing of CO_2 from Groundwater Withdrawals. The degassing of CO_2 supersaturated groundwater withdrawals across the US is known to contribute to the country's atmospheric CO_2 emissions.[21,23,25] The research reported here uses a more robust methodology to estimate the subnational and sectoral contributions to a national-level CO_2 emission of 3.6 Tg CO_2 yr^{-1} (Figure 1a). This value is 112% larger than the 1.7 Tg CO_2 yr^{-1} previously reported,[21] primarily due to the use of total groundwater withdrawal volumes within our calculations, as opposed to the lower volumes that represent groundwater depletion, or net withdrawals used by Wood and Hyndman.[21] Although our research uses larger (gross) withdrawal volumes for estimating WD-$CO_{2\ gw}$ emissions, as opposed to net (depletion) withdrawal volumes, the excess groundwater CO_2 concentrations (E-[$CO_{2\ gw\text{-}atm}$]) determined and used within our research are on average lower than those adopted in previous work.[21] We believe that the approach reported in the current paper is conceptually more representative of the amount of CO_2 degassed, as withdrawn groundwater will degas more rapidly than the time it takes for it to be returned to an aquifer,[39,40] and that the use of THINCARB has modeled more spatially resolved and accurate E[$CO_{2\ gw\text{-}atm}$] concentrations across the US than in previous research. The use of lab-measured pH values within calculations, due to a lack of reported field pH values, may lead to an underestimate of CO_2 emissions from groundwater.[40] The use of both in-field and lab-measured pH values in the determination of WD-$CO_{2\ gw}$ emissions is therefore discussed in Supplementary Note 1.

Ninety-six percent of the 1401 counties that have WD-$CO_{2\ gw}$ emissions exceeding those from major emitting facilities (Figure 3b) have no emissions reported as part of the GHGRP,[45] which is assumed to largely reflect the fact that any emissions from facilities within those counties are below the reporting threshold.[46] Despite this, our identification of regions where WD-$CO_{2\ gw}$ emissions are important in relation to other major CO_2 emission sources (Figure 3b) suggests that these emissions should be included within regional and local-scale C budgets, C footprint assessments, and Net Zero efforts by the US water supply sector.[65]

Previous work has generally focused on quantifying the CO_2 emissions associated with degassing groundwater withdrawals for irrigation use.[23−25] A more comprehensive assessment of the sectoral withdrawals that can contribute to the total withdrawal of CO_2 emissions has been made in our current research, with observed sectoral differences in WD-$CO_{2\ gw}$ emissions driven by the contrasting dependence of each water use sector on groundwater withdrawals. Although irrigation groundwater withdrawals make a dominant contribution to total national-level WD-$CO_{2\ gw}$ emissions, neglecting groundwater withdrawals from other water use sectors would cause a 27% underestimate of WD-$CO_{2\ gw}$ emissions (Figure 1a). With the volume of groundwater withdrawals anticipated to increase across many regions of the US,[66] WD-$CO_{2\ gw}$ emissions are likely to persist or even increase into the future. While beyond the scope of this research, the E[$CO_{2\ gw\text{-}atm}$] data set and methodology presented in the current paper should facilitate a more detailed investigation into the mechanisms controlling E[$CO_{2\ gw\text{-}atm}$] concentrations and thus WD-$CO_{2\ gw}$ emissions. This is likely to include consideration of land use[67,68] and hydrogeological setting[69] (e.g., Figure S3). An improved understanding of these mechanisms would then support more sustainable groundwater management strategies, not only for the purpose of conserving fresh groundwater resources but also for the regulation of atmospheric CO_2 emissions.

4.4. Future Priorities for Estimating Net DIC Fluxes. Estimating net US irrigation WD-DIC fluxes is complex and beyond the scope of this research. As the largest sector contributing to the gross national-level WD-DIC flux, estimating the net impact of irrigation withdrawals on DIC cycling may impact the determination of other sectoral net WD-DIC fluxes and thus warrants additional research. This will require comprehensive country-wide data sets detailing the amount of water withdrawn that is subsequently used for irrigation, as any spare water withdrawn will be stored within reservoirs.[70] Data disclosing the varying proportion of water returned to either surface waters or groundwaters post irrigation,[28] as well as the physiochemical changes associated with this redistribution of water will also be needed.[14] Modeling the fate of DIC both during and post irrigation will also be required to determine how much DIC is taken up by crops, precipitated as carbonate within soils, or degassed as CO_2. This will require a substantial range of input data sets. For example, the amount of DIC degassed as CO_2 both during and post irrigation may require data relating to irrigation system type (flood, sprinkler, or drip), irrigation efficiency, return flows, as well as soil and crop type.[71−74] While research has estimated the energy-derived CO_2 emissions from surface water pumping and running of surface irrigation systems across the US,[25] understanding the impact of different irrigation systems on CO_2 degassing from both withdrawn surface waters and groundwaters across the country remains an important area of research.[71]

