The Impacts of Water Supply Processes on Macronutrient Cycling Across the United States

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Abstract

Anthropogenic activities modify biogeochemical cycles of the macronutrients carbon (C), nitrogen (N) and phosphorus (P) worldwide. This has resulted in a need for more effective nutrient management practices that are informed by accurate nutrient budgets. This thesis uses publicly available data to assess the impacts that human uses of fresh water across the contiguous United States (US) can have upon N, C and P cycles. Freshwater withdrawals were estimated to delay the downstream export of 417 kt NO_3-N yr^{-1}, a flux equivalent to 57% of total US river denitrification. Freshwater withdrawals were estimated to delay the downstream export of 15.1 Tg DIC yr^{-1}, a flux equivalent to 51% of the total DIC exported to the oceans from the US by surface waters and subterranean groundwater discharge. On a national level, the degassing of CO_2 supersaturated groundwater following withdrawal was estimated to emit 3.6 Tg CO_2 yr^{-1}, an emission equivalent to 1.2% of CO_2 emissions from outgassing lakes and rivers. Degassing groundwater withdrawals are now estimated to be an important component of overall emissions of CO_2 on localised scales, with 45% of US counties estimated to have CO_2 emissions from degassing groundwater withdrawals that exceed those from major emitting facilities. Contributions of major water use sectors to freshwater withdrawal retention fluxes and degassing groundwater withdrawal CO_2 emissions have been detailed for the first time anywhere globally, with emissions due to irrigation groundwater withdrawal alone (2.6 Tg CO_2 yr^{-1}) equivalent to 25% of the CO_2 emissions associated with electricity generation for irrigation groundwater pumping. The mass flux of phosphate (PO_4) added to potable water, for the purpose of minimising metal corrosion within US water distribution networks, was estimated as being up to 14.9 kt PO_4-P yr^{-1}. On a national level, subsequent leakage of water from watermains was estimated to release up to 2.6 kt PO_4-P yr^{-1} and 7.7 kt NO_3-N yr^{-1} into the environment, with these fluxes equivalent to 1.2% and 1.4 % of P and N from point sources, respectively. On a national level, the loss of PO_4 dosed water from water supply networks due to outdoor water use at domestic residences was estimated to release up to 3.1 kt PO_4-P yr^{-1}, a flux equivalent to 1.4% of

P input from point sources. Leakage and outdoor water use fluxes are a locally important sources of N and P across urban areas, with county-level leakage N fluxes >10% of leached agricultural N fertilizer inputs across 265 counties and combined leakage and outdoor water use P fluxes exceeding point source P inputs across 541 counties. This research suggests that N, C and P fluxes associated with water supply processes should be integrated into future local-level and sectoral nutrient budgets, policy making and management practices. For example, the loss of PO_4 from water supply networks due to leakage has implications for economic level of leakage assessments, Lead and Copper Rule revisions and the sustainability of P use across the country. Similarly, the application of corrosion inhibitor derived PO_4 due to outdoor water use may help inform state-level policy that seeks to regulate the use of P based lawn fertilizers at domestic residences. The contribution of degassing irrigation and public supply groundwater withdrawals to overall sectoral CO_2 emissions may have implications for the sustainable use of groundwater, policy surrounding preferential irrigation method and the ability for water systems to achieve net-zero. The methodology developed here should be used to quantify similar fluxes across other countries with extensive freshwater use, as part of a global assessment.

Contents

Acronyms

AQUA-NO_3-N	Nitrate flux due to freshwater aquaculture withdrawals
C	Carbon
CH_4	Methane
CO_2	Carbon dioxide
$CO_{2\ gw}$	Concentration of CO_2 in groundwater
$CO_{2\ sw}$	Concentration of CO_2 in surface water
$C_{r\ (GW\text{-}NO3\text{-}N)}$	Raw concentrations of nitrate (as nitrogen) in groundwater
$C_{r\ (SW\text{-}NO3\text{-}N)}$	Raw concentrations of nitrate (as nitrogen) in surface water
$C_{t\ (NO3\text{-}N)}$	Concentrations of nitrate (as nitrogen) in treated potable water
$C_{t\ (PO4\text{-}P)}$	Concentrations of phosphate (as phosphorus) in potable water due to corrosion control treatment
$DI_{domestic}$	Volumetric flow rate of freshwater delivered to domestic residences
DIC	Dissolved inorganic carbon
DOMESTIC-NO_3-N	Nitrate retention flux due to non-publicly supplied domestic freshwater withdrawals
DOSE-PO_4-P_{pws}	Flux of phosphate added to the water distribution network due to phosphate dosing of publicly supplied water
DOSE-PO_4-P_{wwtp}	Flux of phosphate into wastewater treatment plants due to phosphate dosing of publicly supplied water
$E[CO_{2\ gw\text{-}atm}]$	Excess CO_2 concentration in groundwater, when in equilibrium with the atmosphere
$E[CO_{2\ gw\text{-}sw}]$	Excess concentration of CO_2 in groundwater, when in equilibrium with surface water
$E[CO_2]_{eff}$	Excess concentration of CO_2 within thermoelectric plant effluent
$EpCO_2$	Excess partial pressure of CO_2 in groundwater, when compared to the atmosphere
f_{dosed}	Fraction of publicly supplied water dosed with phosphate for corrosion control
$f_{leakage}$	Leakage factor
f_{owu}	Fraction of water supplied to domestic residences used outdoors
IND-NO_3-N	Nitrate retention flux due to freshwater industry withdrawals
IRR-NO_3-N	Nitrate retention flux due to freshwater irrigation withdrawals
LIVE-NO_3-N	Nitrate retention flux due to freshwater livestock withdrawals
LV	Volumetric flow rate of water leakage from watermains

MINE-NO_3-N	Nitrate retention flux due to freshwater mining withdrawals
N	Nitrogen
N_2	Nitrogen gas
N_2O	Nitrous oxide
NO_3-N	Nitrate (as nitrogen)
OWU-PO_4-P	Flux of phosphate lost from public supply network due to outdoor water use at domestic residences
P	Phosphorus
$pCO_{2\ atm}$	Partial pressure of CO_2 in the atmosphere
$pCO_{2\ gw}$	Partial pressure of CO_2 in the groundwater sample
$pCO_{2\ gw\text{-}atm}$	Partial pressure of CO_2 in groundwater, when in equilibrium with the atmosphere
PO_4-P	Phosphate (as phosphorus)
Pop_{dosed}	Population served by phosphate dosed water
Pop_{pws}	Population served by public water systems
PWS-NO_3-N	Flux of nitrate due to freshwater public water supply withdrawals
SDWIS	Safe Drinking Water Information System
THERM-NO_3-N	Flux of nitrate due to freshwater thermoelectric withdrawals
US	United States
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
$Vol_{pws\text{-}dosed}$	Volumetric rate of phosphate dosed water entering the public supply network
WD-$CO_{2\ gw}$	Emissions of CO_2 due to the degassing of CO_2 supersaturated groundwater withdrawals
WD-DIC_{gw}	Dissolved inorganic carbon retention flux due to fresh groundwater withdrawals
WD-DIC_{sw}	Dissolved inorganic carbon retention flux due to fresh surface water withdrawals
WD_{gw}	Fresh groundwater withdrawals
WD-NO_3-N_{total}	Total nitrate retention flux due to freshwater withdrawals
$WD_{pws\text{-}total}$	Freshwater withdrawals for public supply use
WD_{sw}	Fresh surface water withdrawals
WML-NO_3-N	Flux of nitrate lost from the public supply network due to watermains leakage
WML-PO_4-P	Flux of phosphate lost from the public supply network due to watermains leakage
WWTP	Wastewater treatment plant

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Acknowledgements

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Declaration

I declare that this thesis is my own work and has not been submitted for the award of a higher degree elsewhere. Discussion as to the general direction of the thesis was undertaken between myself and my supervisory team throughout the PhD, which included Matthew Ascott, Daren Gooddy, Ben Surridge and Mason Stahl. Support given by my supervisory team for the publication of results chapters has been clearly identified and certified at the start of each results chapter, and they have been acknowledged as co-authors accordingly.

Elizabeth Flint

24/09/2024

“Recommit yourself to the healing of the world

And to the welfare of all creatures upon it

Pursue a practice

That will strengthen your heart”

John K. Samson

1. Introduction

1.1 Background

The macronutrients nitrogen (N), carbon (C) and phosphorus (P) are essential elements for metabolism and life in all biological systems. The production of crops and feeding of livestock to support a growing global population has relied heavily on the widespread use of inorganic N and P fertilizers (Tilman et al., 2011), fossil fuel combustion and extensive land use change (Lal, 2004). These activities have contributed to global N, C and P fluxes that exceed safe planetary boundaries (Steffen et al., 2015). Globally, the doubling of total N and P deliveries to freshwaters over the 20th century has resulted in the persistent eutrophication of fresh water and marine ecosystems (Beusen et al., 2016; UNEP/WHO, 1988). Eutrophication is both a natural and anthropogenically induced process that occurs due to the over enrichment of aquatic ecosystems with nutrients, including N and P (Akinnawo, 2023). This over enrichment leads to pervasive growth of algal blooms, that in turn can lead to depleted oxygen levels and hypoxia in aquatic ecosystems. Eutrophication poses a threat to environmental and human health, with some algal blooms resulting in fish kills, decreased drinking water quality and toxin release (Davis and Shaw, 2006). The economic costs associated with the impacts and management of eutrophication are also vast (Dodds et al., 2009; Garcia-Hernandez et al., 2022). Increases in greenhouse gas emissions due to fossil fuel combustion and land-use change have also led to a 50% increase in atmospheric CO_2 levels since pre-industrial times and resulted in global climate change (NOAA, 2022).

Sustaining a growing global population, whilst preventing pollution of aquatic ecosystems and the atmosphere, remains a significant challenge (Sutton et al., 2013). Attempts to sustainably manage N, C and P fluxes within the environment, including the development of legally binding legislation and reduction targets (European Commission, 1991; UNFCCC, 2015; USEPA, 1972) and the adoption of best management practices (Liu et al., 2017; Sharpley et al., 2006), have largely been unsuccessful (Lintern et al., 2020; Maslin et al., 2023). This is in part due to the lag time between both the identification of impacts associated with perturbed N, P and C cycles and the

implementation of policy, and between the implementation of policy and observed water quality improvements (Brown et al., 2019a; Meals et al., 2010), as well as legacy N and P pollution of soils and groundwaters (Haygarth et al., 2014; Van Meter et al., 2016). Effective policies for sustainably managing N, C and P cycles must also be informed by robust and integrated nutrient budgets that identify and quantify all sources, transformations, and outputs of these nutrients on spatial and temporal scales that are relevant to management decisions (Grizzetti et al., 2015; USGCRP, 2018; Wu and Ma, 2015). The omission of nutrient fluxes within budgets and management strategies can also be responsible for the discrepancy between implemented nutrient management and observed improvements in water quality and aquatic ecology.

A small body of research has identified several anthropogenic freshwater supply processes as mechanisms capable of perturbing N, C and P cycles, on magnitudes that have implications for the development of accurate nutrient budgets and environmental health. The construction of reservoirs and dams around the world for water storage has increased freshwater N, C and P retention (Akbarzadeh et al., 2019; Beusen et al., 2016; Maavara et al., 2017; Maavara et al., 2015; Wang et al., 2022). It should be noted that this thesis defines retention as a process that can prevent or delay the downstream delivery of nutrients from the land to the oceans (Grizzetti et al., 2015), and thus accounts for the difference between inputs and exports of nutrients to a catchment (De Klein, 2008). Fresh surface water and groundwater withdrawals have been identified as important mechanisms for the retention of both inorganic and organic C and N within freshwater environments (Ascott et al., 2018b; Finlay et al., 2016; You et al., 2023), with groundwater withdrawals capable of moving nutrients between subsurface and surface environments (McDonough et al., 2022; Stahl, 2019). Upon withdrawal, the degassing of groundwaters supersaturated with carbon dioxide (CO_2) and methane (CH_4), when compared to the atmosphere, have also been identified as a source of greenhouse gas emissions to the atmosphere (Gooddy and Darling, 2005; Kulongoski and McMahon, 2019; Mishra et al., 2018; Wood and Hyndman, 2017). The treatment and transfer of untreated (raw) water (USEPA, 2020a), as well as the leakage of treated water during distribution (Ascott et al., 2016; Ascott et al., 2018b; Gooddy et al., 2017; Gooddy et al., 2015; Holman et al., 2008; Lerner et al., 1999), can

also impact the cycling of N and P within the environment and be sources of atmospheric CO_2 (Finlay et al., 2016; Plappally and Lienhard V, 2012).

These studies have highlighted a need to make more comprehensive estimates of the impacts that water supply processes can have on macronutrient cycling both for individual countries around the world and on a global scale. The United States (US) has some of the largest per capita rates of freshwater use anywhere globally (FAO, 2024) and is a country subjected to persistent freshwater eutrophication (Malone and Newton, 2020; Manning et al., 2020). An understanding of how water supply processes can impact macronutrient cycling across the US is limited, however. For example, there have been no assessments of the potential for net N and C retention due to freshwater withdrawals by each of the country's major water use sectors, or for the release of nutrients into the environment via watermains leakage and outdoor water use. In addition, although emissions of CO_2 from degassing groundwater withdrawals have been estimated on a national level (Wood and Hyndman, 2017), calculations made use of nationally averaged values. Results also neglected to identify both the relative contribution that groundwater withdrawals that each major water use sector made to the national-level estimate, as well as any regional variation in CO_2 emissions. Neglecting to accurately quantify the impacts of water supply processes upon macronutrient cycles across the US hinders the development of integrated nutrient budgets on both a national and global scale. This in turn will compromise both an ability to accurately assess the extent to which N, C and P management policies can deliver environmental improvements and the effectiveness of existing and future environmental policies when they are implemented.

1.2 Thesis Aim, Objectives and Scope

With the US a significant contributor to global freshwater use and a country subjected to persistent eutrophication, this core aim of this thesis is to increase understanding of the impacts that water supply processes can have on macronutrient (N, P and C) cycles across the US. This is achieved by addressing the following objectives:

1. To review the current state of science related to the impacts of water supply processes upon N, C and P cycling around the world and across the US
2. To quantify the impact of freshwater withdrawal and use on N and C cycling across the US
3. To evaluate how PO_4 dosing practices for corrosion control can impact P cycling across the US
4. To identify future research needs with respect to understanding the impacts of water supply processes upon N, C and P cycling across the US and around the world

This thesis will focus on the impacts of water supply processes on fluxes of N and P, specifically in their bioavailable and inorganic form (as nitrate; NO_3 and phosphate; PO_4). This is due to the fact they are readily available for aquatic organisms and thus have heightened importance for ecological functioning and eutrophication in fresh waters (Akinnawo, 2023). Similarly, this work also focuses on the impact of water supply processes on fluxes of inorganic C (as dissolved inorganic carbon; DIC), since DIC is the dominant form of C exported within fresh waters (Chaplot and Mutema, 2021). Understanding the impacts of water supply processes upon fluxes of organic and particulate fractions of N, C and P is beyond the scope of this thesis. Whilst the macronutrients oxygen, hydrogen, magnesium and potassium are also fundamental for biological life (Hawkesford et al., 2023), understanding the impact of water supply processes upon these nutrients is also beyond the scope of this thesis.

1.3 Thesis Structure

The research objectives outlined in Section 1.2 are addressed throughout the chapters of this thesis. Chapter two delivers objective one in relation to objectives 2-4. Chapters 3-5 form the results chapters of this thesis and answer one or more of the research objectives, with each results chapter modified from a published paper. Research objectives, their corresponding thesis chapter and associated publication are outlined in Table 1.1.

Table 1.1. Research objectives with corresponding thesis chapter and research publication.

Objective (chapter)	Publication Title	Journal and DOI
1 (2)	-	-
2 (3 and 5)	Water supply processes are responsible for significant nitrogen fluxes across the United States	Global Biogeochemical Cycles 10.1029/2022GB007340
	Anthropogenic water withdrawals modify freshwater carbon fluxes across the United States	Environmental Science and Technology 10.1021/acs.est.4c09426
3 (4)	Watermains leakage and outdoor water use are responsible for significant phosphorus fluxes to the environment across the United States	Global Biogeochemical Cycles 10.1029/2022GB007614
4 (3,4,5,6)	Water supply processes are responsible for significant nitrogen fluxes across the United States	Global Biogeochemical Cycles 10.1029/2022GB007340
	Watermains leakage and outdoor water use are responsible for significant phosphorus fluxes to the environment across the United States	Global Biogeochemical Cycles 10.1029/2022GB007614
	Anthropogenic water withdrawals modify freshwater carbon fluxes across the United States	Environmental Science and Technology 10.1021/acs.est.4c09426

2. The Impacts of Water Supply Processes on Macronutrient Cycling: Current Understanding, Knowledge Gaps and Research Needs

2.1 Introduction

The macronutrients N, C and P play a critical role within metabolic processes and are therefore fundamental elements for supporting life. The heavy reliance upon inorganic N and P fertilizers for enhancing food production has caused global N and P deliveries to freshwaters to double over the 20th century and has resulted in persistent eutrophication of freshwater and marine ecosystems around the world (Beusen et al., 2016; UNEP/WHO, 1988). Eutrophication induced algal blooms pose a threat to both environmental and human health and drinking water quality (Davis and Shaw, 2006), with the impacts and management of eutrophication having significant economic implications (Dodds et al., 2009; Garcia-Hernandez et al., 2022). Fossil fuel combustion and extensive land-use change have also facilitated global population growth, accelerated the cycling of C between terrestrial, freshwater and atmospheric pools (Regnier et al., 2022). This has resulted in the significant rise of atmospheric CO_2 levels and changing of the global climate (NOAA, 2022).

Sustaining a growing global population, whilst preventing the pollution of aquatic ecosystems and the atmosphere, remains a significant global challenge (Sutton et al., 2013). The development of legally binding legislation and the adoption of best management practices for more sustainably managed cycles of N, C and P within the environment have largely been unsuccessful (Lintern et al., 2020; Liu et al., 2017; Maslin et al., 2023; Sharpley et al., 2006). This is partially due to a lag time between the implementation of a management practice and response time of the environment (Brown et al., 2019a; Meals et al., 2010) and legacy N and P pollution of soils and groundwaters (Haygarth et al., 2014; Van Meter et al., 2016). More effective nutrient management and water quality policies must also be informed by more robust and integrated nutrient budgets that identify and quantify all sources, transformations and outputs of a given system (Grizzetti et al., 2015; Wu and Ma, 2015).

Research has recently identified a range of anthropogenic water supply processes as mechanisms capable of impacting nutrient cycles on magnitudes that have implications for environmental health. Much of this research has been undertaken in the form of isolated and small-scale case studies. This has resulted in a continued limited understanding of how water supply processes can impact macronutrient cycling around the world and means that achieving a comprehensive global understanding remains an ongoing area of research. This literature review firstly provides a brief overview of the key natural and anthropogenic processes that can influence macronutrient cycles within fresh waters (Section 2.2). It then presents the state of scientific knowledge with regards to the impacts that water supply processes can have upon macronutrient (N, C and P) cycles around the world (Section 2.3), with a specific focus on the US (Section 2.4). It also identifies the knowledge gaps associated with macronutrient cycling and water supply processes that need to be addressed, in order to develop more integrated nutrient budgets and effective nutrient management policy (Section 2.4). Finally, the knowledge gaps to be addressed specifically within this thesis are detailed (Section 2.5). An in-depth review of literature surrounding agriculture and wastewater effluent as sources of N and P pollution, the combustion of fossil fuels and terrestrial land-use change as sources of atmospheric CO_2, and the impacts of water supply processes upon macronutrients exclusive of N, C and P (e.g. oxygen, hydrogen and potassium) are outside the scope of this review.

2.2 An Overview of Macronutrient Cycling in Fresh Waters

2.2.1 Natural Cycling and Speciation of Macronutrients in Fresh Waters

The essential need for N, C and P within metabolic reactions means that any change to the abundance of these nutrients within fresh waters, particularly when in their bioavailable forms, may change the ecological productivity and community structure of freshwater environments (Durand et al., 2011; Weigelhofer et al., 2018). In natural freshwater environments, the concentration and form of these nutrients can vary substantially and are controlled by a vast range of physical, chemical and biological processes. Some of the key processes controlling N, C and P cycles in fresh surface waters are detailed in Figure 2.1. Freshwater N can be found in

organic or inorganic forms and in a range of different oxidation states, with bioavailable forms of N (as nitrite; NO_2, nitrate; NO_3 or ammonium; NH_4) able to be assimilated by living organisms for primary production. Natural inputs of N to freshwater environments include atmospheric deposition and the biological fixation of N gas (N_2). In-stream retention processes, such as denitrification and burial in sediments, act to temporarily retain or permanently remove N. Physical characteristics, such as stream order and residence time, largely control the fate of N. Within fresh groundwaters, N is predominantly dissolved in the form of NO_3 and is sourced via leaching from soils or surface water (Durand et al., 2011; Grizzetti et al., 2015).

Phosphorus within fresh surface waters can be in soluble and particulate form. Naturally, it is sourced from the weathering of finite phosphate bedrock reserves, meaning that releases of bioavailable P (as phosphate; PO_4) are extremely slow (Cordell and White, 2014). In-stream PO_4 retention processes include biotic assimilation by living organisms and abiotic processes of sedimentation, precipitation and adsorption to sediments (Reddy et al., 1999). Although geogenic P within groundwaters can be a source of P to surface water environments (Kazmierczak et al., 2021), it is generally assumed that naturally occurring P concentrations within groundwaters are negligible due to the sorption of PO_4 to soils and sediments above (Domagalski and Johnson, 2012). A complex mixture of organic, inorganic, dissolved and particulate forms of C are found within fresh surface waters. These C species can enter freshwater via runoff up-stream, diffusion of atmospheric CO_2 or by fixation of CO_2 by photosynthesising aquatic plants. Carbon retention in fresh waters can occur through processes including storage in sediments, emission to the atmosphere as CO_2 or export downstream (Vachon et al., 2021). Groundwaters contain both organic and inorganic C in dissolved form, most of which is sourced from plant and microbial respiration above (Ward et al., 2017). Despite the important role that fresh waters play in moderating exports of C to the ocean and emitting CO_2 to the atmosphere, their importance for global carbon cycling has only been acknowledged during the last few decades (Cole et al., 2007).