Similarly, a lack of comprehensive national-level data detailing potable water treatment and in-pipe processes that may affect DIC speciation and retention, such as pH adjustment and the precipitation of carbonates within potable water distribution pipes,[75] limits our ability to accurately determine a net WD-DIC_{sw} flux at this time (Figure 2b). We estimate the input of DIC via public supply return flows (WWTP effluent) to be 2.9 Tg C yr^{-1} (Supplementary Note 2), a flux that exceeds the retention capacity provided by withdrawals, with combined WD-DIC_{gw} and WD-DIC_{sw} fluxes (1.2 Tg C yr^{-1}) equivalent to 41% of the WWTP effluent DIC flux. Despite this exceedance, future research should continue to resolve the retention of DIC within the water distribution system and the degree to which freshwater withdrawals can moderate the downstream export of potentially environ-

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mentally disruptive DIC inputs from municipal wastewater effluents.[76]

Although withdrawals for industrial, aquaculture, and mining water use sectors are minor on a large (global and national) spatial scale, when compared to irrigation and public supply sectors, they can make major contributions to overall freshwater withdrawals on more localized scales. In addition, these sectors often withdraw water within environmentally sensitive locations,[52] meaning they may have an important impact on overall freshwater nutrient cycling within an area. Data detailing the proportion of water withdrawn for industrial, aquaculture, and mining water use sectors that is stored and returned to surface water and groundwater environments,[50,58] as well as any associated DIC concentration changes, are currently limited on a national scale. Annual county-level WD-DIC fluxes neglect to account for both the seasonality and the spatial heterogeneity in both freshwater use and DIC concentrations.[77,78] A lack of data has also prevented the use of sector-specific DIC concentrations within flux calculations. Should calls for more widespread and regular in situ monitoring of freshwater quality determinants (including pH, CO_2, and DIC) be answered[11,79] and more spatially and temporally resolved water use data released, uncertainties associated with gross and net sectoral WD-DIC fluxes should also be reduced. With 10% of counties responsible for over 70% of total freshwater consumption across the country,[50] efforts to determine net WD-DIC fluxes could be prioritized in these areas. While this work highlights the localized importance of WD-$CO_{2\ gw}$ emissions, future work must also determine to what extent human-induced groundwater withdrawal CO_2 emissions affect the amount of CO_2 degassing by natural discharge downstream.[40]

This paper considers freshwater withdrawals and reservoir creation, through the damming of surface waters, to be distinct processes capable of impacting freshwater DIC cycling.[12] Fresh surface water withdrawal data used in this paper do not distinguish between withdrawal from reservoirs or other surface water bodies.[33] However, approximately 15% of US dams are constructed for municipal and irrigation water supply purposes,[80] and processes controlling DIC concentrations within the lentic environment of reservoirs often differ substantially from those within the wider lotic network of a river or stream.[81] If future data allow differentiation between freshwater withdrawals from reservoirs versus other surface waters, it will be important that research more accurately constrains the specific controls exerted by reservoirs on DIC concentrations and thereby on withdrawal DIC fluxes from these freshwaters. Integrating the impacts of water supply reservoirs and fresh surface water and groundwater withdrawals upon DIC cycling across the contiguous US (e.g., ref 28) is beyond the scope of this study, however constitutes an important piece of future research. Subsequent withdrawals of freshwater from these dammed areas can also lead to a release of atmospheric CO_2 emissions due to an increase in drawdown area.[27,82] Future work should integrate degassing groundwater withdrawal CO_2 emissions with other water supply-related CO_2 emissions, including those from drawdown, surface water withdrawal degassing, thermoelectric effluents, and aeration during irrigation.