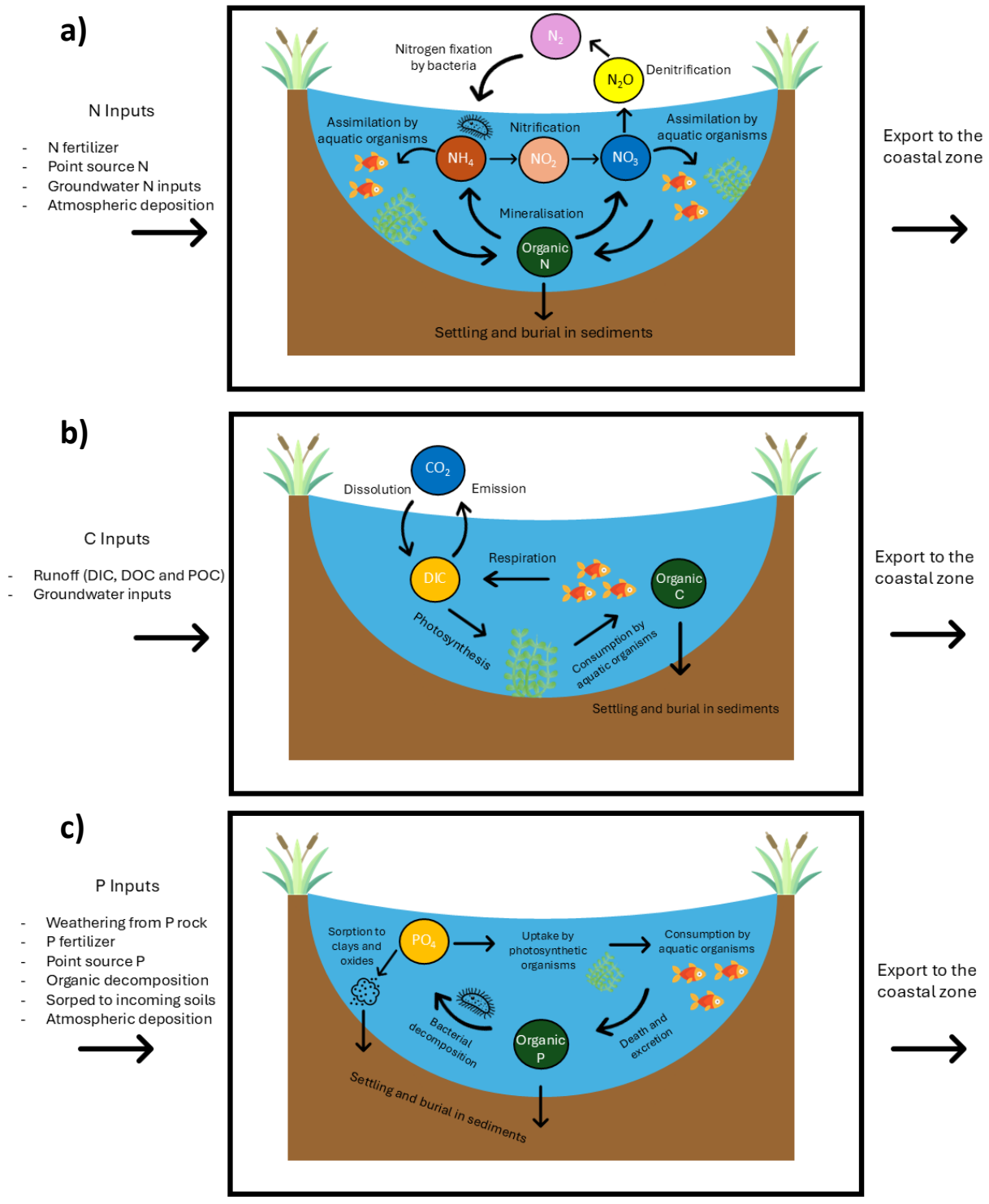

Figure 2.1. Schematic showing a simplified depiction of key biological, physical and chemical processes that control cycles of a) nitrogen (N), b) carbon (C) and c) phosphorus (P) within fresh surface water environments.

2.2.2 Anthropogenic Perturbations to Macronutrient Cycling

Anthropogenic activity has contributed to global N, C and P fluxes exceeding safe planetary boundaries (Steffen et al., 2015). A rising global population continues to drive industrialisation and increases in agricultural production around the world, both of which cause pervasive pollution of fresh waters and the atmosphere (Sinha et al., 2019). Due to their limiting effects on global food production, N and P are widely used within agrochemical fertilisers to enhance food security (Guignard et al., 2017). Facilitated by the development of the Haber-Bosch process in the early 20th century (Erisman et al., 2008; Fowler et al., 2013), humans produced twice as much reactive N globally than natural processes at the turn of the millennium (EPA Science Advisory Board, 2011). The widespread mining of PO_4 rock, largely for the production of inorganic P fertilizers, has tripled global P mobilisation (Yuan et al., 2018). The utilisation of fossil fuels for energy generation and major land use change, including deforestation, have both contributed to the accelerated cycling of C between terrestrial, freshwater and atmospheric pools (Regnier et al., 2022).

The unsustainable application of inorganic N and P fertilizers has contributed to wide-spread and long-term accumulation of nutrients within soils (Lun et al., 2018; Van Meter et al., 2016). The subsequent runoff of excess soil N and P into aquatic environments has significantly altered global N and P cycles (Bouwman et al., 2013; Fowler et al., 2013) and is a pervasive source of diffuse (non-point) nutrient pollution within surface waters, groundwaters and other sensitive receiving waters (Bijay and Craswell, 2021; Munn et al., 2018; Sun et al., 2012; Xie and Ringler, 2017). Whilst these agricultural practices are responsible for the majority of freshwater and coastal eutrophication (Poore and Nemecek, 2018), urban areas also generate both point and non-point sources of N and P. These include from wastewater treatment and industrial plant effluents, atmospheric deposition, lawn fertilization, stormwater runoff from impermeable surfaces and leakages from septic systems and urban sewers (Brown and Froemke, 2012; Groffman et al., 2004; Hobbie et al., 2017; Lerner et al., 1999; Lerner, 2003; Wakida and Lerner, 2005; Winiwarter et al., 2020). The combined impacts of these anthropogenic perturbations have

resulted in the doubling of the global delivery of N and P to fresh waters over the 20th century (Beusen et al., 2016).

The enrichment of N and P within aquatic ecosystems is the leading cause of water quality issues within both developed and developing countries around the world (Howarth, 2008; Jarvie et al., 2015; Metson et al., 2020a; Suh and Yee, 2011; Sutton et al., 2011; United Nations, 2018). As nutrients often limit primary production (Whitehead and Crossman, 2012), excess N and P concentrations, specifically when in their bioavailable forms as NO_3 and PO_4, have caused severe eutrophication of many inland and coastal waters (Bijay and Craswell, 2021; Howarth, 2008; McDowell et al., 2020). Eutrophication has been a global issue since the 1980's (UNEP/WHO, 1988) and is characterised by excessive phytoplankton and algal growth that can lead to hypoxia, harmful algal blooms, habitat degradation, loss of biodiversity and reduced potable water quality (Camargo and Alonso, 2006; Mekonnen and Hoekstra, 2015; Shukla and Saxena, 2018; United Nations, 2018; Whitehead and Crossman, 2012). There is also evidence linking drinking water with elevated N concentrations to infant methemoglobinemia, elevated risk of cancer and adverse birth outcomes (Temkin et al., 2019; Ward et al., 2018). The adverse effects of algal blooms on human health (Davis and Shaw, 2006; World Health Organization, 1999), tourism and commercial fishing have significantly impacted the worldwide economy (Dodds et al., 2009; Pretty et al., 2003; Sanseverino et al., 2016; Sobota et al., 2015; Strokal et al., 2020; Van Grinsven et al., 2013). The costs associated with water quality monitoring and management policies that aim to decrease nutrient pollution are one of the largest environmental expenditures for many developed countries (Keiser et al., 2019).

Other environmental impacts of an anthropogenically enhanced N cycle include climate change, acid rain, biodiversity decline, and changes to the ozone (Houlton et al., 2013). The production and transport of synthetic N fertilizers, along with field emissions of nitrous oxide (N_2O) subsequent to their use, were responsible for 2.1% of global greenhouse gas emissions in 2018 (Menegat et al., 2022). The non-renewable nature of geological P reserves, in the face of rising

global demand for P fertilizers, has also led to concerns of future P scarcity and thus future food security (Nedelciu et al., 2020). The prevailing paradox of simultaneous P scarcity and excess makes the sustainable use of P a pressing global challenge (Leinweber et al., 2018). Since the industrial revolution, fossil fuel combustion and land use change have increased levels of atmospheric CO_2 by over 50% and contributed to global climate change (NOAA, 2022). Along with other anthropogenic pressures, changes to land use and climate have also extensively impacted a range of freshwater C fluxes, including terrestrial C inputs, CO_2 emissions, primary production and the export and burial of C (Butman et al., 2015; Pilla et al., 2022; Tian et al., 2023). For example, anthropogenic activities have caused the delivery of C from land to fresh waters to increase by 0.8 Pg C yr^{-1}, relative to the pre-industrial era (Regnier et al., 2013). This increase has implications for accurately estimating other components of the global carbon budget, including the attribution of CO_2 emissions to either natural or anthropogenic sources (Pilla et al., 2022; Regnier et al., 2022; Tian et al., 2023).

2.2.3 The Need for Integrated Macronutrient Budgets and Targeted Management Strategies

Enhancing food production in the face of a rising global population, whilst preventing nutrient pollution of aquatic environments and climate change, is a major global challenge and requires more sustainable nutrient use (Leinweber et al., 2018; Xie and Ringler, 2017; Zhang et al., 2020). Despite huge investments and decades of effort around the world, policies aiming to improve water quality and meet climate change related targets have not resulted in expected trajectories of improvement (Keiser et al., 2019; Maslin et al., 2023). Observable improvements to both water and air quality have often been slower than anticipated and atmospheric pollution and poor water quality still widely persist (Manuel, 2014; Meals et al., 2010; USEPA, 2010). Although this is partially due to legacy pollution and the inherent time lag between policy implementation and observed improvements (Brown et al., 2019a; Chang et al., 2021; Chen et al., 2018; Haygarth et al., 2014; Jarvie et al., 2013; Liptzin and Dahlgren, 2016; Meals et al., 2010; Sharpley et al., 2013; Stackpoole et al., 2019; Van Meter et al., 2016; Van Meter et al., 2021), accurately apportioning sources of nutrients and developing effective and targeted management practices remain

significant challenges (Davies et al., 2014; Gooddy et al., 2015; Kirk et al., 2024; Shortle et al., 2020; Young et al., 2009; Zhang et al., 2020).

Nutrient budgets seek to identify and quantify all inputs, stores, and losses of nutrients within a defined boundary. This boundary can be based upon a range of spatial scales including individual properties (Baker et al., 2007), watersheds (Metson et al., 2020b; Sabo et al., 2022), regions (Baron et al., 2012; Environment Agency, 2019; European Environment Agency, 2005) and the globe (Chowdhury et al., 2014; Zhang et al., 2020). Budgets can also be made for individual economic sectors (Liu and Mauter, 2022; Metson et al., 2020a; Suh and Yee, 2011) and ecosystems (Najjar et al., 2018; Winiwarter et al., 2020; Zhang et al., 2020). Improving nutrient budgets will firstly require a reduction in the numerical uncertainties that are associated with estimates of anthropogenic pressures on N, C and P fluxes (Baron et al., 2012; Fowler et al., 2013; McGrane, 2016; Sobota et al., 2013). Accurate nutrient budgets and effective nutrient management strategies will also require an integrated approach. This means that all nutrient inputs, transformations and outputs that impact a system (on a spatial and temporal scale that is relevant to management decision making) must be accurately quantified and managed (Baker et al., 2007; Chowdhury et al., 2014; EPA Science Advisory Board, 2011; Grizzetti et al., 2015; Malone and Newton, 2020; Metson et al., 2020b; Pilla et al., 2022; Shen et al., 2023; Shortle et al., 2020; Vachon et al., 2021; Wu and Ma, 2015; Zhang et al., 2020).

The importance of accounting for all nutrient input, transformation, and output mechanisms within nutrient budgets is highlighted by the fact that many budgets utilise a mass balance approach in order to estimate their components (Zhang et al., 2020). For example, the denitrification and aquatic storage of N are often assumed to be the difference between anthropogenic inputs and riverine outputs of a catchment (EPA Science Advisory Board, 2011; van Breemen et al., 2002; Van Meter et al., 2016; Worrall et al., 2012), and the input of C to inland waters from land is often calculated as the residual of an inland water mass balance equation (Pilla et al., 2022). Determining net anthropogenic inputs of N and P to rivers around the world,

as a useful predictor for the export of these nutrients to the ocean, also makes use of a mass balance approach (Algren et al., 2023; Hong et al., 2011; Mao et al., 2021; Russell et al., 2008; Swaney et al., 2012). It has been suggested that the disconnect between the nutrient inputs and exports quantified within some watershed nutrient budget studies may be due to the omission of certain retention processes (Grieger and Harrison, 2021; Metson et al., 2020b). The importance of integrating freshwater C fluxes into wider C budget assessments has also been highlighted (Cole et al., 2007; Vachon et al., 2021). Specifically, the omission of freshwater C fluxes within C budgets can lead to biased estimation and uncertainty of other constituent C fluxes, including emissions of CO_2 from surface waters to the atmosphere, thus hindering the ability to respond effectively to a changing C cycle (Butman et al., 2018; Chaplot and Mutema, 2021; Drake et al., 2018; Regnier et al., 2013; Regnier et al., 2022; Zhang and Planavsky, 2019).

An integrated nutrient management approach also requires simultaneous consideration of all nutrients and freshwater environments. For example, the impacts of perturbed N, P and C cycles are now thought to amplify one another (Allesson et al., 2020; Anderson et al.; Beaulieu et al., 2019; Cross et al., 2022; Downing et al., 2021; Pilla et al., 2022; Sinha et al., 2019) and N and P can be co-limiting nutrients for primary production (USEPA, 2015). Additionally, the movement of water, N, C and P between fresh surface water and groundwater environments results in both compartments having influence on overall nutrient cycles, and the need for them to both be considered when creating nutrient management strategies (Jakeman et al., 2016). For example, although groundwaters are a relatively slow changing component within overall cycles of N and P, they have a direct influence on recipient surface and drinking waters (Puckett et al., 2011; Stuart and Lapworth, 2016).

2.3 Water Supply Processes: An Emerging Caveat for Integrated Nutrient Budgets and Management

Anthropogenic pressures upon global resources of fresh water are substantially increasing. Global demand for fresh water has increased six-fold over the past century and will continue to

increase in the wake of both anticipated population growth and economic development (Boretti and Rosa, 2019; Wada et al., 2016). Globally, fresh water is predominantly used for industrial, agricultural and domestic uses, with agricultural use representing around 70% of the total global use of fresh water (WWAP, 2018). Fresh water use varies significantly between countries, with Central Asia and the United States having some of the largest per capita withdrawal rates anywhere globally (FAO, 2024). Fresh water is then treated and supplied for different end uses via a range of different processes. Firstly, raw water must be withdrawn from either a surface water or groundwater source, via surface water intakes and groundwater wells, respectively. It is then pumped or passively transported to a location of use or to a place of storage, such as within tanks and reservoirs. Water to be used for human consumption then undergoes varying levels of treatment, before being piped to users and returned to wastewater treatment plants for treatment and release back into the environment.

Whilst the demand for fresh water will likely increase in the future, climate change and water pollution will continue to increase the variability of fresh water as a resource. As a result, the need for enhanced treatment processes (such as desalination), the recycling of wastewater and large-scale transfers of water from areas of surplus to deficit are anticipated to increase (He et al., 2021). Despite the significant perturbations that human water use continue to cause to the natural water cycle, integration of anthropogenic water management within depictions of the global water cycle has historically been lacking (Abbott et al., 2019). Growing recognition for the importance of human perturbations upon the global water cycle is reflected by the United States Geological Survey's (USGS) recent integration of these human interactions within a recently published water cycle figure (Figure 2.2).

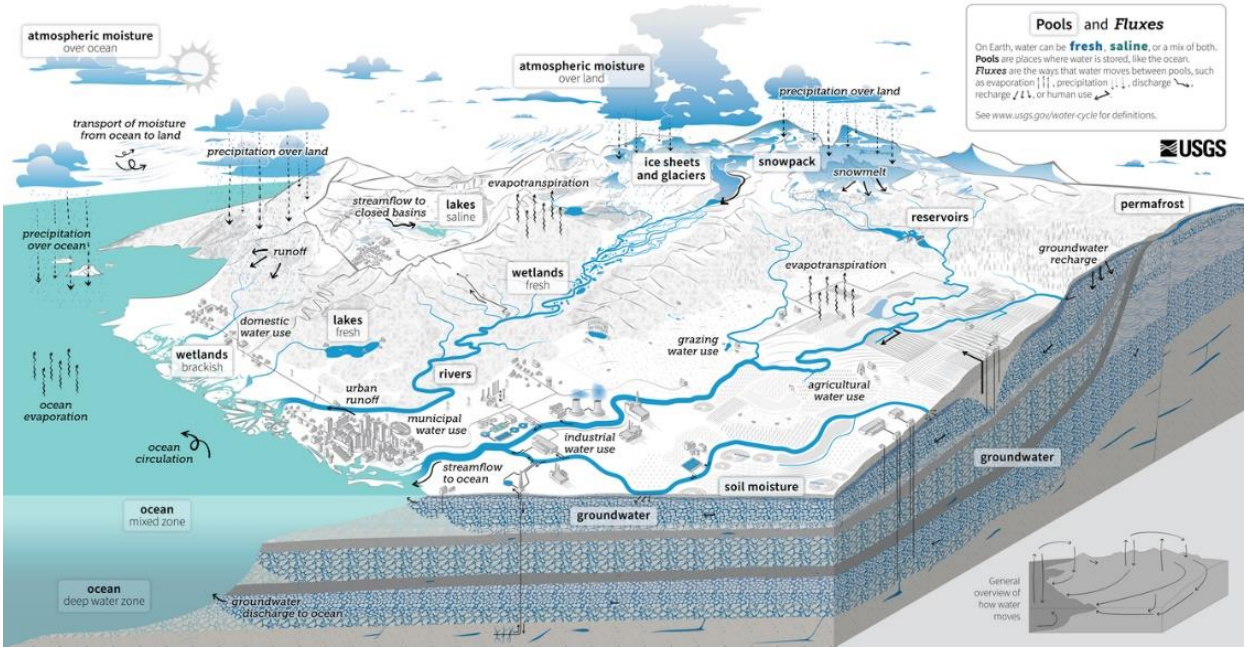

Figure 2.2. A modified version of a schematic detailing major components of the global water cycle. The schematic shows how both natural and anthropogenic processes can impact where water is stored, how it is moved and how clean it is. Specifically, this schematic explicitly acknowledges that human water use for municipal, agricultural and industrial purposes can impact both water quality and quantity, as well as the time frame in which water is cycled. Image credit to the USGS VizLab (USGS, 2022).

A small body of recent research has identified a number of these anthropogenic freshwater supply processes as mechanisms that can impact nutrient cycling (Table 2.1). Withdrawals of fresh surface water and groundwater for public supply across the United Kingdom (UK) have been estimated to retain 4 and 46 kt organic N and C yr^{-1}, respectively (Finlay et al., 2016). Similarly, freshwater withdrawals across England, UK, have been estimated to retain 24.2 kt NO_3-N yr^{-1} (Ascott et al., 2018b). Global-level freshwater withdrawals and reservoir interception have been estimated to reduce the downstream export of dissolved organic C to the ocean by 13.36 Tg C yr^{-1} (You et al., 2023). Fresh groundwater withdrawals have also been estimated to bring 19 Tg total C yr^{-1}, 1.2-3.7 Tg dissolved organic C yr^{-1} and 3.55 Tg N yr^{-1} to the surface (Downing and Striegl, 2018; McDonough et al., 2022; Stahl, 2019). The alteration of stream-groundwater

interactions caused by groundwater withdrawals are also thought to reduce the N retention capacity of streams (Azizian et al., 2017). Withdrawals of groundwater, that are supersaturated with respect to CO_2 and CH_4, have also been identified as a source of greenhouse gas emissions to the atmosphere. Specifically, 1.7 and up to 131 Tg CO_2 yr^{-1} were estimated to be emitted due to degassing groundwater withdrawals across the US and India, respectively (Mishra et al., 2018; Wood and Hyndman, 2017). Degassing groundwater withdrawals across the UK and US have also been estimated to be responsible for the emission of $2.2x10^{-6}$ and $4.4x10^{-2}$ Tg CH_4 yr^{-1} to the atmosphere, respectively (Gooddy and Darling, 2005; Kulongoski and McMahon, 2019).

The need for treated water transfers is also continuing to increase around the world (Palmer and Characklis, 2009; Water UK, 2016). The ongoing transfer of raw water from areas of surplus to those of stress can also affect nutrient cycling, as nutrients can be introduced into the receiving system in association with the transferred water (Zeng et al., 2015; Zhuang, 2016). Research has highlighted the impact of these transfers upon the quality of potable water (CIWEM, 2014) and greenhouse gas emissions (Griffiths-Sattenspiel and Wilson, 2009; Reffold et al., 2008). A number of countries, including the US, the UK and Canada, also dose their potable water with PO_4 in order to prevent lead and copper corrosion within distribution pipes (Akoumainaki, 2017; Health Canada, 2009; Lamb, 2020; McNeill and Edwards, 2002). Most potable water ends up as wastewater treatment plant effluent, where PO_4 can then be released into surface water environments. The proportional contribution of dosing sourced P to wastewater treatment plant influent and effluent P loads continues to be an active area of research (Gooddy et al., 2015; USEPA, 2020a). Leakages of treated potable water and sewage from pipes were first hypothesised as sources of groundwater nutrient pollution over two decades ago (Holman et al., 2008; Lerner et al., 1999). Leakage fluxes of both NO_3 and PO_4 from distribution pipes have since been quantified on both catchment (Ascott et al., 2018a; Gooddy et al., 2017; Wakida and Lerner, 2005) and national scales, with 3.62 kt NO_3-N yr^{-1} and 1.2 kt PO_4-P yr^{-1} estimated to be input to the environment due to watermains leakage across England, UK (Ascott et al., 2016; Ascott et al., 2018b). The construction of reservoirs and dams around the world have also impacted the retention of macronutrients within freshwater (Beusen et al., 2016; Wang et al., 2022) through

their enhancement of N and P accumulation and burial within sediments, and alteration of C and N mineralisation (Akbarzadeh et al., 2019; Maavara et al., 2017; Maavara et al., 2015). Specifically, the construction of reservoirs around the world have been estimated to prevent the downstream export of 6.48 and 1.1 Tg N and P yr^{-1}, respectively (Beusen et al., 2016).

The end use of freshwater can also alter the movement of macronutrients within the environment, with major water use sectors having different controls on nutrient cycling. The use of water for irrigation can impact the amount of C storage and N and P retention within a watershed (Grieger and Harrison, 2021; Zhu et al., 2020). A range of treatment and distribution processes associated with the use of water for public supply can also impact the cycling of N, C and P. For example, there are embedded greenhouse gas emissions associated with the treatment of potable water (Finlay et al., 2016; Plappally and Lienhard V, 2012), however the removal of dissolved organic C from raw water through the process of coagulation has also been found to slow the speed at which C enters the atmosphere (Jones et al., 2016).

The importance of water supply processes as mechanisms perturbing overall nutrient cycles has been assessed through the comparison of anthropogenic water supply fluxes with natural fluxes (Klee and Graedel, 2004). For example, the flux of organic N removed from aquatic environments due to freshwater withdrawals across the UK (4 kt N yr^{-1}) exceeded the amount of N retained by transient floodplain storage, and the amount of organic C diverted by these withdrawals (46 kt C yr^{-1}) was equivalent to up to 1.3% of the UK's total fluvial organic C flux (Finlay et al., 2016). The retention flux of NO_3 from aquatic environments due to withdrawals across England (24.2 kt N yr^{-1}) was estimated to be equivalent to up to 39% of N removal due to denitrification in surface waters, groundwaters and coastal marine environments (Ascott et al., 2018b). The flux of N removed due to irrigation groundwater withdrawals was estimated to be significant in the context of fertilization requirements across regions of the US (Stahl, 2019). Globally, the estimated retention flux of organic C due to groundwater withdrawals (1.2 Tg C yr^{-1}) was equivalent to 41% of the total organic C exported to the oceans by subterranean groundwater

discharge (McDonough et al., 2022). The withdrawal and use of freshwater for irrigation is a potential N retention mechanisms that, due to the potential for increased denitrification and sorption, may account for the disconnect observed between estimated nutrient inputs and exports within watershed-scale nutrient budgets (Grieger and Harrison, 2021).

It has been estimated that by 2030, around 15%, 17% and 19% of the global riverine N, P and organic C loads may be retained within reservoirs, respectively (Akbarzadeh et al., 2019; Maavara et al., 2017; Maavara et al., 2015). Inputs of NO_3 and PO_4 across England's urban areas due to leakage from watermains (3.62 and 1.2 kt N and P yr^{-1}, respectively) were estimated to be equivalent to 20% and 30% of total N and P inputs in these areas, respectively (Ascott et al., 2016; Ascott et al., 2018b). The greenhouse gas emissions that are associated with different facets of water supply have also been found to be non-trivial, with the release of CO_2 from degassing groundwater withdrawals (1.7 Tg CO_2 yr^{-1}) estimated to be in the top third of CO_2 emissions sources across the US (Wood and Hyndman, 2017). The significance of these fluxes, in the context of other budget components, not only supports their inclusion within nutrient budget studies, but also suggests they represent a risk of resulting in ecological and environmental harm.

Table 2.1. Previous estimates of nitrogen (N), carbon (C) and phosphorus (P) fluxes that are associated with water supply processes on a global and national level. The term 'freshwater withdrawals' refers to withdrawals of both fresh groundwater and surface water.

Flux	Spatial Scale	Reference	Value
Carbon (C)			
Retention of organic C due to freshwater withdrawals across the United Kingdom	National	Finlay et al. (2016)	46 kt C yr^{-1}
Global retention of dissolved organic C due to freshwater withdrawals and reservoir interception	Global	You et al. (2023)	13.36 Tg C yr^{-1}
Global input of C into surface waters due to groundwater withdrawal	Global	Downing and Striegl (2018)	19 Tg C yr^{-1}
Global removal of dissolved organic C from groundwaters due to groundwater withdrawal	Global	McDonough et al. (2022)	1.2 - 3.7 Tg C yr^{-1}
Carbon dioxide emissions due to the degassing of fresh groundwater withdrawals across India	National	Mishra et al. (2018)	31 - 131 Tg CO_2 yr^{-1}
Carbon dioxide emissions due to the degassing of depleted fresh groundwater across the United States	National	Wood and Hyndman (2017)	1.7 Tg CO_2 yr^{-1}
Methane emissions due to the degassing of fresh groundwater withdrawals across the United Kingdom	National	Gooddy and Darling (2005)	$2.2x10^{-6}$ Tg CH_4 yr^{-1}
Methane emissions due to the degassing of fresh groundwater withdrawals across the United States	National	Kulongoski and McMahon (2019)	$4.4x10^{-2}$ Tg CH_4 yr^{-1}
Nitrogen (N)			
Retention of organic N due to freshwater withdrawals across the United Kingdom	National	Finlay et al. (2016)	4 kt N yr^{-1}
Retention of nitrate due to fresh public supply withdrawals across England, United Kingdom	National	Ascott et al. (2018b)	24.2 kt N yr^{-1}
Retention of N due to construction of reservoirs globally	Global	Beusen et al. (2016)	6.48 Tg N yr^{-1}
Mass flux of N removed from aquifers due to global groundwater withdrawal	Global	Stahl (2019)	3.55 Tg N yr^{-1}
Return of nitrate to the environment due to watermains leakage across England, United Kingdom	National	Ascott et al. (2018b)	3.62 kt N yr^{-1}
Phosphorus (P)			
Retention of P due to construction of reservoirs globally	Global	Beusen et al. (2016)	1.1 Tg P yr^{-1}
Input of phosphate to the environment due to watermains leakage across England, United Kingdom	National	Ascott et al. (2016)	1.2 kt P yr^{-1}

2.4 The United States: A Globally Important Exemplar

2.4.1 Anthropogenic Impacts upon Nitrogen, Carbon and Phosphorus Cycles Across the United States

The US is a developed country with disparate climate, ecology and geography and has the third largest population of any country globally (United States Census Bureau, 2024). Anthropogenic use of N across the US has been inefficient and has resulted in five times the amount of reactive N being lost to the environment since the industrial revolution (Houlton et al., 2013), the proportion of which is nearly double that of the global average (Sobota et al., 2015). Similarly, the manufacturing, export and use of inorganic P across the US is globally significant (MacDonald et al., 2012). The inefficient use of P fertilizer across the country has caused P accumulation within agricultural soils (Frei et al., 2021; MacDonald et al., 2012; Sabo et al., 2021b; Suh and Yee, 2011). Point sources, such as industrial and municipal wastewater treatment plant effluents, are also inputting large N and P loads into the country's freshwater environments (Skinner and Wise, 2019). Poor nutrient management across the US has resulted in most of the country's fresh surface waters having N and P concentrations that compromise their ecological health (Manning et al., 2020). Fresh and coastal water eutrophication across the country is severe, with the impacts of eutrophication within Chesapeake Bay ranked to be the greatest of anywhere globally (Malone and Newton, 2020). The US is also one of the top greenhouse gas emitters with respect to emissions from the unsustainable use of synthetic N fertilizers (Menegat et al., 2022), which has complex implications for radiative forcing and respiratory health of the population (Pinder et al., 2013; Sobota et al., 2015).

The importance of understanding US inland water C fluxes in the context of the global C cycle is reflected by the incorporation of North American C fluxes within the most recent State of Carbon Cycle Report (USGCRP, 2018). Human activities have impacted freshwater C fluxes across the country, with land management practices and irrigation increasing US riverine C exports (Raymond et al., 2008; Ren et al., 2016; Ren et al., 2015; Tian et al., 2015) and man-made reservoirs acting as sources of atmospheric CO_2 (Beaulieu et al., 2020; Soumis et al., 2004). The

relative contributions of individual fresh surface water C fluxes (C burial, CO_2 emissions and C export to the oceans) to total freshwater C cycling are proportionally similar on a global and US level (USGCRP, 2018), highlighting the US an exemplar location for investigating anthropogenic influences on freshwater C cycling.

Impacts of altered N, C and P cycles across the US, including loss of aquatic life and decreased quality of recreational and drinking waters, result in significant economic costs for the country (Dodds et al., 2009; Langholtz et al., 2021; Mosheim and Sickles, 2021). In order to reduce both point and non-point source N and P water pollution, the US has developed federal laws, including the Clean Water Act (USEPA, 1972) and Safe Drinking Water Act (USEPA, 1974). A vast array of best management practices for N and P have also been implemented within both agricultural and non-agricultural settings (Ice et al., 2010; Liu et al., 2017; Sharpley et al., 2006). Some attempts to curb nutrient pollution have been successful, with the National Pollutant Discharge Elimination System program (part of the Clean Water Act) resulting in major declines of N and P release from point sources since the 1970's (Manuel, 2014; USEPA, 2024). Instances of freshwater C management are less widespread than those for N and P (Stanley et al., 2012) and the rapid changes in fresh surface water chemistry make evaluating the effectiveness of freshwater C management inherently difficult (USGCRP, 2018). Minimising current knowledge gaps and uncertainties surrounding both natural and anthropogenic freshwater C fluxes on a regional level across the US remains an important area of future research (Butman et al., 2018).

Despite huge financial investments in regulating nutrient inputs across the US (Keiser and Shapiro, 2019), improvements to freshwater quality have generally been slower than anticipated and nutrient pollution of fresh and coastal waters continues to persist (Frei et al., 2021; Keiser et al., 2019; Oelsner and Stets, 2019). Hypotheses explaining a lack of observed water quality improvements across many parts of the US include the remobilisation of historically accumulated N and P within the terrestrial and aquatic environments (Haygarth et al., 2014; Stackpoole et al., 2019; Van Meter et al., 2016; Van Meter et al., 2021; Van Meter et al., 2018) and the impact that

climate change can have upon the release of nutrients from these stores and overall nutrient export (Sabo et al., 2023; Sinha et al., 2019; Zia et al., 2022). Studies across the US have also suggested that observed decoupling between estimated inputs of N and P and their export downstream may be due to a lack of accounting for their respective input and retention processes (Grieger and Harrison, 2021; Metson et al., 2020b). There are also critical knowledge gaps and large uncertainties surrounding both natural and anthropogenically impacted freshwater C fluxes across the US (Butman et al., 2018). This continues to hinder the accuracy of C source apportionment and carbon balance assessments, as well as the efficacy of integrated land and water management strategies, with implications for managing atmospheric CO_2 emissions (Butman et al., 2016; Casas-Ruiz et al., 2023; USGCRP, 2018). By the year 2050, the US Department for Agriculture has set a target for increasing agricultural production by 40%, whilst reducing nutrient losses by 30% (USDA, 2020b). Although the US has made positive progress in reducing its CO_2 emissions, it remains a globally significant emitter of CO_2 (Ritchie, 2019) and further reductions will require ever more accurate carbon budget assessments. Achieving targets and more sustainably managing N, C and P cycling across the US will ultimately require a more integrated approach (Casas-Ruiz et al., 2023; Haque, 2021; Sabo et al., 2021a; USGCRP, 2018) that moves beyond conventional budget development and nutrient management strategies.

2.4.2 The Impacts of Water Supply Processes on Macronutrient Cycling Across the United States

The US has some of the largest per capita rates of freshwater use anywhere globally (FAO, 2024). Water use estimates made by the USGS suggest that water withdrawn for irrigation and thermoelectric power sectors are accountable for the majority of freshwater withdrawals on a national level, at around 42% and 34% of the total, with other water use sectors, including public supply, industry, domestic, aquaculture, livestock and mining, being locally significant users of fresh water across the country (Dieter et al., 2018b). The volume of freshwater withdrawals from surface water environments varies across the US and reflect its availability, with drier regions and seasons of the year that lack a supply of fresh surface water relying more on groundwater withdrawals to meet demand (Dieter et al., 2018b; Scanlon et al., 2012). Disparities between freshwater demand and supply prevail across the country and result in the need for large scale

transfers of both raw and treated water, particularly for irrigation and public supply uses (Siddik et al., 2023; Young and Brozovik, 2019). The treatment and fate of withdrawn water then varies between each major water use sector. For example, water used for public supply across the US is subjected to extensive treatment processes including pH adjustment, corrosion control and disinfection (Patel et al., 2020), whereas water used for irrigation is largely untreated prior to use.

Emerging research has identified water supply processes across the US, including freshwater withdrawals, water impoundments and potable water treatment, as mechanisms impacting cycles of N, C and P. The flux of N removed due to groundwater withdrawals for irrigation was estimated to be significant in the context of fertilization requirements across regions of the country (Stahl, 2019), however the impact of freshwater withdrawals (both surface water and groundwater) upon freshwater N retention across the US is yet to be determined. As part of a global assessment, fresh surface water and groundwater withdrawals across the country were also identified as a mechanism capable of preventing downstream export of organic C (You et al., 2023). The US has globally significant riverine and subterranean groundwater discharge exports of DIC to the ocean (Chaplot and Mutema, 2021; Liu et al., 2024) and the loading of DIC to fresh waters is a major control on CO_2 emissions (McDonald et al., 2013). Estimates of C fluxes (both organic and inorganic) through fresh inland waters of the US, and the anthropogenic influences on these fluxes, remain poorly constrained, however (Butman et al., 2018). Estimating the impact of fresh surface water and groundwater withdrawals upon freshwater DIC retention across the US therefore remains an important area of research. The degassing of fresh groundwater withdrawals across the US were also found to be an important source of CO_2 emissions (Wood and Hyndman, 2017), however the national-level estimate was determined using a range of nationally-averaged values and didn't reveal any localised hotpots of CO_2 release. The extent of PO_4 dosing across the US has only been characterised on a national-level (USEPA, 2020a), and although the subsequent leakage of PO_4 and NO_3 from treated potable water supplies has been identified as an important source of N and P across urban environments in the UK (Ascott et al., 2016; Ascott et al., 2018b), sub-national level estimates of PO_4 dosing practices and watermains

leakage fluxes of N and P are missing across the US. Excessive lawn irrigation has been identified as a significant contributor to summer base flow across some areas of the US (Fillo et al., 2021). An understanding of how the use of PO_4 dosed water for lawn irrigation across the country might be acting as a P release mechanism is also lacking. Freshwater use across the US is globally significant and nutrient pollution and greenhouse gas emissions are persistent problems for the country. Given US water supply infrastructure, management and use are reflected across other well-developed countries and regions around the world (e.g. Canada, Australia, Europe and China), the US makes is an appropriate exemplar for further investigating the impacts of water supply processes upon macronutrient cycling.

2.5 Knowledge Gaps

2.5.1 Knowledge Gaps Identified in Previous Work

Research has shown that a range of anthropogenic water supply processes can alter the movement of N, C and P between terrestrial, freshwater, atmospheric and marine systems, on magnitudes that have implications for the development of accurate nutrient budgets and environmental health. Although much of the work done in this research area has provided a foundational understanding of the impacts that these processes can have upon macronutrient cycling, these studies have identified a wide range of knowledge gaps and future research needs, including:

- Ensuring comprehensive freshwater biogeochemical and withdrawal volume datasets are used to estimate freshwater withdrawal macronutrient fluxes, for both organic and inorganic fractions of nutrients, across other countries around the world (Ascott et al., 2018b; Stahl, 2019; You et al., 2023).

- Reducing the number of assumptions, including the use of globally and nationally averaged nutrient concentration and water withdrawal volume data (Downing and Striegl, 2018; McDonough et al., 2022; Wood and Hyndman, 2017), that are adopted within studies seeking to understand the impact of water supply processes on

macronutrient cycles on larger spatial (continental and global) scales, as a way of reducing uncertainties and revealing hotspots of these fluxes.

- Estimating the magnitude and fate of watermains leakage NO_3 and PO_4 fluxes across other countries with developed water distribution networks that utilise PO_4 as a corrosion inhibitor (Ascott et al., 2018a; Ascott et al., 2016; Ascott et al., 2018b; Gooddy et al., 2017).

2.5.2 Knowledge Gaps to be Addressed

Several of the research gaps identified in Sections 2.4.2 and 2.5.1 will be addressed within this thesis, including:

- Estimating the impact of freshwater withdrawals (both surface water and groundwater) upon the freshwater NO_3 retention across the US. This will be the first time that freshwater withdrawal NO_3 retention fluxes have been estimated across the country. It is also the first time that water use sector contributions to freshwater withdrawal NO_3 retention fluxes will have been identified anywhere globally.

- Estimating the impact of freshwater withdrawals (both surface water and groundwater) upon the freshwater DIC retention across the US. This will be the first time that freshwater withdrawal DIC retention fluxes have been estimated across the country and anywhere globally. It is also the first time that water use sector contributions to freshwater withdrawal DIC retention fluxes will have been identified anywhere globally.

- Estimating the emissions of CO_2 due to degassing fresh groundwater withdrawals across the US. This will be the first time that CO_2 emissions from this source will have been estimated on a county level across the country, as a way of investigating spatial variability. It is also the first time that water use sector contributions to these emissions will have been identified anywhere globally.

- Estimating the mass flux of PO_4 added to the US water supply network due to corrosion control dosing practices and subsequent release of PO_4 to the environment due to watermains leakage and outdoor water use on a county level across the US. This will be the first time that watermains leakage and outdoor water use PO_4 fluxes have been estimated on a county level across the country and the spatial variability of these fluxes evaluated. It is also the first time that outdoor water use will be evaluated as a PO_4 release mechanism anywhere globally.

- Estimating the mass flux of NO_3 released to the environment due to watermains leakage on a county level across the US. This will be the first time that watermains leakage NO_3 fluxes have been estimated across the country and the spatial variability of this flux evaluated.

The fluxes estimated in relation to addressing these gaps in research are illustrated in Figure 2.3.

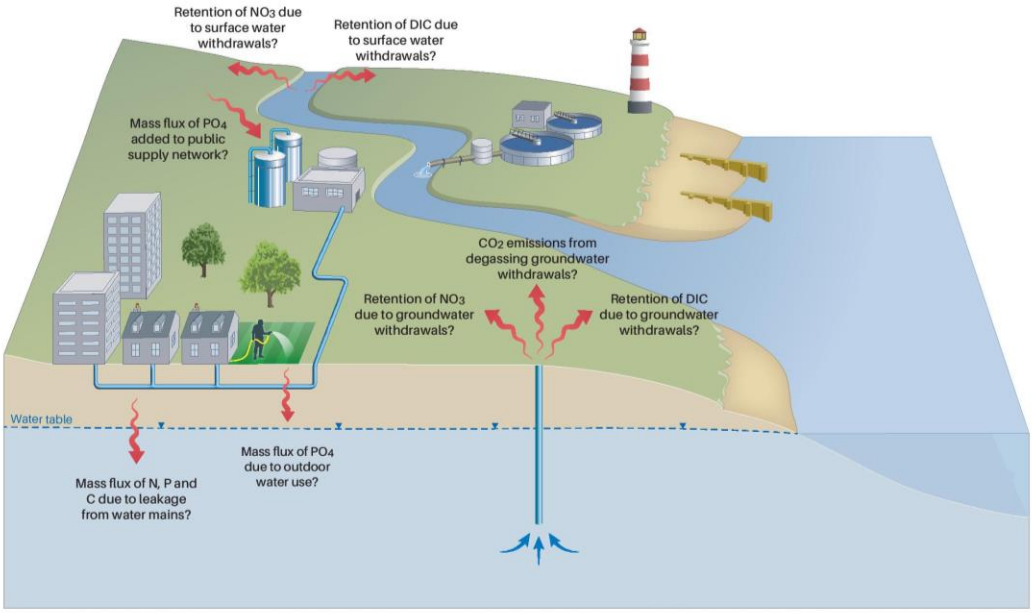

Figure 2.3. Schematic detailing the nitrogen (N), carbon (C) and phosphorus (P) fluxes associated with water supply processes across the United States that will be investigated in this thesis.

2.6 Conclusion

Natural N, C and P cycles have been significantly altered by human activity. Despite decades of effort to control the movement of these nutrients within the environment, perturbations to these cycles continue to cause widespread environmental damage through eutrophication of both fresh waters and coastal ecosystems and climate change. Developing more integrated N, C and P budgets and management strategies, where inputs, transformations and outputs within a given system are accurately quantified, will play an essential role in preventing and mitigating impacts of eutrophication and climate change. Despite recent advances in understanding of how anthropogenic use of freshwater can impact the movement of N, C and P in the environment, research in this area is still scant and global estimates of associated fluxes are either absent or poorly resolved. The use of freshwater use across the US is globally significant and nutrient pollution and greenhouse gas emissions are persistent across the country. The supply infrastructure, processing and usage of fresh water across the US also reflects those of many other developed nations around the globe. These considerations make the US an appropriate exemplar for further investigating the impacts of water supply processes upon N, C and P cycling. Specifically, this thesis will investigate knowledge gaps surrounding how the withdrawal, treatment, distribution and use of freshwater can modify N, C and P cycles across the country. The understanding facilitated through this research will make a valuable contribution to the development of integrated nutrient budgets and sustainable N, C and P management strategies across the US and globally. This thesis will also provide recommendations for future work, should the impacts of water supply processes upon macronutrient cycling around the globe be further understood.

3. Water Supply Processes are Responsible for Significant Nitrogen Fluxes Across the United States

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Author contributions are as follows:

Flint conceptualised research questions and developed the methodology used for data analysis. Flint acquired and analysed freshwater nitrate concentrations and treated drinking waters, freshwater withdrawal rates and leakage rates. Flint developed figures and wrote and revised the manuscript. Co-authors Ascott, Gooddy, Surridge and Stahl have signed below to confirm that they provided general support for development of conclusions during project meetings and provided several rounds of feedback on manuscript drafts.

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3.1 Introduction

Nitrogen (N) plays a crucial role in the metabolic functioning of biological systems and thus global food production (Fields, 2004; Fowler et al., 2013). Anthropogenic activity, in particular the unsustainable application of fertilizer, have caused fluxes of N to exceed safe planetary boundaries (Steffen et al., 2015). The pollution of fresh waters due to excess nitrate (NO_3) concentrations has led to significant, adverse effects on human and environmental health around the globe. These include severe eutrophication of inland and coastal waters (Bijay and Craswell, 2021; Howarth, 2008; McDowell et al., 2020), and decreases in potable water quality (Camargo and Alonso, 2006; Mekonnen and Hoekstra, 2015). Human influences on the N cycle have been pervasive across the US, with the country's anthropogenic production of reactive N five times that of its natural production (EPA Science Advisory Board, 2011). Subsequent nutrient pollution is now a leading cause of degraded freshwater quality across the country (USEPA, 2015) and the effects on environmental and human health are widespread (Bouwman et al., 2013; Munn et al., 2018). Eutrophication of inland and coastal waterbodies has persisted for decades across the US (Bricker et al., 2008; Oelsner and Stets, 2019; Oswald and Golueke, 1966), and the decrease in potable (Kozacek, 2014) and recreational water quality (World Health Organization, 1999), loss of aquatic habitats and disruption to food chains (Munn et al., 2018) are estimated to cost billions of dollars a year (Dodds et al., 2009; Sobota et al., 2015).

Since the Clean Water Act was brought into practice (USEPA, 1972), overall improvements to US freshwater quality have been slow, and elevated N concentrations continue to contribute to persistent poor water quality across the country (Keiser et al., 2019; Manuel, 2014; USEPA, 2010). The sustainable and effective use of nutrients requires an integrated management approach, meaning that nutrient balances for a given system must identify and regularly quantify processes influencing all known inputs, transformations and outputs (EPA Science Advisory Board, 2011; Grizzetti et al., 2015; Roy et al., 2021; Sabo et al., 2019; Wu and Ma, 2015). Delays in freshwater quality improvements reflect the response time of the system (Meals and Dressing, 2008) and associated legacy stores of N in soil, the vadose zone and groundwater (Ascott et al., 2017; Chang et al., 2021). Estimates of these processes, as well those of both established and emerging

anthropogenic pressures on aquatic N cycling, often carry large uncertainty. For example, within national-level budgets, fluxes of N associated with livestock production carry particularly high levels of uncertainty (Sabo et al., 2019). On more localised scales, N fluxes characteristically occurring in urban areas, such as N sourced from combined sewer overflows, urban runoff and atmospheric deposition, are often more poorly constrained than those across agricultural areas, such as agricultural fertilizer input (Chung et al., 2023; Decina et al., 2018; McGrane, 2016). Ultimately, improvements to freshwater N mass balances, policy and management require greater methodological consistency and consideration for the spatial and temporal heterogeneity of anthropogenic influences upon N cycling in these ecosystems (Sabo et al., 2019; Sabo et al., 2021a; Sobota et al., 2013).