A. Global Perspective on the Impacts of Water Withdrawals on Freshwater−Carbon Fluxes. While the research reported here has estimated the impacts of freshwater withdrawals on freshwater C fluxes across the contiguous US, withdrawals of fresh water are likely to perturb freshwater C fluxes globally. Using global net groundwater and surface water withdrawal volumes[83] and adopting median US DIC_{gw} and DIC_{sw} concentrations determined in this study, we estimate net global WD-DIC_{gw} and WD-DIC_{sw} fluxes to be 12.4 and 35.0 Tg C yr^{-1}, respectively. We estimate the global subterranean groundwater discharge (SGD) DIC flux (DIC_{SGD}), using lower and upper fresh global SGD volume estimates[7] and the median US DIC_{gw} concentration determined in this study, to be 269.6−770.3 Tg C yr^{-1}. Net global WD-DIC_{gw} and WD-DIC_{sw} fluxes may therefore be equivalent to approximately 1.6−4.6% of the global DIC_{SGD} flux and 8.6% of global riverine DIC export,[6] respectively. These coarse calculations highlight the potential importance of net freshwater withdrawal DIC fluxes, with respect to global freshwater DIC cycling. Using recent global groundwater withdrawal volumes (959 km^3 yr^{-1}, for the year 2017)[84] and the median excess groundwater CO_2 concentration estimated in this study (13.7 mg CO_2 L^{-1}), we estimate the global WD-$CO_{2\ gw}$ flux to be 13.1 Tg CO_2 yr^{-1}. This estimate is slightly lower than the upper depletion WD-$CO_{2\ gw}$ flux (9.7−13.5 Tg CO_2 yr^{-1}) made by Wood and Hyndman,[21] an artifact of the simultaneously higher gross WD_{gw} value but lower E-$[CO_{2\ gw\text{-}atm}]$ concentration adopted in the research we report here. This estimate is much lower than the 36.7−110 Tg CO_2 yr^{-1} estimated by Macpherson[40] due to the lower E-$[CO_{2\ gw\text{-}atm}]$ concentration adopted in this study. Emerging global data sets estimating sectoral water use and consumption should be used to resolve similar fluxes elsewhere around the world,[85] with priority given to countries undertaking globally significant withdrawals of fresh water.

To conclude, fresh surface water and groundwater withdrawals across the US were estimated to result in gross dissolved inorganic carbon (DIC) retention fluxes of 6.7−9.9 and 5.3−8.8 Tg C yr^{-1}, respectively. The degassing of CO_2 supersaturated groundwater following withdrawal was estimated to emit 2.2−5.5 Tg of CO_2 yr^{-1}, 112% larger than previous estimates, with county-level CO_2 emissions exceeding CO_2 emissions from major emitting facilities across 45% of US counties. Future work should continue to resolve net US freshwater withdrawal DIC fluxes and CO_2 emissions as more data becomes available. Results should then be integrated into wider carbon budget assessments and help inform more sustainable management of freshwater resources and carbon cycling.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.4c09426.

Additional details regarding data quality assurance and methodologies used throughout the manuscript are detailed in Supporting Information document (PDF)

The dataset disclosing fresh groundwater and surface water DIC concentrations and excess CO_2 concentrations of fresh groundwaters across the United States, including steps taken to calculate excess CO_2 concentrations of fresh groundwaters are also detailed (XLSX)

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AUTHOR INFORMATION

Corresponding Author

Elizabeth M. Flint − *British Geological Survey, Wallingford, Oxfordshire OX10 8BB, U.K.; Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, U.K.;* orcid.org/0000-0002-5781-2523; Email: efli1@bgs.ac.uk

Authors

Matthew J. Ascott − *British Geological Survey, Wallingford, Oxfordshire OX10 8BB, U.K.;* orcid.org/0000-0002-4868-2069

Daren C. Gooddy − *British Geological Survey, Wallingford, Oxfordshire OX10 8BB, U.K.; Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, U.K.; UK Centre for Ecology and Hydrology, Wallingford, Oxfordshire OX10 8BB, U.K.;* orcid.org/0000-0002-6015-1332

Mason O. Stahl − *Department of Geosciences, Union College, Schenectady, New York 12308, United States*

Ben W. J. Surridge − *Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, U.K.;* orcid.org/0000-0003-2425-1739

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.est.4c09426

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. E.M.F.: Conceptualisation, Methodology, Formal Analysis, Writing Original Draft. M.J.A., D.C.G., M.O.S., B.W.J.S.: Conceptualisation and Supervision, Writing: Reviewing and Editing.

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Notes

The authors declare no competing financial interest.

All data used within this research are publicly available. Volumetric rate data of freshwater withdrawals were sourced from the USGS[33] and DIC concentrations were modeled using data from the Water Quality Portal.[34] Data surrounding processes affecting DIC returns were available from a variety of sources, see Supporting Information. Linework on map figures were created using the "usmap" package in R.[48]

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