Research has begun to highlight the potential role that water supply processes play in N cycling both across the US and around the globe, including their effect on N retention, which is defined here as processes that prevent or delay the delivery of N from the land to the oceans (Grizzetti et al., 2015). For example, the manipulation of water resources through dam construction has been found to impact major retention processes of denitrification and burial of N in sediments both across the US (Baron et al., 2012) and around the world (Beusen et al., 2016; Seitzinger et al., 2007; Wisser et al., 2010). Recent research has found groundwater withdrawal to be a mechanism capable of perturbing the global N cycle (Stahl, 2019). Research in England, UK, has shown that withdrawal of fresh water for public supply acts as a nationally significant transient retention mechanism for organic N (Finlay et al., 2016) and NO_3 (Ascott et al., 2018b), with these results highlighting the need for the inclusion of these fluxes in future nutrient budgets.

The US has one of the largest freshwater withdrawal volumes per capita in the world (FAO, 2024). Freshwater use sectors are defined by the USGS, with sectoral withdrawal volumes estimated every five years (Dieter et al., 2018b). Whilst approximately 14% of country's total freshwater withdrawal in 2015 was for public supply (water withdrawn by both public and private suppliers), the remainder of withdrawals were for non-public and self-supplied uses including for irrigation,

thermoelectric, industry, livestock, aquaculture, domestic (i.e. private wells) and mining (Dieter et al., 2018b).

Leakage of water from the mains distribution network is known to return nutrients to the environment (Holman et al., 2008; Lerner et al., 1999). Recently, research has also begun to quantify these fluxes (Ascott et al., 2016; Ascott et al., 2018b; Gooddy et al., 2017) and investigate how to identify the fate of these fluxes isotopically (Gooddy et al., 2015). Results from a study in England, UK, highlighted the significance of these fluxes, with watermains leakage fluxes equivalent to up to 20% of all N inputs across some urban areas (Ascott et al., 2018b), and thus the need for their incorporation into nutrient budgets and consideration in policy decision making. The declining condition of water infrastructure across the US means watermains leakage is a persistent yet spatially variable problem (Folkman, 2018; Rosario-Ortiz et al., 2016), and results in the USEPA reported average loss of 16% of the water initially entering the country's watermains distribution network (USEPA, 2013).

In this research, the US is used as an exemplar to quantify NO_3 fluxes associated with non-public supply withdrawal for the first time anywhere globally. Public supply NO_3 withdrawal fluxes and watermains leakage NO_3 fluxes are quantified for the first time across the US. It was hypothesised that:

1. Freshwater withdrawals by all water use sectors will constitute a significant transient NO_3 retention mechanism across the US, with the resulting flux making a significant contribution to global withdrawal NO_3 flux estimates.
2. Across the US, watermains leakage will return a spatially heterogeneous and locally significant flux of NO_3 back to the environment.

Publicly available freshwater withdrawal and watermains leakage volumetric rate data, along with untreated (raw) and treated water NO_3 concentrations, were used to quantify fluxes of NO_3

associated with freshwater withdrawals and watermains leakage across the contiguous US, herein referred to as the US. The environmental significance of county, state, and national-scale estimates were evaluated through their comparison with estimates of other N budget components. The implications of results are discussed in both a national and global context and recommendations for future research are made.

3.2 Methods

3.2.1 Quantification of National Withdrawal and Watermains Leakage Nitrate Fluxes

County-level fluxes of NO_3 associated with fresh surface water and groundwater withdrawals for public water supply (PWS-NO_3-N) and self-supplied irrigation (IRR-NO_3-N), thermoelectric power (THERM-NO_3-N), industry (IND-NO_3-N), mining (MINE-NO_3-N), livestock (LIVE-NO_3-N), aquaculture (AQUA-NO_3-N) and domestic (DOMESTIC-NO_3-N) water use sectors were estimated across the 48 states that form the US, and aggregated to give a total national-level withdrawal flux (WD-NO_3-N_{total}) using equation 3.1.

$$WD\text{-}NO_3\text{-}N_{total} = (WD_{sw} \times C_{r\,(SW\text{-}NO3\text{-}N)}) + (WD_{gw} \times C_{r\,(GW\text{-}NO3\text{-}N)}) \quad (3.1)$$

Surface water (WD_{sw}) and groundwater (WD_{gw}) withdrawal data, in L yr^{-1}, were provided for each water use sector within each county for the year of 2015 by the USGS (Dieter et al., 2018a), representing the most up to date freshwater withdrawal estimates across the US. With surface water intake locations not disclosed by the EPA, coordinates of active surface water intakes between 2013-2020 provided by the United States Environment Protection Agency (USEPA, 2021c), were geocoded from intake location names using Google's Geocoding API web service (Google, 2021) in conjunction with R's 'ggmap' package (Kahle and Wickham, 2013). Intake coordinates were then matched to USGS and EPA site coordinates of surface water sites through use of the 'Fuzzyjoin' package using a 5-mile buffer in R (Robinson et al., 2020). Returned sites were queried on the Water Quality Portal (WQP, 2023) for raw dissolved NO_3 and raw dissolved

NO_3 + NO_2 concentrations that were measured between 01.01.2010 and 31.12.2020 using the 'dataRetrieval' package in R (De Cicco et al., 2018). The Water Quality Portal sources its data from the USGS NWIS (USGS, 2021) and the EPA's STORET-WQX (USEPA, 2021d) databases. Due to the negligible concentrations of NO_2 in surface waters, returned dissolved NO_3-N and dissolved NO_3 + NO_2 concentrations were assumed to represent raw surface water NO_3 concentrations ($C_{r\,(SW\text{-}NO3\text{-}N)}$), in mg N L^{-1}.

Raw groundwater NO_3 concentrations ($C_{r\,(GW\text{-}NO3\text{-}N)}$), in mg N L^{-1}, were sourced from USGS National Water Quality Assessment studies (Arnold et al., 2017; Arnold et al., 2018; Arnold et al., 2016; Arnold et al., 2020). To increase the number of data points, $C_{r\,(SW\text{-}NO3\text{-}N)}$ and $C_{r\,(GW\text{-}NO3\text{-}N)}$ values were obtained between 2010-2020 and 2012-2016 respectively. Despite expanding C_r concentration datasets to additional years surrounding 2015, the lack of comprehensive county-level datasets meant that state-level median values of both $C_{r\,(SW\text{-}NO3\text{-}N)}$ and $C_{r\,(GW\text{-}NO3\text{-}N)}$ were assigned to each state's constituent counties. Sector-specific $C_{r\,(GW\text{-}NO3\text{-}N)}$ concentration values were also only available for determination of PWS-NO_3-N and DOMESTIC-NO_3-N fluxes (Appendix 1-4), resulting in remaining $C_{r\,(GW\text{-}NO3\text{-}N)}$ and all $C_{r\,(SW\text{-}NO3\text{-}N)}$ values being uniform across all other sectors (Appendix 5-8). These limitations are discussed further in Section 3.4.1. The resulting concentration datasets were non-normally distributed (Kolmogorov Smirnov test $p < 0.01$), so median concentrations for each state were assigned to their constituent counties and used within equation 3.1. Estimated county fluxes for each water use sector were aggregated to give total county, state and national-level WD-NO_3-N fluxes, in metric kt NO_3-N yr^{-1}. County and state-level estimates were also normalised for land area and expressed as kg NO_3-N km^{-2} yr^{-1}, allowing counties and states of contrasting area to be compared.

County-level NO_3 fluxes due to watermains leakage (WML-NO_3-N) were derived using equations 3.2 and 3.3. Estimated volumetric leakage rates have not been reported by the USGS since 1995 (Dieter et al., 2018b), thus volumetric leakage rates for each county (LV), in L yr^{-1}, were calculated using equation 3.2. With public supply distribution input estimates also omitted from water use

reports, and given the majority of losses are from pipes downstream of the water treatment works (Van Hecke, 2020), distribution inputs were assumed to equal the total volume of freshwater withdrawn for PWS in each county ($WD_{pws\text{-}total}$), in L yr^{-1}. Freshwater withdrawals for PWS (assumed to be distribution inputs) are reported by the USGS (Dieter et al., 2018a). These estimates include unaccounted for water, including system losses (i.e. leakage) and so must be corrected using a leakage factor. With the exception of California and Georgia (see Section 3.2.2), a lack of county-level leakage factor data meant that state-level leakage factors, $f_{leakage}$ (unitless), were obtained from various sources and assigned to their respective counties. Where possible, $f_{leakage}$ values were determined by dividing volume of real water loss by volume of total water supplied from validated American Water Works Association water utility audits for the year of 2016 (American Water Works Association, 2021). Utility $f_{leakage}$ values were then averaged and extrapolated for the relevant state (see Kunkel Water Efficiency Consulting (2018)). In the absence of water audit data, state values were sourced from various reports (Appendix 9), or as a last resort a USEPA reported national average of 16% was assumed for that state (USEPA, 2013). Due to the absence of county-level data, average treated water NO_3-N concentrations ($C_{t\text{-}(NO3\text{-}N)}$) for each state between 2014-2019, in mg N L^{-1}, were sourced from the Environmental Working Group database (EWG, 2019) and assigned to all of its constituent counties. County fluxes were aggregated to give state and national-level WML-NO_3-N estimates, as well as normalised for land area, expressed as kg NO_3-N km^{-2} yr^{-1}. A summary of data sources used to estimate both WD-NO_3-N and WML-NO_3-N fluxes is provided in Table 3.1.

$$LV = WD_{pws\text{-}total} \times f_{leakage} \quad (3.2)$$

$$WML\text{-}NO_3\text{-}N = C_{t\ (NO3\text{-}N)} \times LV \quad (3.3)$$

Table 3.1. Table summarising data sources for key terms used for the estimation of freshwater withdrawal nitrate fluxes (WD-NO_3-N) and watermains leakage nitrate fluxes (WML-NO_3-N), on both a national level and for the states of California and Georgia.

Term	Term Description	Reference
National WD-NO_3-N		
WD_{gw}	Fresh groundwater withdrawals	Dieter et al. (2018a)
WD_{sw}	Fresh surface water withdrawals	Dieter et al. (2018a)
$C_{r\ (SW\text{-}NO3\text{-}N)}$	Raw surface water NO_3 concentrations	WQP (2023)
$C_{r\ (GW\text{-}NO3\text{-}N)}$	Raw groundwater NO_3 concentrations	Arnold et al. (2017), Arnold et al. (2018), Arnold et al. (2016), (Arnold et al., 2017; Arnold et al., 2018; Arnold et al., 2016); Arnold et al. (2020)
California WD-NO_3-N		
$C_{r\ (GW\text{-}NO3\text{-}N)}$	Raw groundwater NO_3 concentrations	Jurgens et al. (2021)
National WML-NO_3-N		
$WD_{pws\text{-}total}$	Total freshwater public supply withdrawals	Dieter et al. (2018a)
$\boldsymbol{f}_{leakage}$	Leakage factor	Various (see Appendix 9)
State-level $C_{t\ (NO3\text{-}N)}$	Treated water NO_3 concentrations	EWG (2019)
California WML-NO_3-N		
LV	Volumetric leakage rate	California Department of Water Resources (2019)
Utility-level $C_{t\ (NO3\text{-}N)}$	Treated water NO_3 concentrations	EWG (2019)
Georgia WML-NO_3-N		
LV	Volumetric leakage rate	Georgia EPD (2016)
Utility-level $C_{t\ (NO3\text{-}N)}$	Treated water NO_3 concentrations	EWG (2019)

3.2.2 Freshwater Withdrawal and Watermains Leakage Nitrate Flux Method Validation

Due to greater availability of $C_{r\,(GW\text{-}NO3\text{-}N)}$ data in California (Jurgens et al., 2021), WD-NO_3-N fluxes were calculated separately for this state, allowing for an estimate derived from data at greater spatial resolution to be compared with the national-scale method detailed in Section 3.2.1. Utility-level LV values for the year 2016 and their corresponding $C_{t\,(NO3\text{-}N)}$ values were available in both California and Georgia (California Department of Water Resources, 2019; EWG, 2019; Georgia EPD, 2016), allowing utility WML-NO_3-N fluxes to be estimated and aggregated to give final county-level estimates. Derived from the most credible volumetric leakage rate and treated water concentration datasets, these fluxes were then compared to second state estimates made using the most assumptive method used in this work, whereby the national average leakage factor of 0.16 was applied to estimated state-level public supply withdrawals to give LV, and $C_{t\,(NO3\text{-}N)}$ was assigned as the respective average state values. This allowed the effect of these assumptions upon WML-NO_3-N estimates to be evaluated.

3.2.3 National Freshwater Withdrawal and Watermains Leakage Nitrate Flux Uncertainties

Uncertainty associated with the national WD-NO_3-N flux estimate was determined by aggregating upper and lower state-level WD-NO_3-N flux estimates. These were determined using equation 3.1, where withdrawal volumes were adjusted for ±10%, and concentrations at the 75th and 25th percentile were applied to each state. Due to the vast range of data sources used to derive USGS water use data, the inherent uncertainty associated with this data is currently not reported (Bradley, 2017; National Research Council, 2002). An uncertainty of ±10% was therefore adopted for all withdrawal volume values, which corresponds with the uncertainty assigned in other USGS publications (Maupin and Weakland, 2009). Raw surface water and groundwater concentrations at the 75th and 25th percentiles were chosen to represent upper and lower concentrations within upper and lower uncertainty bounds flux estimates. This prevented outliers from skewing uncertainty calculations, whilst retaining an ability to reflect the variability in raw water NO_3 concentrations and thus the potential bounds of uncertainty that are associated with adopting median concentration values in flux calculations. Due to a single mean $C_{t\,(NO3\text{-}N)}$

value reported for each state by the EWG, uncertainty associated with the national WML-NO_3-N flux is represented by upper and lower estimates made solely through adjustment of leakage volumes for ±10% within equation 3.3, using the same rational as for WD-NO_3-N uncertainties. Lower and upper uncertainty bounds surrounding national WD-NO_3-N and WML-NO_3-N estimates are reported in parentheses after flux values in Section 3.3.

3.2.4 Comparison of Freshwater Withdrawal and Watermains Leakage Nitrate Fluxes with Other Nitrogen Fluxes

National-scale WD-NO_3-N and WML-NO_3-N fluxes were conceptualised to be internal within national-scale N budgets. The significance of national WD-NO_3-N fluxes should therefore, ideally, be determined through its comparison to other national-level internal N retention flux estimates. Such estimates are scant across the US. In this research, the national-level WD-NO_3-N flux was compared to both a previously published estimate of a national scale internal retention flux (total pastureland N uptake (Byrnes et al., 2020)), and external N fluxes at the system boundary (total denitrification from US rivers (Baron et al., 2012)). The national-level WD-NO_3-N estimate was also compared to an initial global WD-NO_3-N flux estimate (Ascott et al., 2018b). California's total WD-NO_3-N flux estimate was conceptualised as an internal flux of N within state-scale budgets. Due to the total annual change in internal N storage within the California's surface waters and groundwaters being calculated as the difference between all major inputs and outputs of N to the state's surface waters and groundwaters by Liptzin and Dahlgren (2016), the proportional contribution that the California WD-NO_3-N flux could make to this value was estimated. The state's WD-NO_3-N flux was compared to external N retention fluxes at the system boundary (surface water N exports to the ocean, and total denitrification within surface waters and groundwaters (Liptzin and Dahlgren, 2016)). Finally, the state's IRR-NO_3-N flux was compared to a previous irrigation withdrawal NO_3 flux estimate (Liptzin and Dahlgren, 2016).

The relative importance of the national WML-NO_3-N flux was evaluated by its comparison to other national-level and internal N input flux estimates, including: N leached to groundwaters

from septic tanks (Sobota et al., 2013), total N input to streams from point sources (Skinner and Wise, 2019), and an initial global WML-NO_3-N estimate (Ascott et al., 2018b). National and county-level WML-NO_3-N fluxes were also compared to the amount of N applied to land as agricultural fertilizer that is then leached from the soil to groundwater. Due to the absence of a published gridded soil N leaching dataset for the US, agricultural N fertilizer application values from Swaney et al. (2018a) were corrected with a fixed leaching emission factor of 0.18 (Mekonnen and Hoekstra, 2015). It should be noted that assigning a single leaching emission factor (which ignores its large variability around the globe) has a large associated uncertainty (Bijay and Craswell, 2021; Goulding et al., 2000; Wang et al., 2019; Zhou and Butterbach-Bahl, 2014). However, this method provides a comparison flux that is useful for contextualising county-level WML-NO_3-N fluxes. California's WML-NO_3-N flux was compared to estimates of N leaching from agricultural fertilizer input (Swaney et al., 2018a), leaching from urban land, leaking sewers and wastewater to groundwater (Liptzin and Dahlgren, 2016), as well as N input into streams from point sources (Skinner and Wise, 2019).

3.3 Results

3.3.1 Freshwater Withdrawal Nitrate Fluxes

The total freshwater withdrawal flux (WD-NO_3-N_{total}) for the US was estimated to be 417 (190-857) kt NO_3-N yr^{-1}, with 45% and 55% of this total being due to surface water and groundwater withdrawals, respectively (Table 3.2). State-level WD-NO_3-N fluxes range from 0.08 - 42.7 kt NO_3-N yr^{-1}, with Nebraska, California and Illinois having the largest fluxes (Figure 3.1a). Contributions of each water use sector to the national-level WD-NO_3-N_{total} flux are 44% from irrigation, 29% from thermoelectric, 13% from public water supply, 6% from industry, 4% from domestic and 3% combined from aquaculture, livestock and mining (Figure 3.1b). The sectoral contributions to state-level WD-NO_3-N fluxes vary geographically, with irrigation (IRR-NO_3-N) and thermoelectric (THERM-NO_3-N) fluxes dominating from western to eastern regions, respectively, and public water supply (PWS-NO_3-N) and self-supplied domestic (DOMESTIC-NO_3-N) fluxes dominating northeastern states (Figure 3.1b and Appendix 10). Total

area-normalised WD-NO_3-N_{gw} and WD-NO_3-N_{sw} county fluxes range from 0-1,024 and 0-8,249 kg NO_3-N km^{-2} yr^{-1}, respectively (Figure 3.2a and b). Counties within the states of California, Kansas and Nebraska are associated with the larger area-normalised WD-NO_3-N_{gw} fluxes (Figure 3.2a). Counties within states of California, Oregon and Montana are associated with the larger area-normalised WD-NO_3-N_{sw} fluxes (Figure 3.2b). The WD-NO_3-N flux estimate for the US is equivalent to 57% of estimated total denitrification within the US rivers, 21% of pastureland N uptake, and 2% of the estimated global WD-NO_3-N flux (Table 3.2). California's WD-NO_3-N_{total} estimate (38 kt NO_3-Nyr^{-1}) is equivalent to 97% of the export of N to the ocean by rivers, 31% of denitrification within the states surface waters and groundwaters and 12% of total change in state-wide N storage internally within surface waters and groundwaters (Table 3.2). The California estimate made using the national dataset is in close agreement with the California estimate made using the more comprehensive state-level dataset (Table 3.2). The California IRR-NO_3-N estimate made in this work (29 kt NO_3-N yr^{-1}) is equivalent to 70% of the previous estimate (41 kt NO_3-N yr^{-1}) for 2005, as reported by Liptzin and Dahlgren (2016).

Table 3.2. Total freshwater withdrawal nitrate fluxes (WD-NO_3-N) for the United States and California, compared to previously determined nitrogen retention and export fluxes.

Flux	Reference	Value (kt NO_3-N yr^{-1})[a]	WD-NO_3-N/flux (%)
National Level			
WD-NO_3-N_{total}	This study	417 (0-8,267)	-
WD-NO_3-N_{sw}	This study	189	-
WD-NO_3-N_{gw}	This study	228	-
Total denitrification within rivers across the United States	Baron et al. (2012)	730	57
Pastureland N uptake across the United States	Byrnes et al. (2020)	2,016	21
Global-level WD-NO_3-N	Ascott et al. (2018b)	22,600	2
California			
WD-NO_3-N_{total}	This study	38	-
WD-NO_3-N_{total}	This study [b]	39	
Total N export from rivers to ocean	Liptzin and Dahlgren (2016)	39	97
Total denitrification of N within surface waters and groundwaters	Liptzin and Dahlgren (2016)	121	31
Change in N storage within surface waters and groundwaters	Liptzin and Dahlgren (2016)	331	12

[a] Values in parentheses are minimum and maximum county flux values, in units of kg N km^{-2} yr^{-1}

[b] This estimate was made using the national-level dataset

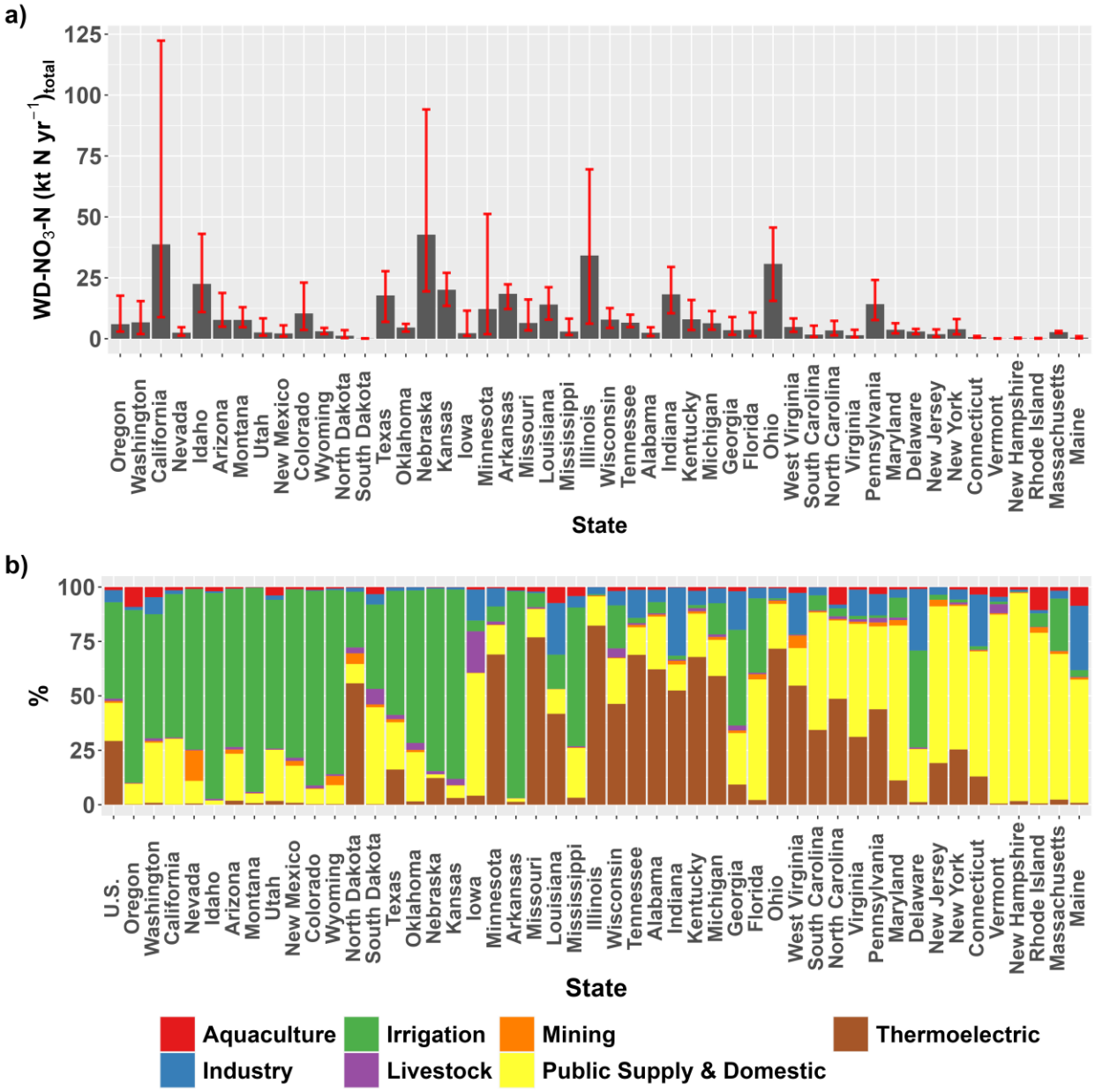

Figure 3.1. a) Total freshwater withdrawal fluxes of nitrate ($WD\text{-}NO_3\text{-}N_{total}$) for each state across the United States. States on the x-axis are ordered from west to east and red error bars represent uncertainties on state fluxes. b) Percentage contribution of each water use sector to the national and state $WD\text{-}NO_3\text{-}N_{total}$ fluxes.

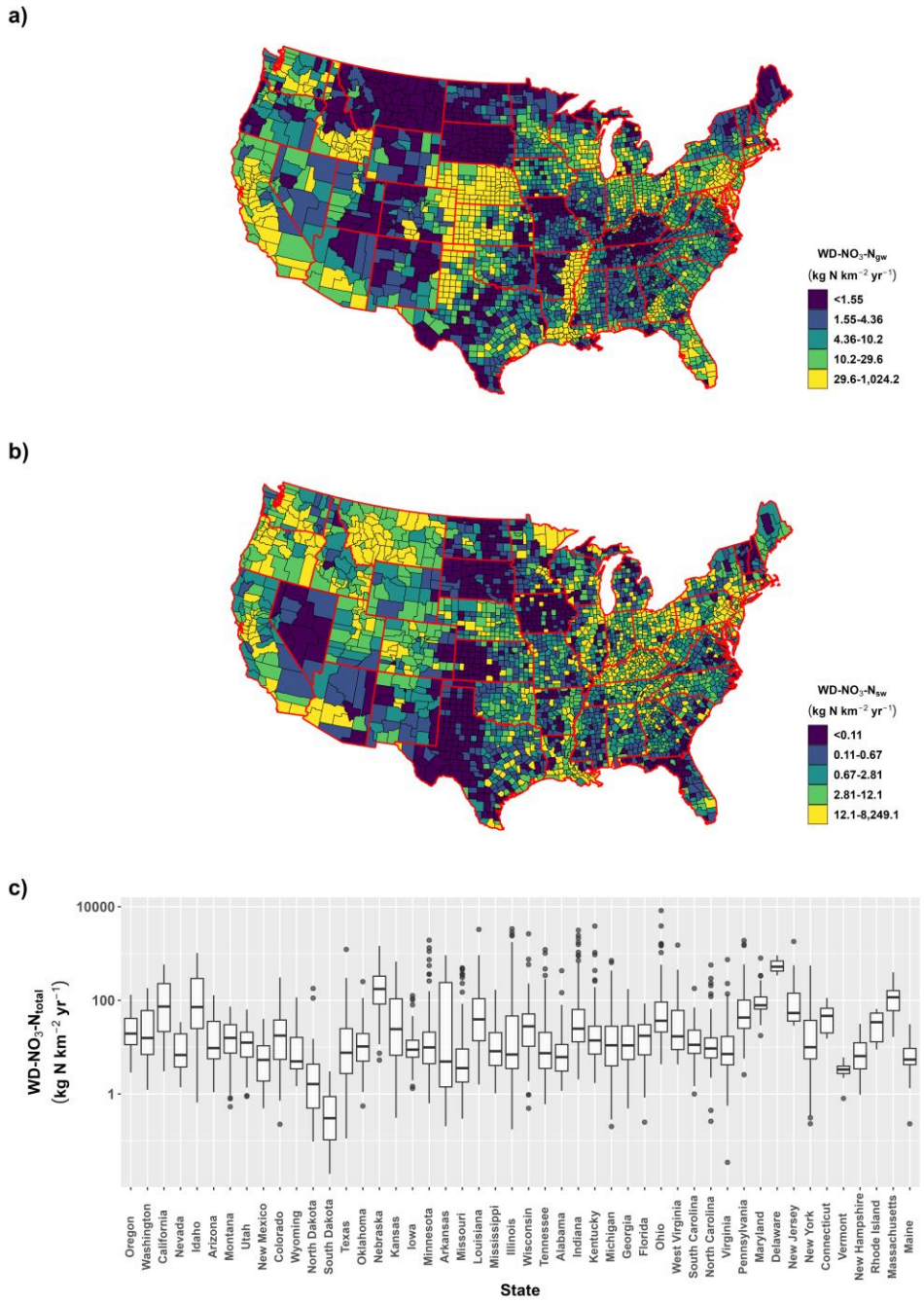

Figure 3.2. a) Area-normalised fresh groundwater withdrawal fluxes of nitrate (WD-NO_3-N_{gw}) for each county across the United States. b) Area-normalised fresh surface water withdrawal fluxes (WD-NO_3-N_{sw}) for each county across the United States. Breaks in the colour scale are defined as separate quintile groups. Linework was created using the 'usmap' package on R (Di Lorenzo, 2022). c) Boxplot showing the distribution of county-level WD-NO_3-N_{total} flux values for each state across the United States. States are ordered from west to east.

3.3.2 Watermains Leakage Nitrate Fluxes

The national-level watermains leakage (WML-NO_3-N) flux for the US was estimated to be 7.0 (6.3-7.7) kt NO_3-N yr^{-1}, returning 13% of PWS-NO_3-N back to the environment (Table 3.3). Area-normalised county WML-NO_3-N fluxes range from 0 to 576 kg NO_3-N km^{-2} yr^{-1}, with the highest values observed in many urbanised counties (Figure 3.3 and Figure 3.5) and a general trend of increasing fluxes from west to east (Figure 3.6). The national WML-NO_3-N flux is equivalent to 16% of N leached from non-agricultural fertilizer application, 4% of N leached from septic tanks, 1.4% of total N from point sources, 0.3% of N leached from agricultural fertilizer input and 1.3% of the global WML-NO_3-N flux estimate (Table 3.3). There is also large inter-county variability in the relative importance of WML-NO_3-N fluxes. This flux is equivalent to >10% of N inputs from leaching of agricultural fertilizer across 265 counties, often across the northeast and western coastal areas, with some county WML-NO_3-N fluxes even exceeding this input (Figure 3.4).

Table 3.3. Total watermains leakage nitrate fluxes (WML-NO_3-N) compared to public supply freshwater withdrawal nitrate fluxes (PWS-NO_3-N) and other sources of nitrogen (N), for the United States and states of California and Georgia.

Flux	Reference	Value (kt NO_3-N yr^{-1})[a]	WML-NO_3-N/flux (%)
National Level			
WML-NO_3-N	This study	7.0 (0-576)	-
PWS-NO_3-N	This study	55.5	13
N leached from non-agricultural fertilizer input	Swaney et al. (2018a)[b]	44.6	16
N leached from septic tanks	Sobota et al. (2013)	200	4
N from point source facilities	Skinner and Wise (2019)	503	1.4
N leached from agricultural fertilizer input	Swaney et al. (2018a)[b]	2,155	0.3
Global-level WML-NO_3-N	Ascott et al. (2018b)	525	1.3
California			
State-level WML-NO_3-N	This study	0.758 ($1x10^{-4}$ – 65)	-
State-level WML-NO_3-N [c]	This study	2.1	36
State-level N leached to groundwater from urban land	Liptzin and Dahlgren (2016)	1	76
State-level N to groundwater from leaking sewers	Liptzin and Dahlgren (2016)	15	5
State-level N leached to groundwater from treated wastewater	Liptzin and Dahlgren (2016)	27	2.8
State-level N to rivers from point source facilities	Skinner and Wise (2019)	33.3	2.3
State-level N leached to groundwater from agricultural fertilizer input	Swaney et al. (2018a)[a]	88	0.9
Georgia			
State-level WML-NO_3-N	This study	0.110 (0-17)	-
State-level WML-NO_3-N [c]	This study	0.108	-

[a] Values in parentheses are minimum and maximum county flux values, in units of kg N km^{-2} yr^{-1}

[b] Input of N from agricultural and non-agricultural fertilizer were for corrected using a leaching emission factor of 0.18, sourced from Mekonnen and Hoekstra (2015)

[c] These estimates were made using national average leakage factor (0.16) and a state average $C_{t\ (NO3\text{-}N)}$

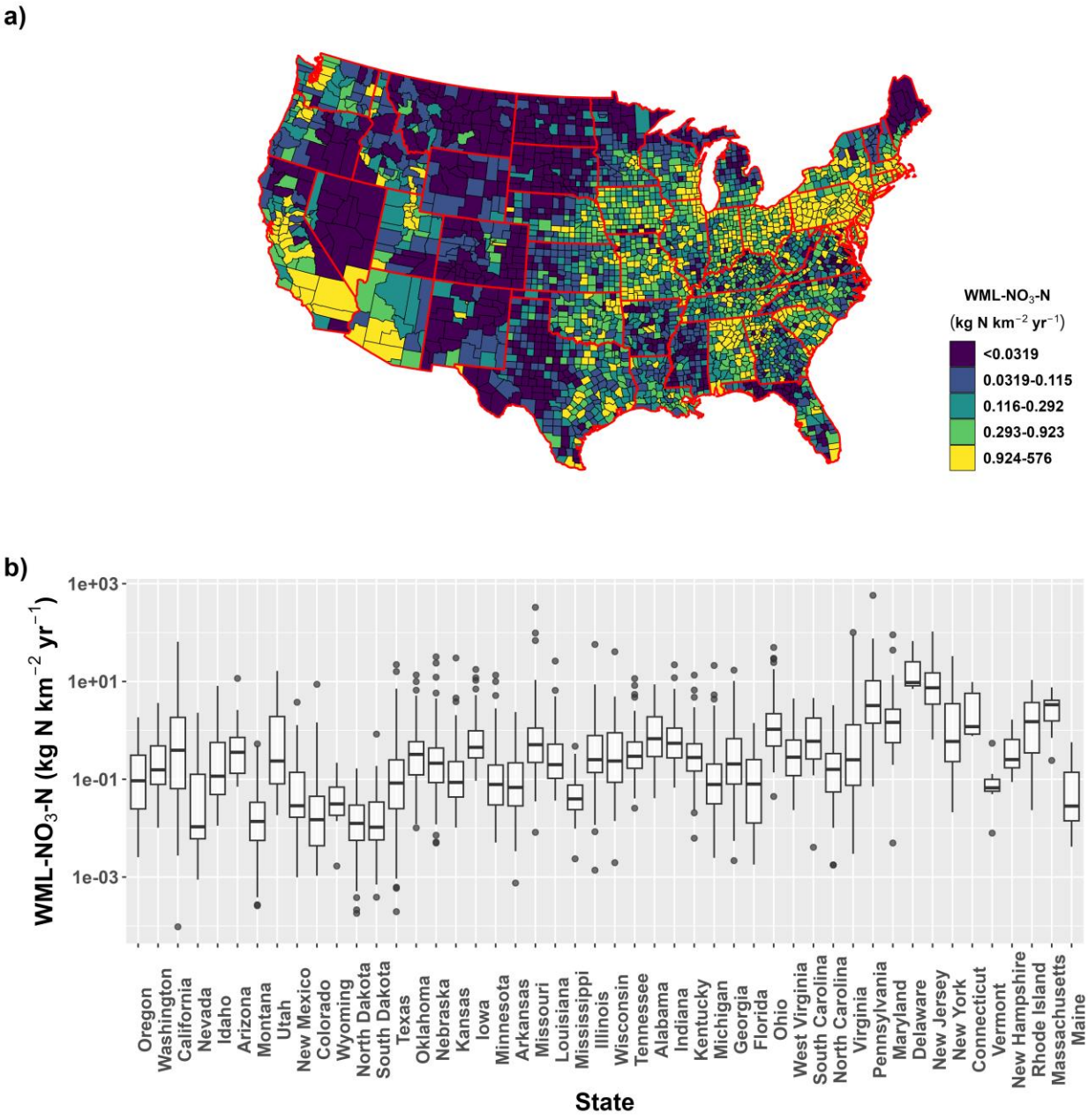

Figure 3.3. a) Total area-normalised watermains leakage fluxes of nitrate (WML-NO_3-N) for each county across the United States. Breaks in the colour scale are defined as separate quintile groups. Linework was created using the 'usmap' package on R (Di Lorenzo, 2022). b) Boxplot showing the distribution of county-level WML-NO_3-N flux values across each state. States are ordered from west to east.

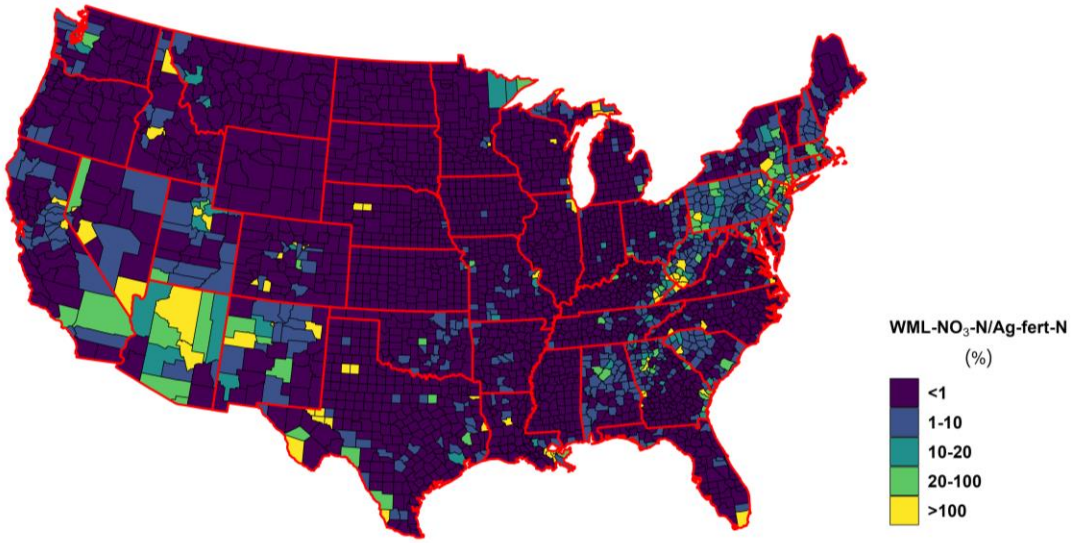

Figure 3.4. County-level watermains leakage nitrate fluxes (WML-NO_3-N) expressed as a percentage equivalence of nitrogen leached to groundwater from agricultural fertilizer application. Linework was created using the 'usmap' package on R (Di Lorenzo, 2022).

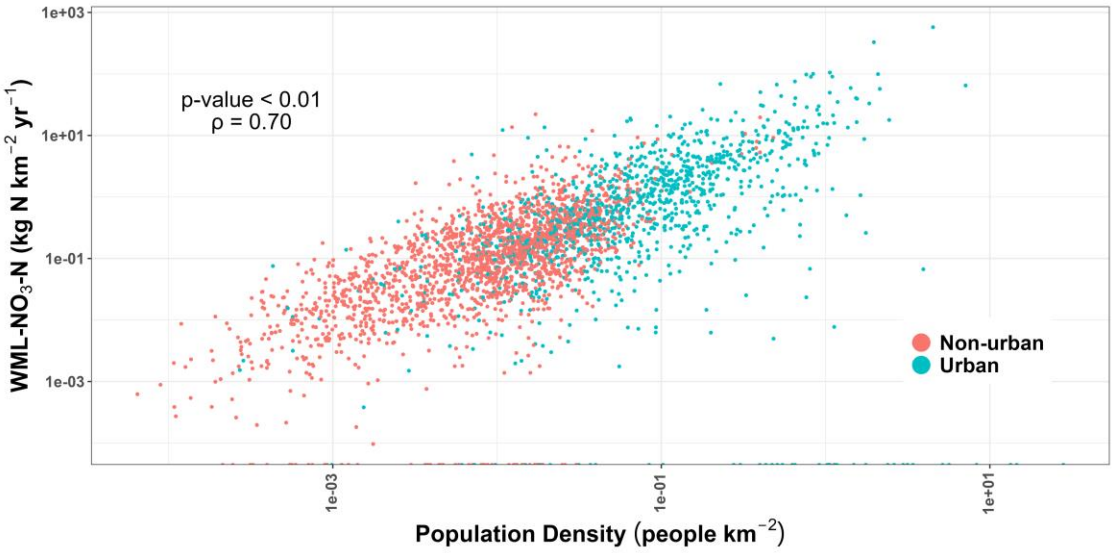

Figure 3.5. Plot showing the relationship between watermains leakage nitrate fluxes (WML-NO_3-N) and population density for urban and non-urban counties across the United States. Urban counties are those defined as 'metro' and 'nonmetro' within the US Department of Agriculture's Rural Urban Continuum Codes, respectively (USDA, 2020a). Spearman's rank correlation test returned a p-value < 0.01 and a positive rank correlation ($\rho = 0.70$), suggesting a strong monotonic relationship between WML-NO_3-N fluxes and population density

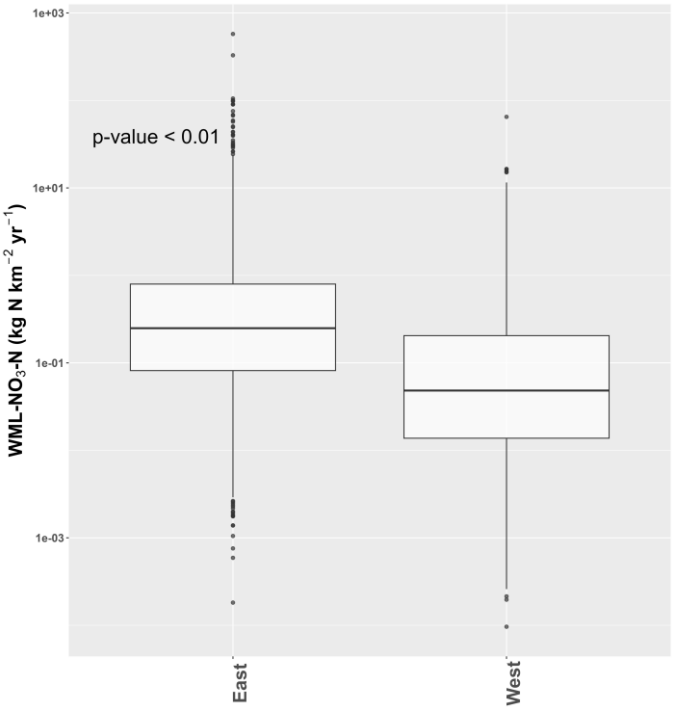

Figure 3.6. Box plot showing the distribution of county-level watermains leakage nitrate fluxes (WML-NO_3-N) across eastern and western regions of the United States. A county was defined as being in either the eastern or western region of the United States due to the longitude of its centroid being east or west of the 100th meridian west, respectively. Running the Mann Whitney U test on WML-NO_3-N fluxes from eastern and western regions of the country returned a p-value < 0.01, suggesting there is statistically significant difference in the magnitude of this flux between the two regions.

The WML-NO_3-N estimates for Georgia, made using both the utility-level dataset and that made by adopting state averages (Section 3.2.2), are in close agreement (Table 3.3). In contrast, California's estimate made using the state-average method is nearly three times as large as that made using more local utility-level dataset (Table 3.3). There is inter-county variation in area-normalised WML-NO_3-N fluxes within both states (Figure 3.7). Urban counties in both California and Georgia (e.g. San Francisco and Fulton, respectively) are associated with larger estimated fluxes than more rural counties (e.g. Alpine and Burke, respectively) (Figure 3.7a and b).

California's total WML-NO_3-N flux is equivalent to 76% of N leached to groundwater from urban soils, 5% of N leached to groundwater from leaking sewers, 2.8% of N leached to groundwater from treated wastewater, 2.3% of total N released to rivers from point source facilities and 0.9% of N leached to groundwater from agricultural fertilizer inputs across the state (Table 3.3). There is also significant inter-county variation in the relative importance of these fluxes, when compared to leached N and PWS-NO_3-N withdrawal fluxes across both states (Figure 3.8).

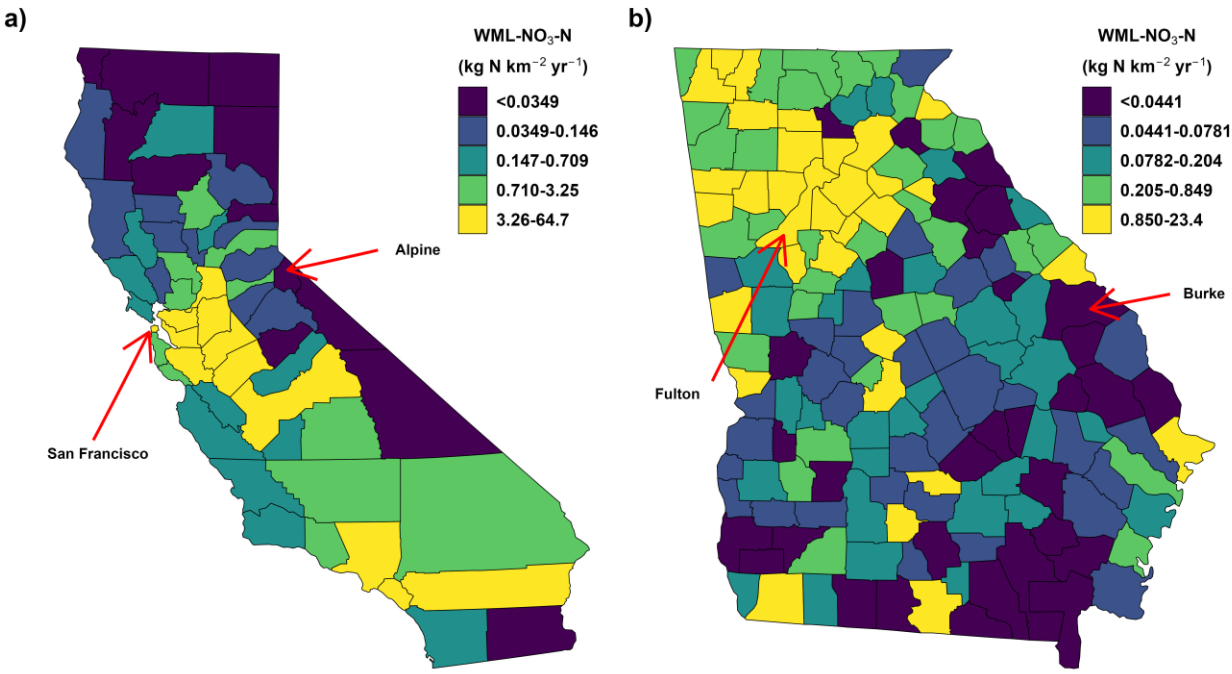

Figure 3.7. Area-normalised watermains leakage nitrate fluxes (WML-NO_3-N) for each county within the states of a) California and b) Georgia, calculated using utility-level audit data. Breaks in colour scales are defined as separate quintile groups. Linework was created using the 'usmap' package on R (Di Lorenzo, 2022).

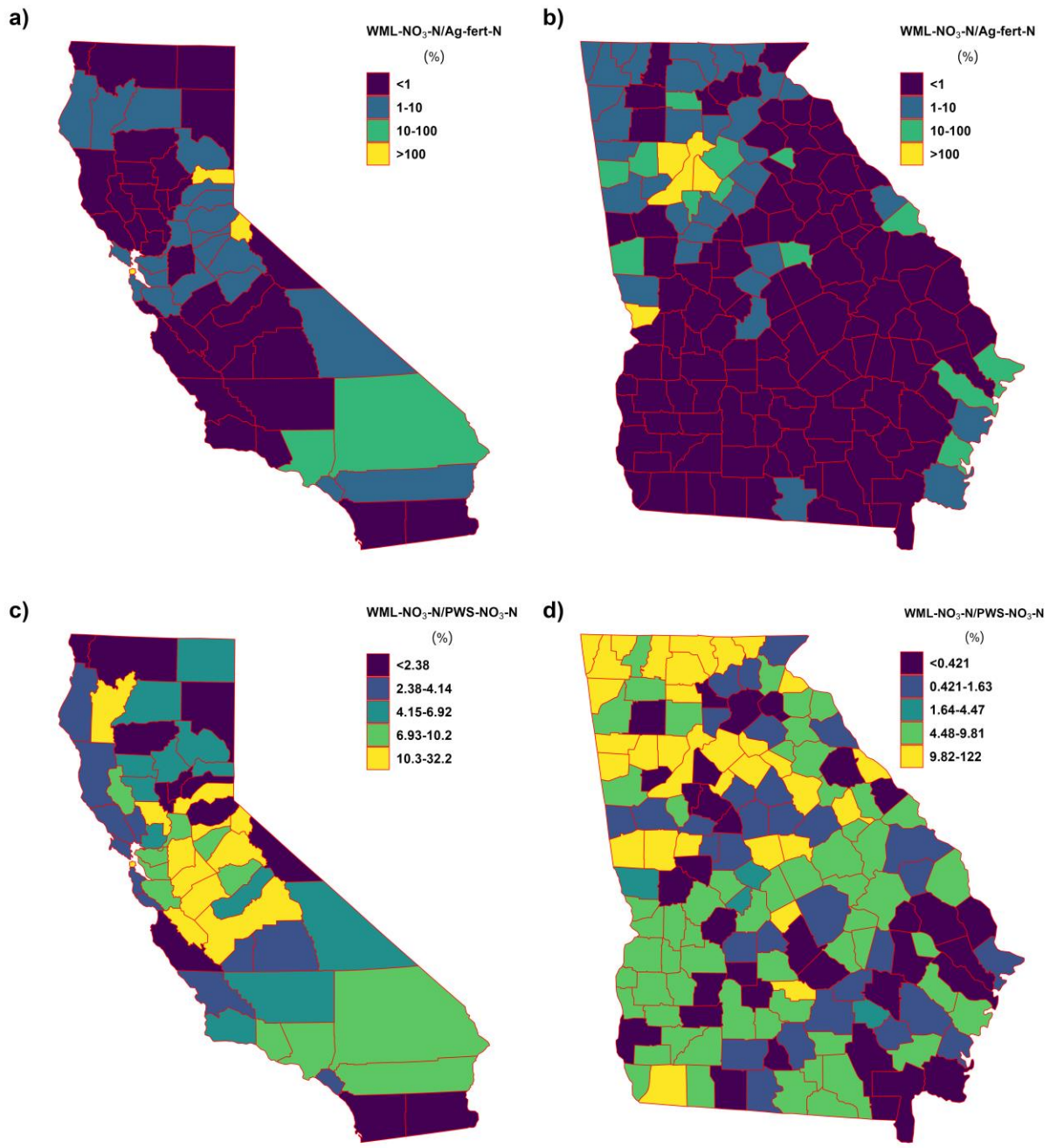

Figure 3.8. County-level watermains leakage nitrate fluxes (WML-NO_3-N) expressed as a percentage equivalence of leached nitrogen from agricultural fertilizer application across a) California and b) Georgia. County-level WML-NO_3-N fluxes expressed as percentage equivalence of public supply withdrawal fluxes of nitrate (PWS-NO_3-N) across c) California and d) Georgia. Breaks in colour scales in Figures c and d are defined as separate quintile groups. Linework was created using the 'usmap' package on R (Di Lorenzo, 2022).

3.4 Discussion

3.4.1 Controls Upon Freshwater Withdrawal Nitrate Fluxes

Retention processes control both the amount of N within inland fresh waters and the amount exported downstream to coastal environments (Baron et al., 2012; Saunders and Kalff, 2001). This research has quantified the significance of freshwater withdrawals for both public and non-public supply uses as NO_3 retention mechanisms for the first time across the US. These WD-NO_3-N fluxes have largely been neglected in N cycling research and this work begins to address specific calls for an increased understanding of these fluxes globally (Ascott et al., 2018b; Stahl, 2019). Whilst freshwater withdrawals across the US account for approximately 10% of global freshwater withdrawals (FAO, 2024), the WD-NO_3-N estimate made in this work accounts for only 2% of initial global WD-NO_3-N estimates (Table 3.3). This is likely due to relatively low NO_3 concentrations within raw surface waters and groundwaters across the US, when compared to other countries that make globally significant freshwater withdrawals, such as India (FAO, 2024; Zhou, 2015). Despite the small contribution from the US to global WD-NO_3-N estimates, the transferable methodology presented here will allow this flux to be estimated in other countries, thus further resolving the global WD-NO_3-N estimate.

Contributions from different water use sectors to the national WD-NO_3-N_{total} flux largely reflect sectoral water withdrawal volumes, with freshwater withdrawals for irrigation, thermoelectric power and public supply collectively accounting for 90% of the country's annual total water withdrawal volume (Dieter et al., 2018b) and 89% of the WD-NO_3-N_{total} flux (Figure 3.1b). Variations between county WD-NO_3-N fluxes (Figure 3.2) and the sectoral contributions to state-totals (Figure 3.1b) also reflect strong regional differences in the use of freshwater resources and thus withdrawal volumes. For example, IRR-NO_3-N fluxes dominate in western states, whereas this flux only accounts for 37% of the national WD-NO_3-N_{total} flux. Conversely, THERM-NO_3-N fluxes dominate in eastern states, facilitating 70% of net US power generation (Dieter et al., 2018b), despite collectively only accounting for 27% of the national WD-NO_3-N_{total} flux.

Counties and states whose water use sectors have a larger dependency on groundwater withdrawals are likely to have withdrawal fluxes relatively larger than surface water withdrawals of the same volume would have, due to the higher NO_3 concentrations generally found within groundwaters compared to surface waters (Appendices 1, 2, 5 and 6) (Pennino et al., 2017). The influence of $C_{r\ (GW\text{-}NO3\text{-}N)}$ concentrations upon final WD-NO_3-N fluxes is illustrated by the fact that although freshwater withdrawals for public supply made up 46% of New York's total freshwater withdrawals, they are responsible for 51% of the state's WD-NO_3-N flux (Figure 3.1b). Across New York, freshwater withdrawals for public supply are 25% from groundwater and 75% from surface water (Dieter et al., 2018a). However, due to the fact that groundwater NO_3-N concentrations are over four times that of surface water (Appendices 1 and 5), groundwater and surface water withdrawals contribute 60% and 40% to the state's total PWS-NO_3-N flux, respectively. The adoption of a median state-level $C_{r\ (NO3\text{-}N)}$ concentration for each county results in high levels of uncertainty surrounding state-level WD-NO_3-N fluxes (Figure 3.1a). State-level WD-NO_3-N flux estimates with higher levels of uncertainty, such as for California (Figure 3.1a), reflect the greater inter-quartile range of raw water NO_3-N concentrations used to derive median values (see Section 3.2.3). In reality, these concentrations are highly spatially variable, even within individual counties (Appendices 3, 4, 7 and 8). Minimising the uncertainties associated with WD-NO_3-N flux estimates should be a future priority, particularly as the availability and spatial distribution of concentration data increases.

This effect of elevated groundwater NO_3 concentrations on withdrawal fluxes is even stronger for self-supplied domestic withdrawals. Although self-supplied domestic withdrawals account for 3.5% of New York's total withdrawals (Dieter et al., 2018a), the state's DOMESTIC-NO_3-N flux constitutes 15% of its WD-NO_3-N_{total} flux (Figure 3.1b). Domestic supply wells often have higher NO_3 concentrations than public supply wells, due to the fact that these wells are screened at shallower depths and are often located in rural areas heavily influenced by agricultural fertilizer practices, and thus closer to anthropogenic sources of NO_3 contamination (Desimone et al., 2009; Johnson and Belitz, 2015). With irrigation withdrawals only decreasing by 23% since 2005, the 40% difference between the IRR-NO_3-N estimate made for California in 2005 by Liptzin and

Dahlgren (2016) compared to that in this work (Table 3.3) is only partially explained by changing withdrawal volumes. Changes to raw water NO_3-N concentrations are also suggested to control the spatial and temporal variations observed in WD-NO_3-N estimates, and geographic areas and sectors withdrawing water with elevated NO_3-N concentrations can have disproportionate impacts on WD-NO_3-N fluxes (Stahl, 2019). Whilst data availability allowed specific public and domestic supply raw groundwater NO_3-N concentration (C_r) datasets to be used in estimating PWS-NO_3-N and DOMESTIC-NO_3-N withdrawal fluxes, the surface water and groundwater $C_{r\text{-}(NO3\text{-}N)}$ datasets for other water uses do not distinguish values between each sector. Future research should investigate the potential differences in $C_{r\ (NO3\text{-}N)}$ values between each water use sector and utilise these sector specific values to further resolve withdrawal flux estimates.

3.4.2 Freshwater Withdrawal Nitrate Fluxes as a Nitrogen Retention Mechanism of Local, National and Global Importance

Whilst denitrification permanently removes N from the freshwater system boundary (Grizzetti et al., 2015), withdrawal fluxes instead temporarily re-route NO_3 internally within the defined system, before being returned to the environment. Such a distinction reflects that made by Liptzin and Dahlgren (2016), in which the irrigation withdrawal N flux estimate was represented as an internal flux between different sub-systems, as opposed to a permanent removal from the state-level system. Whilst this work acknowledges the limitation of comparing transient and internal N fluxes with longer-term external boundary fluxes (see Section 3.2.4), the 57% and 97% equivalence of national-level and California state-level WD-NO_3-N fluxes made in this work (respectively) to total denitrification provides an initial insight into the potential importance of these internal fluxes (Table 3.2).

Contrasting patterns in transport, consumption and fate of fresh waters withdrawn for different uses will likely have varying effects upon N cycling. Deducing the implications of these withdrawal fluxes thus requires a disaggregation of WD-NO_3-N_{total} fluxes into their constituent sectors. With regards to PWS-NO_3-N fluxes, the average residence time for water in the US public supply

distribution system is estimated at 1.3 days (USEPA, 2002). Therefore WML-NO_3-N fluxes could be expected to return some of the PWS-NO_3-N flux within a similar timeframe. Despite this, denitrification can be used as an intentional treatment option, either pre-supply (Hunter, 2008) or as a wastewater treatment process, and will result in the long-term removal of NO_3 from water and the release of N into the atmosphere (USEPA, 2007). In addition, water that is withdrawn and transported across catchment boundaries, often for agricultural and municipal use (Dickson and Dzombak, 2017; Young and Brozovik, 2019), can be thought of as a permanent removal from the catchment of withdrawal and as an input into the receiving catchment. This invalidates the assumption that withdrawal fluxes merely occur internally between sub-systems and instead contribute to net anthropogenic inputs of N (Hong et al., 2011; Swaney et al., 2018a).

The exceedance of WML-NO_3-N fluxes when compared to PWS-NO_3-N fluxes across some counties (Figure 3.8) may potentially be attributable to freshwater transfers across county boundaries (Dickson and Dzombak, 2017), where low PWS-NO_3-N fluxes are a result of water imports offsetting the need for freshwater withdrawals. Many urbanised areas across the US are particularly reliant on such transfers, such as in San Francisco and counties in the San Joaquin Valley (e.g. Fresno, Stanislaus and San Joaquin) and Greater Sacramento areas (Placer and Yolo). In these counties, a significant amount of fresh water for public use is sourced from imports via the State Water and Central Valley Projects (Feinstein and Thebo, 2021; USBR, 2021). Similarly, many of the counties across northwest Georgia, where WML-NO_3-N fluxes return a large proportion of the PWS-NO_3-N flux (Figure 3.8), receive drinking water from inter-basin transfers (Metropolitan North Georgia Water Planning District, 2017). Under predicted future water stress (Brown et al., 2019b), the influence of increasing water transfers upon N fluxes across hydrological and administrative boundaries will add nuance to many of the existing input-output anthropogenic N budget methodologies (Byrnes et al., 2020; Swaney et al., 2018a).

The timeframe and spatial distribution of NO_3 return fluxes, and the overall effect of withdrawals for non-public water use sectors upon N cycling remain largely unknown. Unlike public supply

withdrawals, where water is often distributed large distances via distribution networks, irrigation withdrawals (responsible for IRR-NO_3-N fluxes) are often done on-site or near to the location of irrigation (Young and Brozovik, 2019). Whilst some of the water withdrawn for irrigation use is returned to the environment, including via seepage from irrigation canals (Hrozencik et al., 2021), more than 50% of irrigation withdrawals are consumptive (Dieter et al., 2018a). The consumptive use of water for irrigation could act as a mechanism that retains substantial masses of N from freshwater systems on timeframes relevant to nutrient budgets that inform nutrient management plans (Zhang et al., 2020). With over half of nation-wide irrigation water withdrawals being from groundwater, this flux also represents substantial movement of NO_3 from the subsurface to surface environment, where different environmental conditions will significantly affect the behaviour of NO_3 (Winter et al., 1998). Once applied on land, the NO_3 deposited on agricultural soils may become concentrated due to the large volumes of water applied being subjected to evapotranspiration (Dieter et al., 2018b). This N can either accumulate in the soil, be taken up by plants, be emitted to the atmosphere or leached back to groundwater, resulting in IRR-NO_3-N fluxes operating over a range of timescales (Galloway et al., 2003).

Thermoelectric water withdrawals are also typically self-supplied and often undertaken on-site, however are predominantly taken from (and returned to) surface water. On a national level, water use for the thermoelectric power generation is largely non-consumptive, with 64% of the total freshwater withdrawn for this sector returned to its source (Dieter et al., 2018b). Whilst the elevated temperatures of return flows are known to impact the quality of source water bodies, NO_3 concentrations within these waters may also be more concentrated as a result of water evaporation during the cooling process (Petrakopoulou, 2021). Whilst low on a national level, consumptive water use for the generation of thermoelectric power is proportionally higher across certain regions. Due to the lower availability of fresh water, the majority of thermoelectric power plants across western US states continually circulate water through heat exchangers, which leads to a larger proportion of water consumption. In contrast, the higher availability of fresh water across eastern states means that once water has passed through heat exchangers, it is then returned to its source, thus consuming less water (Lee et al., 2018). Although

THERM-NO_3-N fluxes make a smaller relative contribution to overall WD-NO_3-N fluxes in western states (Figure 3.1b), the higher proportion of water consumption in these areas will result in these fluxes acting as a transient anthropogenic store of N. Whilst the timescale and magnitude of N retention associated with consumptive withdrawals may be transient when compared with more permanent removals, such as denitrification and burial in sediments (Baron et al., 2012), they may become relevant when considered in relation to nutrient balances and management decisions related to smaller sub-national (e.g. catchment-scale) systems (Ator and Denver, 2015). With Europe also dedicating large volumes of water to thermoelectric power generation (Magagna et al., 2018), the potential for THERM-NO_3-N fluxes to retain N across the US warrants their quantification elsewhere around the globe.

Comprehensive consumptive water use data for the remaining water use sectors (industry, domestic, aquaculture, livestock and mining) are unavailable across the US, however regional assessments have been made (Shaffer, 2008; Shaffer and Runkle, 2007). In addition, consumptive use volumes of fresh water for thermoelectric use exceed total fresh water thermoelectric withdrawals in Arizona, California and Oregon, potentially due to this sector receiving water transfers in these states (see previous discussion on the effects of transfers). The amount of water consumed by these water use sectors depends on a wide range of processes that vary geographically across the US, including evapotranspiration, incorporation of water into products, as well as livestock and human consumption (Shaffer and Runkle, 2007).

An improved understanding of the different effects that sectoral withdrawal fluxes may have upon N cycling across the US is imperative in order to further resolve nuances within nutrient budget methodologies, with implications within the nutrient spiralling paradigm (Ensign and Doyle, 2006). For example, changes to the internal storage of N within surface waters and groundwaters is a component of the California Nitrogen Assessment (Liptzin and Dahlgren, 2016) and is quantified as the difference between the other input and output N fluxes that are defined within budgets of these sub-systems. The transient anthropogenic store of N that California's

WD-NO_3-N flux represents may thus account for 12% of the internal storage of N within California's surface waters and groundwaters (Table 3.2), thus emphasizing the importance of its inclusion within future state-level N balances.

The annual WD-NO_3-N flux estimates presented here neglect seasonal fluctuations in both volume and quality of withdrawn water (Bexfield and Jurgens, 2014; Josset et al., 2019; Lee et al., 2020; Ornelas Van Horne et al., 2019; Wiener et al., 2020). As more temporally and spatially resolved water withdrawal volume and quality data becomes available, future research should seek to assess the seasonality in, and reduce uncertainties associated with, WD-NO_3-N flux estimates. Anticipated increases in the human population and a changing climate will also affect future WD-NO_3-N fluxes across the US and around the world (Brown et al., 2013; Harris and Diehl, 2019; McDonald and Girvetz, 2013; Pickard et al., 2017; Wada and Bierkens, 2014), thus making estimates of these fluxes in the future an important area of research.

3.4.3 Watermains Leakage Nitrate Fluxes Return Variable Amounts of Nitrogen Back to the Environment

The national WML-NO_3-N estimate returns a relatively small flux of NO_3 to the environment when compared to other global and national N input and return fluxes (Table 3.3). Despite the volume of leaked water within the US accounting for around 11% of the estimated global total (Wyatt and Liemberger, 2019), the WML-NO_3-N estimate made here accounts for only 1.3% of the global WML-NO_3-N estimate made by Ascott et al. (2018b). This potentially reflects the relatively low NO_3 concentrations of treated water across the US as a result of high prevalence and standard of drinking water treatment (EWG, 2019). The ratio of the national-level WML-NO_3-N estimate, when compared to the PWS-NO_3-N estimate (Table 3.3), is also similar to that of England, UK (Ascott et al., 2018b). As developed countries, both the US and England have relatively low average leakage rates and concentrations of NO_3 in drinking water when compared to many developing countries, such as Vietnam (Hung et al., 2020; Kingdom et al., 2006), where area-normalised WML-NO_3-N fluxes may be more significant.

The national-level WML-NO_3-N estimate masks the localised importance of this flux across many urban and coastal counties (Figure 3.3a). Despite the relatively low NO_3 concentrations in treated tap water across the country, leakage from water distribution networks can still lead to large overall nutrient loads due to the large volume of water released into the environment. Higher area-normalised county-level WML-NO_3-N fluxes largely reflect higher population densities of more urbanised counties, that are often situated in coastal areas (Figure 3.7; Appendix 11). These areas have larger volumes of water input into their distribution network and a higher density of watermains pipes with the potential to leak, per unit of land area. The ages of water distribution networks also vary regionally across the US, with older pipes more susceptible to leakage largely found in the older cities in eastern states (Speight, 2015). Although available data is limited, larger $f_{leakage}$ values are concentrated in eastern states (Appendix 9), where together with their larger population densities, larger WML-NO_3-N fluxes are observed (Figure 3.6**Error! Reference source not found.**).

The relative importance of county-level WML-NO_3-N fluxes to overall county-level N cycling (e.g. Figure 3.8) is largely determined by the importance of other N retention and input mechanisms in these areas. For example, the counties of San Francisco (California) and Fulton (Georgia) have WML-NO_3-N fluxes that exceed the amount of N leached from agricultural fertilizer (Figure 3.8). This is due to the likely influence of urbanisation on more intense WML-NO_3-N flux estimates and the simultaneously lower levels agricultural activity (i.e. fertilizer application) in these areas. More broadly, urban counties (those defined as 'metro' by US Department of Agriculture; USDA (2020a)) account for 96% of the total number of counties whose WML-NO_3-N flux exceeds the median WD-NO_3-N flux for all counties. Urban counties are also found to account for 84% of total counties where WML-NO_3-N fluxes exceed N leached from agricultural fertilizer, highlighting the significance of WML-NO_3-N fluxes as a component of overall anthropogenic N cycles in these areas (Figure 3.4). With a trend of decreasing agricultural N fertilizer input across many urban US counties, particularly in the northeast (Sabo et al., 2019), as well as reports of zero agricultural N fertilizer application across many interior and southeastern states (Swaney et al., 2018a), the relative importance of WML-NO_3-N fluxes on overall N inputs may increase. In contrast, in areas

with intensive agricultural activity, such as counties within the midwestern states and California's Central Valley region, N fertilizer application is the largest terrestrial N input (Sabo et al., 2019) and the main cause of elevated groundwater NO_3 concentrations (Exner et al., 2014; Harter et al., 2017). Therefore WML-NO_3-N fluxes make a relatively small contribution to local anthropogenic N cycles in these areas (Figure 3.4). Ultimately, whilst N fertilizer application remains the largest anthropogenic N input on a national scale, N inputs on more localised (e.g. sub-watershed) scales can be dominated by other natural and anthropogenic processes, including natural N fixation, rock weathering and human waste (Sabo et al., 2019; Swaney et al., 2018a). This research now highlights the potential for watermains leakage to be an additional locally important, yet previously overlooked, anthropogenic input of N.

Along with contributions of leaky sewers to N within the country's urban streams (Divers et al., 2013; Pennino et al., 2016; Viers et al., 2012), these newly quantified WML-NO_3-N fluxes further develop an understanding of how urban development acts as an agent of environmental change (McGrane, 2016). These results not only contribute to the challenge of understanding non-point source pollution in urban watersheds (Cappiella et al., 2012; Hobbie et al., 2017; Pennino et al., 2016), but also an understanding of the risks to the wider environment. For example, the proximity of many urbanised areas to coastal environments (Appendix 11) means that nutrients delivered to urban fresh waters may be more likely to affect coastal water quality and ecosystems (Sawyer et al., 2016).

In the face of increasing water scarcity, the need to reduce leakage from water distribution networks has been well-established (Speight, 2015; Xu et al., 2014). Although WML-NO_3-N fluxes may have associated environmental impacts, largely due to their potential contribution to NO_3 in groundwaters and other receiving waters downstream, the relatively low NO_3 concentrations within leaked treated water, in comparison to those from nearby sewage network leakage, means WML-NO_3-N fluxes may dilute concentrations of N in groundwater (Yates et al., 1990). Understanding the trade-off between these negative and positive impacts, as well as the fate of

WML-NO_3-N fluxes once leaked into the environment, will be important in future evaluations of environmental impacts and policy surrounding leakage control (Ascott et al., 2018b; Xu et al., 2014).

The consistency of WML-NO_3-N flux estimates in California and Georgia using both methods outlined in Section 3.2.2 indicates that, whilst using utility-level data will likely carry less uncertainty, the suite of assumptions adopted for many states due to the absence of data may still provide a reasonable first estimate of WML-NO_3-N fluxes. With some states planning to legally require validated audits that disclose utility-level volumetric leakage rates (e.g. New Jersey Department of Environmental Protection (2017)), these new datasets will allow WML-NO_3-N fluxes to be determined with lower uncertainties and at finer spatial resolution in the future, such as for individual public water systems and watershed catchments.

Extreme weather events across the US may lead to seasonal WML-NO_3-N fluxes (Folkman, 2018; Healey et al., 2021; Miller, 2021), similar to those observed in England, UK, as a result of winter pipe burst events (Ascott et al., 2018a). Watermains leakage has been found to make significant contributions to baseflow in urban streams during summer months (Fillo et al., 2021), suggesting that the relative importance of WML-NO_3-N fluxes may also change seasonally. Investigating how these fluxes change throughout the year, as well as with anticipated ageing water infrastructure replacement (USEPA, 2021a), should be a focus of future research. Watermains leakage is also an important return mechanism of phosphate in urban areas across England, UK (Ascott et al., 2016; Gooddy et al., 2017; Holman et al., 2008; Wakida and Lerner, 2005). The widespread phosphate dosing of tap water across the US for the purpose of corrosion control (McNeill, 2002) and the known contribution of phosphate to freshwater eutrophication across the US, particularly within urban catchments (Haque, 2021; Hejna and Cutright, 2021; Metson et al., 2017; Watson et al., 2016), warrants estimation of watermains leakage phosphate fluxes.

3.4.4 Policy Implications

Whilst this work does not aim to make prescriptive policy suggestions, the advancement in understanding from this research could contribute to the formulation of more effective and integrated nutrient management strategies (Ator and Denver, 2015; EPA Science Advisory Board, 2011; Grizzetti et al., 2015; Tomich et al., 2016). Now revealed to be a significant retention mechanism on a range of spatial scales, the absence of WD-NO_3-N fluxes and variable return times for this flux in N balances may invalidate many models and budgets used by policymakers in their attempt to manage N (Ascott et al., 2021). For instance, increased understanding of IRR-NO_3-N fluxes will aid the development of optimum N fertilizer application and crop production recommendations, as the movement of N associated with water withdrawals has implications for the amount of N required to be added to soils. The potential impact of water transfers on the balance between PWS-NO_3-N and WML-NO_3-N fluxes could also influence the future regulation of water withdrawal permits and transfers both across the US and around the world (Shumilova et al., 2018). The national-level WML-NO_3-N estimate presented here will facilitate international comparisons (Swaney et al., 2018b). The importance of county-level WML-NO_3-N fluxes should also help resolve urban watershed scale N budgets (Winiwarter et al., 2020) and inform local and state optimum leakage control policy (Xu et al., 2014).

3.5 Conclusions

Understanding anthropogenic controls on the N cycle is imperative for mitigating the effects of human activity on nutrient pollution of fresh waters. This research quantifies how processes associated with water supply can drive changes in the cycling of N across the US. The withdrawal of fresh water for both public and non-public supply has a potentially significant influence on N cycling across the country. Consumptive water use may act as a relatively significant transient internal store of N on a national-level and post-withdrawal water transfers may be a mechanism importing and exporting N across system boundaries on a sub-national-level. These newly quantified processes may occur on timescales relevant to nutrient management, and thus be of interest to stakeholders involved in developing more effective nutrient management strategies.

Their significance in the context of other N fluxes suggests that internal fluxes may be a necessary nuance to be considered within future N budget methodologies. Watermains leakage is estimated to return 7.0 kt NO_3-N yr^{-1} back to the environment across the US. Despite a small flux on a national level when compared to other major N inputs, this estimate masks greater relative importance of watermains leakage fluxes of N on more localised scales, with this flux exceeding the amount of N leached from agricultural fertilizer input within some urbanised counties. The results and transferrable methodology reported here, using the US as an exemplar, should support future research to quantify similar fluxes for other locations around the globe as more data becomes available.

3.6 Data Availability

All data used within this research are publicly available. Withdrawal data are available from Dieter et al. (2018a), raw surface water concentrations were available from the Water Quality Portal (www.waterqualitydata.us), and obtained using the 'dataRetrieval' package in R (De Cicco et al., 2018). Raw groundwater concentrations were sourced from the USGS Groundwater Data Releases as part of the National Water-Quality Assessment (https://www.sciencebase.gov/catalog/item/57f7f703e4b0bc0bec0a1ba8). Treated water concentrations are available from the Environmental Working Group's Tap Water Database via their website (www.ewg.org/tapwater) and volumetric leakage rate data are available from a variety of sources (Appendix 9).

3.7 Acknowledgements

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4. Watermains Leakage and Outdoor Water Use are Responsible for Significant Phosphorus Fluxes to the Environment Across the United States

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Author contributions are as follows:

Flint conceptualised research questions and developed the methodology for data analysis. Flint acquired and analysed data disclosing public water system phosphate dosing, rates of leakage, freshwater withdrawal volumes and rates of outdoor water use. Flint developed figures and wrote and revised the manuscript. Co-authors Ascott, Gooddy, Surridge and Stahl have signed below to confirm that they provided general support for development of conclusions during project meetings and provided several rounds of feedback on manuscript drafts.

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Ben Surridge

Mason Stahl

4.1 Introduction

Human society is reliant on phosphorus (P) for global food production and security (Cordell and White, 2014). However, rising P demands and the non-renewable nature of P reserves have led to global scarcity concerns (Cordell and White, 2014; Nedelciu et al., 2020; Van Vuuren et al., 2010; Yuan et al., 2018). Further, anthropogenic activity is now thought to have caused the global biogeochemical fluxes of P to exceed safe planetary boundaries (Steffen et al., 2015). Excess P inputs from rural and urban environments have substantially increased P availability within fresh and coastal waterbodies around the world (Howarth, 2008; Jarvie et al., 2015; Metson et al., 2020a; Suh and Yee, 2011). These inputs have had widespread effects on both environmental and human health (Carvalho et al., 2013; Davis and Shaw, 2006; Diaz et al., 2004), as well as significant economic costs (Garcia-Hernandez et al., 2022; Pretty et al., 2003; Sanseverino et al., 2016). This simultaneous occurrence of both P scarcity and excess, the so-called paradox of P, has made the sustainable use of P a significant global challenge (Jarvie et al., 2015; Leinweber et al., 2018).

Phosphorus pollution is a leading cause of degraded freshwater quality across the US (USEPA, 2015). High P concentrations have caused 58% of the total miles of US rivers to be rated as having poor status (USEPA, 2020b) and the resulting eutrophication of the country's fresh and marine waterbodies has persisted for decades (Bricker et al., 2008; Oswald and Golueke, 1966). The effects on environmental and human health, including decreases in potable and recreational water quality, loss of aquatic habitats and disruption to food chains (Chorus and Welker, 2021; Erdner et al., 2008; Kozacek, 2014; Munn et al., 2018), are estimated to cost the country billions of dollars a year (Dodds et al., 2009).

Although reducing anthropogenic P inputs has been a focus of US policy for decades (Litke, 1999; USEPA, 1972), water quality improvements are often not timely or sufficient (Lintern et al., 2020; Sharpley et al., 2013; Stackpoole et al., 2019). Whilst this is partially due to the lag time between adoption of management practices and detection of outcomes (Meals et al., 2010), it is also due

to the continued difficulty in identifying and quantifying the vast number of persistent P sources and the release of legacy P from previous land management practices (Sharpley et al., 2013; Smith et al., 2019). As a result, the effectiveness of policies and other attempts to more sustainably manage P across the US, such as the improved management of both point and non-point sources and more extensive P recovery and recycling programs, have been relatively limited (Daneshgar et al., 2018; Haque, 2021; Metson et al., 2016).

The ability for phosphate (PO_4) dosed water to minimize lead and copper corrosion within water distribution networks has been understood for decades (Rice and Hatch, 1939; Schock, 1989). However, the contribution of this practice to the flux of P delivered to surface water environments around the world, via wastewater treatment plant effluents, has not been properly constrained, often due to lack of data which prevents quantification of the relevant P fluxes (van Puijenbroek et al., 2019). The PO_4 dosing of public water supply for corrosion control has been a widespread practice by US public water systems (PWS) since the passing of the Lead and Copper Rule in 1991 (McNeill and Edwards, 2002; National Research Council, 2006; Singley et al., 1984; USEPA, 1991). The importance of this dosing was recently highlighted by the Flint Water Crisis in 2014, where a lack of effective corrosion control practices resulted in multiple impacts, including the increased exposure of children to lead and a range of associated long-term health effects (Edwards et al., 2009; Hanna-Attisha et al., 2015; Pieper et al., 2017).

Understanding the environmental impacts of PO_4 dosing regimens has been an active area of research, however this research has largely focussed on the contribution that this dosing makes to influent loads of P at wastewater treatment plants (USEPA, 2020a; Water Research Foundation, 2017). Beyond a limited number of small-scale studies (McNeill and Edwards, 2002; Rodgers, 2014), the extent of PO_4 dosing practices across the entire US remains poorly constrained. In addition, not all PO_4 dosed water will be returned to wastewater treatment plants (WWTPs). Some PO_4 is thought to be released from the water distribution network and into the environment as a result of outdoor water use at domestic residences, the release of effluent from

industrial cooling processes, and leakage of water from public water supply network pipes (USEPA, 2020a; Water Research Foundation, 2017). Despite this, research investigating and quantifying these processes is lacking across the US.

Research has estimated the leakage flux of PO_4 dosed tap water from the water distribution network to the environment on both a national and catchment level across the UK (Ascott et al., 2018a; Ascott et al., 2016; Gooddy et al., 2017). During periods of high leakage, leakage fluxes of P were found to be equivalent to up to 20% of WWTP P inputs to rivers across urbanised catchments, highlighting their significance in these areas (Ascott et al., 2018a). Leakage from distribution networks is ubiquitous within water systems around the world (Al-Washali et al., 2019; Lerner, 1990). With approximately 16% of the water entering the US watermains distribution network estimated to be lost due to leakage (USEPA, 2013), recent research has demonstrated that watermains leakage can be an important mechanism returning nitrogen to the environment across the US (Flint et al., 2022). Therefore, it is hypothesised that leakage of PO_4 dosed water may also constitute an important source of P across the country. Outdoor water use also represents a large proportion of total potable water use across many countries (Statistics Canada, 2017), with around one third of water supplied to domestic residences across the US being used outdoors each year (USEPA, 2017). As a result, water from public supply that has been used for lawn irrigation has been found to contribute significantly to baseflow across some US cities (Fillo et al., 2021) and PO_4 corrosion inhibitors have been reported as a potential source of P in urban runoff (Clary et al., 2020). Despite this, the fluxes of PO_4 to the environment that are associated with processes of leakage and outdoor water use are lacking, both across the US and around the globe.

In this work, recommended PO_4 dosing concentrations (expressed as P), public water system dosing facility data, volumetric rate estimates of both public and domestic supply distribution inputs, as well as fractions of these inputs lost due to leakage and outdoor water use are synthesised to address the following research questions:

1. What is the spatial variability of PO_4 dosing practices undertaken by public water systems for the purpose of corrosion control across US counties, and thus what is the annual mass flux of PO_4 added to these systems?
2. What is the annual mass flux of PO_4 lost or actively removed from the watermains distribution network across US counties due to leakage and outdoor water use, respectively, and thus what is the residual mass flux of PO_4 returned to wastewater treatment plants per year?
3. What are the significance of, and dominant controls upon, estimated watermains leakage and outdoor water use PO_4 fluxes across the US?

4.2 Methods

4.2.1 Estimating the Extent of Phosphate Dosing by Public Water Systems for Corrosion Control and the Mass Flux of Phosphate Entering the Water Distribution Network

The mass flux of PO_4 entering the water distribution network across each US county due to dosing by public water systems (DOSE-PO_4-P_{pws}) was estimated using equations 4.1 to 4.3. The fraction of a county's population served by public water systems that dose their water with either orthophosphate or polyphosphate (herein referred to as PO_4; f_{dosed}) was determined as the ratio of the county's population served by PO_4 dosed water (Pop_{dosed}) to the total population served by public water systems (Pop_{pws}). Pop $_{dosed}$ values were determined through querying the Safe Drinking Water Information System (SDWIS) (USEPA, 2022b) for PWS that had active PO_4 dosing facilities for the purpose of corrosion control in the year 2015. The resulting dataset disclosed both the counties and the population size that each PWS supplied, and corresponded with the most recent water use data release year (Dieter et al., 2018a). County-level Pop_{pws} values were sourced from Dieter et al. (2018a).

$$f_{\text{dosed}} = \frac{\text{Pop}_{\text{dosed}}}{\text{Pop}_{\text{pws}}} \tag{4.1}$$

f_{dosed} was then applied to county-level volumetric rates of PWS distribution inputs to give the total volumetric rate of PO_4 dosed water entering the public water supply distribution network ($Vol_{pws\text{-}dosed}$), in L yr^{-1} (equation 4.2). With PWS distribution input estimates omitted from water use reports, they were assumed to equal the total volume of freshwater withdrawn for public supply in each county for the year 2015 ($WD_{pws\text{-}total}$) in L yr^{-1}, and were sourced from Dieter et al. (2018a).

$$Vol_{pws\text{-}dosed} = WD_{pws\text{-}total} \times f_{dosed} \quad (4.2)$$

DOSE-PO_4-P_{pws} values for each county, in kg PO_4-P yr^{-1}, were estimated as the product of $Vol_{pws\text{-}dosed}$ and PO_4 concentrations within dosed tap water ($C_{t\ (PO4\text{-}P)}$), in mg PO_4-P L^{-1} (equation 4.3). Due to generally low PO_4 concentrations in natural waters (Hem, 1985; Litke, 1999), and the lack of a health-based PO_4 limit within potable water (USEPA, 2021b; World Health Organization, 2005), PO_4 concentrations are not widely reported for dosed or non-dosed water. It was therefore assumed that concentrations of PO_4 in potable water were only present as a result of dosing practices by public water systems (Cornwell et al., 2015). Given no comprehensive national $C_{t\ (PO4\text{-}P)}$ dataset, USEPA (2016b) recommended lower and upper target residual PO_4 concentrations at the consumers tap (0.33 and 1 mg PO_4-P L^{-1}, respectively) were adopted in order to make both lower and upper DOSE-PO_4-P_{pws} flux estimates. County level DOSE-PO_4-P_{pws} estimates were aggregated to give a final national-level estimate, in metric kt PO_4-P yr^{-1}. The sources of data for all terms used to estimate DOSE-PO_4-P_{pws} fluxes are outlined in Table 4.1.

$$DOSE\text{-}PO_4\text{-}P_{pws} = Vol_{pws\text{-}dosed} \times C_{t\ (PO4\text{-}P)} \quad (4.3)$$

Table 4.1. Table summarising data sources for key terms used to estimate the fluxes of phosphate entering the water distribution network due to corrosion control practices (DOSE-PO_4-P_{pws}), fluxes of PO_4 leaked to the environment from watermains (WML-PO_4-P) and fluxes of PO_4 lost to the environment due to outdoor water use at domestic residences (OWU-PO_4-P) across the United States.

Term	Term Description	Reference
DOSE-PO_4-P		
f_{dosed}	Fraction of population served by PO_4 dosed water	-
Pop_{dosed}	Population served by PO_4 dosed water	USEPA (2022b)
Pop_{pws}	Population served by public water systems	Dieter et al. (2018a)
$Vol_{pws\text{-}dosed}$	Volumetric rate of PO_4 dosed water entering the public water supply distribution network	-
$WD_{pws\text{-}total}$	Volumetric rate of freshwater withdrawn for public supply	Dieter et al. (2018a)
$C_{t\ (PO4\text{-}P)}$	PO_4 concentrations within dosed tap water	USEPA (2016b)
WML-PO_4-P		
$f_{leakage}$	Leakage factor	Various (see Appendix 12)
$Vol_{leaked\text{-}dosed}$	Volumetric rate of PO_4 dosed water leaking from the public water supply distribution network	-
OWU-PO_4-P		
$Vol_{domestic\text{-}dosed}$	Volumetric rate of PO_4 dosed water supplied for domestic use	-
$DI_{domestic}$	Volumetric rate of water supplied for domestic use	Dieter et al. (2018a)
f_{owu}	Outdoor water use factor	Various (see Appendix 14)
$Vol_{owu\text{-}dosed}$	Volumetric rate of PO_4 dosed water lost from the public water supply distribution network due to outdoor water use	-

4.2.2 Estimating Watermains Leakage and Outdoor Water Use Phosphate Fluxes and Their Comparison with Other Phosphorus Fluxes to the Environment

County-level PO_4 fluxes due to watermains leakage (WML-PO_4-P) were estimated across the US using equations 4.4 and 4.5. $Vol_{pws\text{-}dosed}$ was adjusted using a leakage factor ($f_{leakage}$; unitless) to give a final volumetric rate of leaked dosed water ($Vol_{leaked\text{-}dosed}$), in L yr^{-1} (equation 4.4). With the exception of California and Georgia, a lack of county-level leakage factor data meant that state level $f_{leakage}$ values were obtained from various sources and assigned to their respective counties (Appendix 12 and 14). Where possible, $f_{leakage}$ values were determined by dividing volume of real water loss by volume of total water supplied from validated American Water Works Association (AWWA) water utility audits for the year of 2016. Utility $f_{leakage}$ values were then averaged and extrapolated for the relevant state (see Kunkel Water Efficiency Consulting (2018)), with this method applied to 16 states. In the absence of water audit data, $f_{leakage}$ values for seven states were sourced from various reports (Appendix 12). For the 22 states without $f_{leakage}$ values, the national average of 0.16 was used (USEPA, 2013).

$$Vol_{leaked\text{-}dosed} = Vol_{pws\text{-}dosed} \times f_{leakage} \quad (4.4)$$

County-level WML-PO_4-P estimates, in kg PO_4 yr^{-1}, were estimated as the product of $Vol_{leaked\text{-}dosed}$ and $C_{t\ (PO4\text{-}P)}$ (equation 4.5). Effective corrosion control within in-building plumbing requires target $C_{t\ (PO4\text{-}P)}$ values to be met at the consumers tap. Due to PO_4 reacting with other compounds and influencing biological processes within pipe networks (Douterelo et al., 2020), water leaving dosing plants will often have higher PO_4 concentrations than that further along the network (Hill and Cantor, 2011; USEPA, 2016b). Over time, dosing concentrations of PO_4 will equal those at the tap (Comber et al., 2013), however the time to reach this equilibrium remains largely unknown and varies between individual water supply systems (USEPA, 2016b). As a result, it was assumed that $C_{t\ (PO4\text{-}P)}$ values were the same along the entire pipe network. County-level WML-PO_4-P fluxes were aggregated to give a national-level estimate, in metric kt PO_4-P yr^{-1}, as well as normalised

for land area, in kg PO_4-P km^{-2} yr^{-1}. The sources of data for all terms used to estimate WML-PO_4-P fluxes are outlined in Table 4.1.

$$WML\text{-}PO_4\text{-}P = Vol_{leaked\text{-}dosed} \times C_{t\ (PO4\text{-}P)} \quad (4.5)$$

County-level fluxes of PO_4 leaving the distribution network due to the use of PO_4 dosed water outdoors at domestic residences across the US (OWU-PO_4-P) were estimated using equations 4.6 to 4.8. The volume of PO_4 dosed water supplied for domestic use ($Vol_{domestic\text{-}dosed}$) was estimated as the product of public supply delivered to domestic users ($DI_{domestic}$) in L yr^{-1} reported by Dieter et al. (2018a) and f_{dosed} (equation 4.6). $Vol_{domestic\text{-}dosed}$ was corrected using an outdoor water use factor (f_{owu}; unitless) to give the volumetric flow rate of dosed water for outdoor use ($Vol_{owu\text{-}dosed}$) (equation 4.7). Lack of county-level f_{owu} data meant that state-level values, ranging from 0.25-0.6, were obtained from various sources (Appendix 14). For the nine states with a state-level f_{owu} value, this value represented a state average and was sourced from a mixture of Cooperative State Research, Education, and Extension Service reports and state environmental department and agency reports. For the 38 states without f_{owu} values, the national average of 0.3 was used (USEPA, 2017). County-level OWU-PO_4-P fluxes, in kg PO_4-P yr^{-1}, were estimated as the product of $Vol_{owu\text{-}dosed}$ and $C_{t\ (PO4\text{-}P)}$ (equation 4.8) and were both normalised for land area, in kg PO_4 km^{-2} yr^{-1} as well as aggregated to give a national-level estimate in metric kt PO_4-P yr^{-1}. The sources of data for all terms used to estimate OWU-PO_4-P fluxes are outlined in Table 4.1.

$$Vol_{domestic\text{-}dosed} = DI_{domestic} \times f_{dosed} \quad (4.6)$$

$$Vol_{owu\text{-}dosed} = Vol_{domestic\text{-}dosed} \times f_{owu} \quad (4.7)$$

$$OWU\text{-}PO_4\text{-}P = Vol_{owu\text{-}dosed} \times C_{t\ (PO4\text{-}P)} \quad (4.8)$$

Median outdoor water use and watermains leakage fluxes of PO_4 were determined through assuming a dosing concentration of 0.67 mg PO_4-P L^{-1}, the median value between lower and upper target residual concentrations of 0.33 and 1.0 mg PO_4-P L^{-1}, respectively (USEPA, 2016b). Upper and lower estimates of national-level WML-PO_4-P and OWU-PO_4-P fluxes were determined by adjusting $C_{t\ (PO4\text{-}P)}$ to lower and upper target residual concentrations and $WD_{pws\text{-}total}$ and $DI_{domestic}$ values of ±10%, respectively. Although the inherent uncertainty associated with USGS withdrawal data is currently not reported (National Research Council, 2002), a ±10% uncertainty on $WD_{pws\text{-}total}$ and $DI_{domestic}$ values was adopted, reflecting the uncertainty used within previous US water budget research (Maupin and Weakland, 2009).

County-level WML-PO_4-P and OWU-PO_4-P fluxes were summated and normalised for county area, in kg PO_4-P km^{-2} yr^{-1}. The significance of county and national-level WML-PO_4-P and OWU-PO_4-P fluxes, in the context of US P budgets, was evaluated through their comparison with estimates of P fluxes from other sources to the environment, including P fluxes to surface waterbodies from point sources, including both municipal and industrial wastewater treatment plant effluents (USEPA, 2023a), the use of farm and non-farm (urban) P fertilizers and P from manure application (Falcone, 2021). Key controls upon OWU-PO_4-P and WML-PO_4-P fluxes were investigated through their comparison with potentially influencing factors, such as population density.

County-level mass fluxes of PO_4 returned to wastewater treatment plants (WWTPs) due to PO_4 dosing (DOSE-PO_4-P_{wwtp}) were estimated using a mass balance equation (equation 4.9 and Figure 4.1) and aggregated to give a national-level estimate, in metric kt PO_4-P yr^{-1}. It should be noted that whilst leaking and overflowing sewers and septic tanks have been found to be important sources of nutrient loading across the US (Delesantro et al., 2022; Iverson et al., 2018), estimating the loss of drinking water derived PO_4 between domestic residences and WWTPs associated with these processes is beyond the scope of this research.

$$DOSE\text{-}PO_4\text{-}P_{wwtp} = DOSE\text{-}PO_4\text{-}P_{pws} - WML\text{-}PO_4\text{-}P - OWU\text{-}PO_4\text{-}P \quad (4.9)$$

Where $DOSE\text{-}PO_4\text{-}P_{wwtp}$ is the flux of dosing derived phosphate that is returned to wastewater treatment plants. $DOSE\text{-}PO_4\text{-}P_{pws}$ is the flux of phosphate added to the water distribution network due to dosing for the purpose of corrosion control. $WML\text{-}PO_4\text{-}P$ is the flux of phosphate lost from the public supply distribution network due to the leakage of phosphate dosed water from leaking watermains pipes. $OWU\text{-}PO_4\text{-}P$ is the flux of phosphate lost from the public supply distribution network due to outdoor water use at domestic residences. The units for all terms in this equation are in kg and kt PO_4-P for fluxes estimated on a county and national level, respectively.

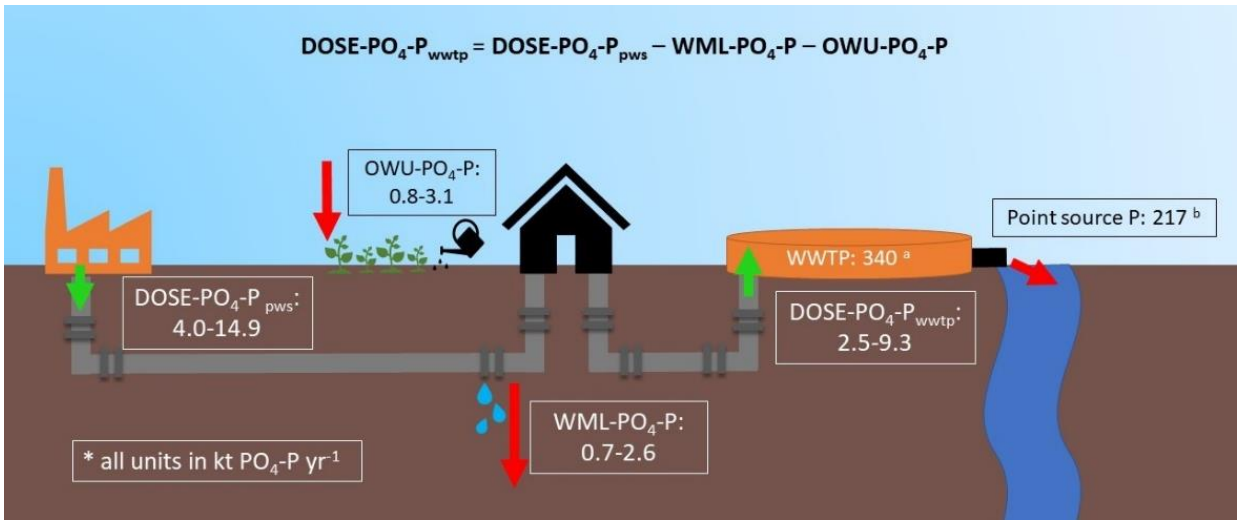

Figure 4.1. Schematic figure showing the national scale mass balance developed to estimate the contribution that phosphate (PO_4) dosed water returned to wastewater treatment plants ($DOSE\text{-}PO_4\text{-}P_{wwtp}$) makes to total estimated loading of phosphorus (P) to municipal wastewater treatment plants (WWTPs) across the United States for the year 2015. Flux ranges represent lower and upper-bound estimates for the input of PO_4 by public water systems ($DOSE\text{-}PO_4\text{-}P_{pws}$), losses from the water distribution network due to watermains leakage ($WML\text{-}PO_4\text{-}P$) and outdoor water use ($OWU\text{-}PO_4\text{-}P$) and $DOSE\text{-}PO_4\text{-}P_{wwtp}$. These flux values may not sum due to rounding. Fluxes sourced from [a] Hallas et al. (2019) and [b] USEPA (2023a).

4.3 Results

4.3.1 The Extent of Phosphate Dosing by Public Water Systems for Corrosion Control and the Mass Flux of Phosphate Entering the Water Distribution Network

This analysis reveals that, in 2015, 4,572 of the 152,104 active public water systems (PWS) across the US (3%) had at least one facility that dosed their water with PO_4 for the purpose of controlling lead and copper corrosion (Table 4.2 and Figure 4.2a). These facilities were found within 1,402 of the 3,109 US counties considered within this research (Figure 4.2b). The percentage of PWS that dose is positively correlated with the size of the PWS, as represented by the size category of population it serves (i.e. the number of people it serves; Table 4.2). For example, 25% of very large PWS (those that serve >100,000 people) dose water with PO_4 for corrosion control purposes, whereas the figure is only 1% for very small systems (that serve <500 people). However, when combined, the large absolute number of 'small' and 'very small' PWS (serving <500 and 501-3,300 people, respectively) means that they contribute over 60% of the total 4,572 PWS that dose with PO_4. Although the absolute number of PWS undertaking PO_4 dosing decreases as PWS size increases, the total population served by PWS that dose is also positively correlated with PWS size (Table 4.2). Consequently, although only 3% of PWS across the US undertook PO_4 dosing in 2015, 25% of the total population were supplied with PO_4 dosed water (Table 4.2). The number of PWS with PO_4 dosing facilities, as well as total and percentage of state populations they serve, are generally larger within constituent counties of Midwestern, Northeastern and Mid-Atlantic states (e.g., Minnesota, Illinois, New York, New Jersey and Pennsylvania), as well as several Californian counties (Figure 4.2). Nationally, it was estimated that 4-14.9 kt PO_4-P yr^{-1} entered the distribution network due to PO_4 dosing (Figure 4.1 and Appendix 15).

Table 4.2. The total number of public water systems (PWS) and the population these systems served across the United States, as well as the number of these systems that undertook phosphate (PO_4) dosing and the population served by PO_4 dosed water, for each defined PWS size category in the year 2015. The percentage of PWS that undertook PO_4 dosing when compared to the total number of PWS, as well as the percentage of the population served by PO_4 dosed water when compared to the total population served by PWS are also shown for each PWS size category.

PWS size (by population served)	Total number of PWS [a]	Total population served [a]	Number of PWS that dose for corrosion control [b]	Population served by PWS that dose [b]	% of PWS that dose [c]	% of population served by PWS that dose [c]
Very Small (< 500)	124,291	13,913,830	1,316	290,260	1.0 (29)	2.0 (0.40)
Small (501 – 3,300)	18,487	24,255,378	1,572	2,358,574	8.5 (34)	10 (3.0)
Medium (3,301 – 10,000)	5,090	29,613,444	777	4,569,572	15 (17)	15 (6.0)
Large (10,000 – 100,000)	3,813	108,954,823	802	23,549,372	21 (18)	22 (30)
Very Large (> 100,000)	422	139,224,370	105	47,436,133	25 (2.0)	34 (61)
PWS (all)	152,104	315,961,845	4,572	78,203,911	3	25

[a] USEPA (2022a)

[b] USEPA (2022b)

[c] Values in parentheses show the percentage contribution that the number of dosing public water systems and the populations they serve in each system size category make to the total number of dosing public water systems and total population served by dosed water (n = 4,572 and n = 78,203,911, respectively).

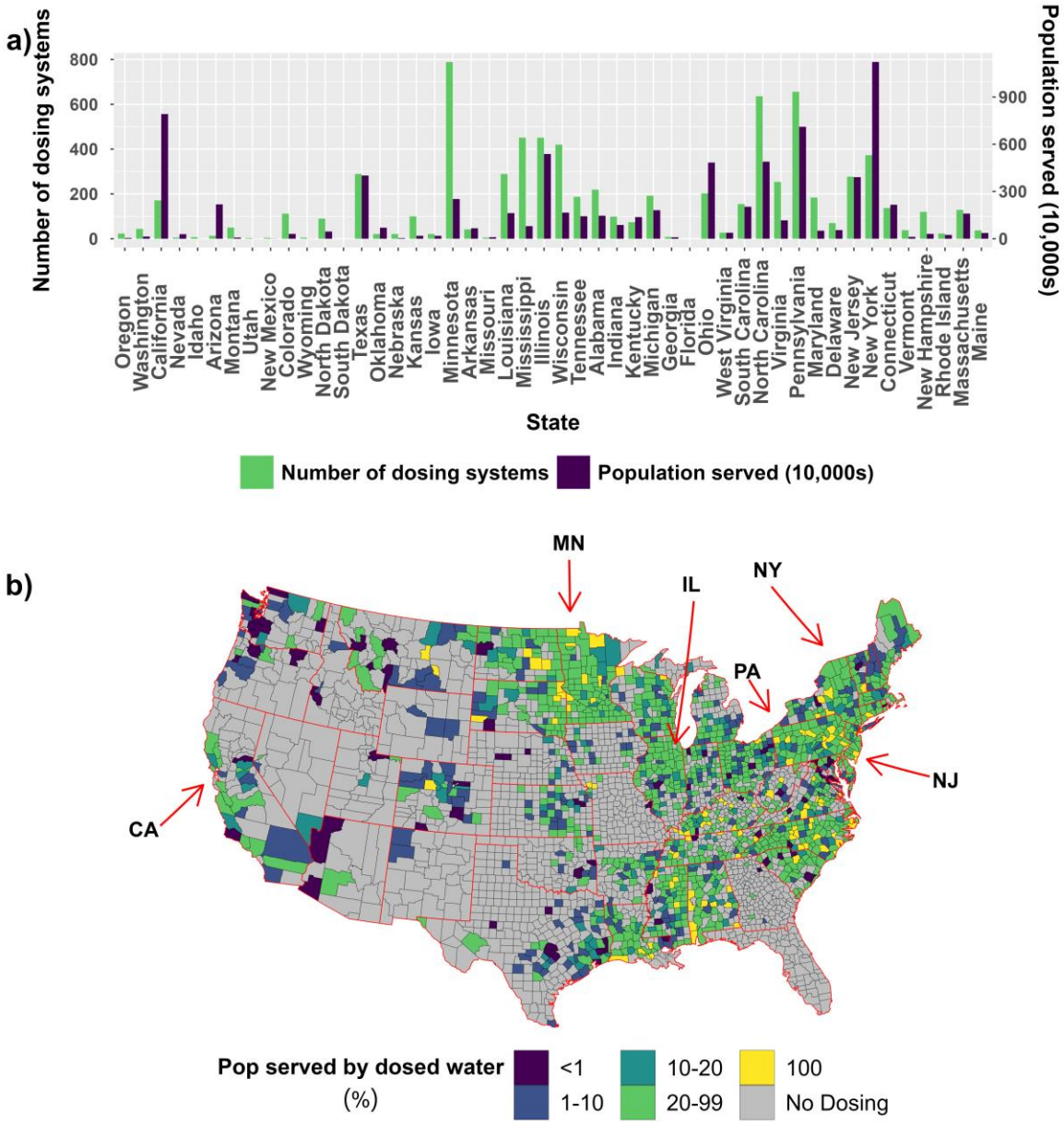

Figure 4.2. a) The number of public water systems with active phosphate (PO_4) dosing facilities across the United States in the year 2015 indicated by purple bars and the total population that these public water systems serve indicated by green bars. States on the x-axis are ordered from west to east. b) Percentage of the population supplied with PO_4 dosed water for each county across the United States, with state labels indicating areas with particularly high values. Linework was created using the 'usmap' package in R (Di Lorenzo, 2022).

4.3.2 Watermains Leakage and Outdoor Water Use Phosphate Fluxes

Nationally, an estimated 5-17% of PO_4 dosed water within the water distribution network was lost due to watermains leakage, with the associated flux of PO_4 (WML-PO_4-P) estimated to be between 0.7-2.6 kt PO_4-P yr^{-1} (Table 4.3), with a median estimated flux of 1.6 kt PO_4-P yr^{-1}. Of the 1,402 counties with at least one PWS that undertook PO_4 dosing in 2015, 58% are defined as urban. A general trend of increasing WML-PO_4-P fluxes from west to east across the US prevails, with the highest estimated fluxes observed in urbanised counties of Midwestern, Northeastern and mid-Atlantic states, such as Philadelphia County in Pennsylvania and Union County in New Jersey (Figure 4.3b).

On a national level, 5-21% of PO_4 dosed water was removed from the water distribution network due to outdoor water use at domestic residences, with the associated PO_4 flux (OWU-PO_4-P) estimated to be 0.8-3.1 kt PO_4-P yr^{-1} (Figure 4.1 and Appendix 14), with a median estimated flux of 1.9 kt PO_4-P yr^{-1}. Counties in the Northeast and state of California had the largest OWU-PO_4-P fluxes (Figure 4.3c). When combined, the upper bound national WML-PO_4-P and OWU-PO_4-P flux estimates (2.6 and 3.1 kt PO_4-P yr^{-1}, respectively) are equivalent to around 12% of P inputs to the environment from urban fertilizer, 2.6% of the P load to surface waterbodies from point sources, and 0.3% of P inputs to the environment from farm fertilizers and manure application (Table 4.3). There is large inter-county variability in combined area-normalised WML-PO_4-P and OWU-PO_4-P fluxes, with estimates ranging from 0-817 kg PO_4-P km^{-2} yr^{-1} (Figure 4.4a). A moderate monotonic relationship was observed between the combination of area-normalised OWU-PO_4-P and WML-PO_4-P fluxes and population density ($\rho = 0.41$, $p < 0.01$; Figure 4.5). When combined, lower and upper county-level WML-PO_4-P and OWU-PO_4-P flux estimates exceed P inputs to the environment from urban and farm fertilizer usage and manure application across 16-56, 13-21 and 17-32 counties respectively, and exceed P inputs from point sources to fresh waters across 461-541 counties, out of a total of 3,101 US counties included in this research (Figure 4.4b-e). In addition, when upper bound county-level estimates are considered, 39 counties have combined WML-PO_4-P and OWU-PO_4-P fluxes that exceed the sum of all major P inputs to the environment

(farm and non-farm fertilizer, manure and point source P inputs). The total mass flux of P returned to US WWTPs due to PO_4 dosing (DOSE-PO_4-P_{wwtp}), having accounted for OWU-PO_4-P and WML-PO_4-P fluxes, was estimated to be 2.5-9.3 kt PO_4-P yr^{-1} (Figure 4.1). Counties with the highest DOSE-PO_4-P_{wwtp} fluxes were found across the Northeast and mid-Atlantic regions and the state of California (Figure 4.3d).

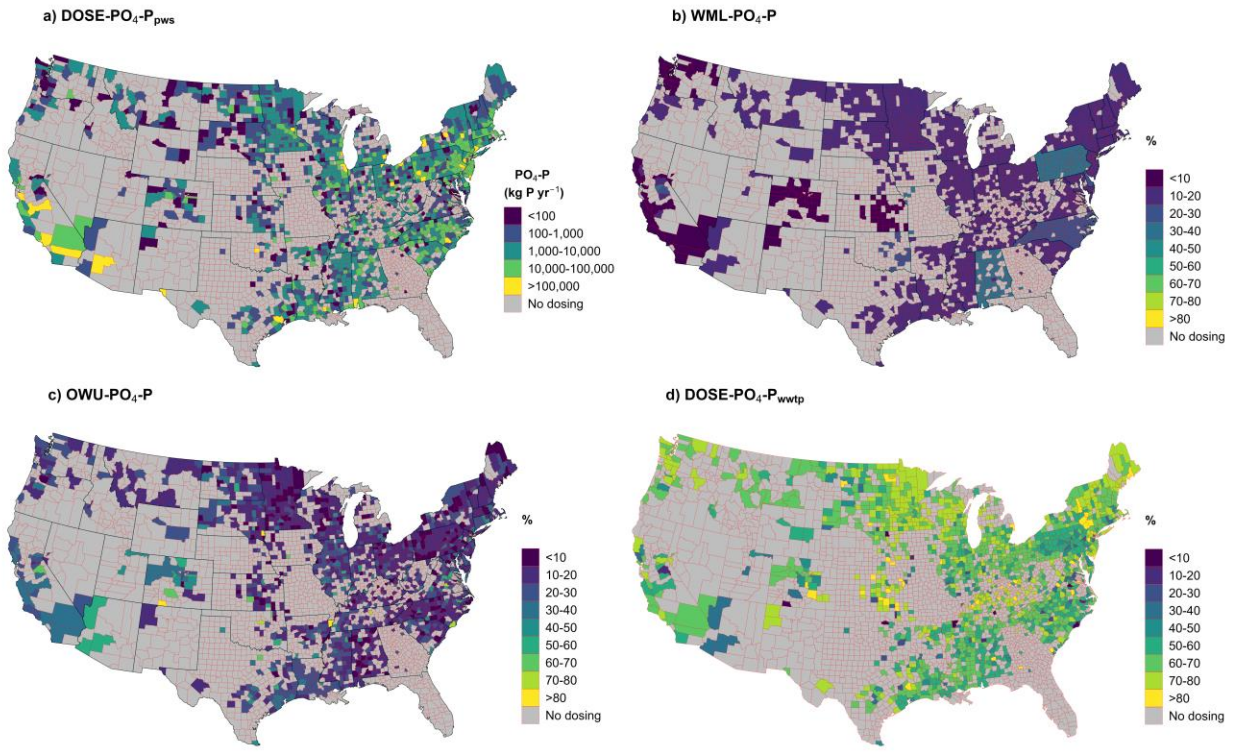

Figure 4.3. a) The mass flux of phosphate (PO_4) added to public water supply distribution networks across each county of the United States due to PO_4 dosing (DOSE-PO_4-P_{pws}). The percentage of each county's estimated DOSE-PO_4-P_{pws} flux that was lost from its water distribution network due to b) watermains leakage (WML-PO_4-P) and removed due to c) outdoor water use (OWU-PO_4-P). d) The percentage of a county's DOSE-PO_4-P_{pws} flux returned to wastewater treatment plants (DOSE-PO_4-P_{wwtp}), once WML-PO_4-P and OWU-PO_4-P fluxes had been accounted for. All fluxes are for the year 2015 and grey areas indicate counties where no PO_4 dosing was reported. Linework was created using the 'usmap' package on R (Di Lorenzo, 2022).

Table 4.3. National-level watermains leakage flux of phosphate (WML-PO_4-P) and outdoor water use flux of phosphate (OWU-PO_4-P) expressed as percentage equivalence of other estimates of major phosphorus (P) inputs to the environment. Values in parentheses are in units of metric kt PO_4-P yr^{-1}.

Flux	**Urban P fertilizer input** (47) [a]	**Loads of P from point sources** (217) [b]	**Farm P fertilizer input** (1,829) [a]	**Manure P input** (1,908) [a]
WML-PO_4-P (0.7-2.6)	1.5-5.5	0.32-1.2	0.038-0.14	0.037-0.13
OWU-PO_4-P (0.8-3.1)	1.7-6.5	0.37-1.4	0.044-0.17	0.042-0.16
WML-PO_4-P + OWU-PO_4-P (1.5-5.6)	3.2-12	0.69-2.6	0.082-0.30	0.079-0.30

[a] Falcone (2021)

[b] USEPA (2023a)

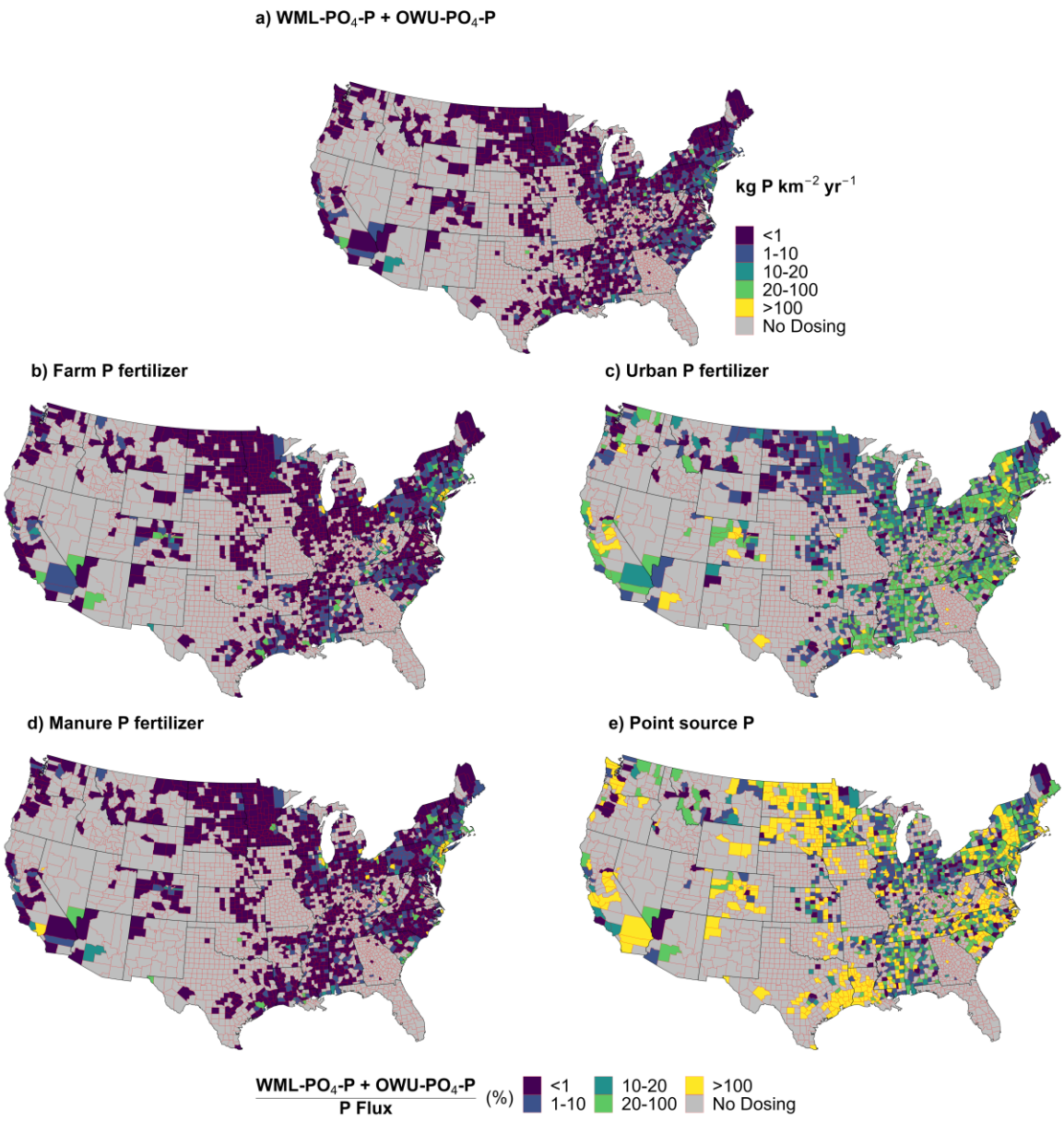

Figure 4.4. a) The sum of estimated area-normalised county-level watermains leakage phosphate fluxes (WML-PO_4-P) and outdoor water use phosphate fluxes (OWU-PO_4-P) across the United States for the year 2015. The sum of estimated county-level WML-PO_4-P and OWU-PO_4-P fluxes expressed as a percentage equivalence of P fluxes from b) farm and c) urban fertilizer inputs, d) manure inputs and e) point sources. Grey areas indicate counties where no phosphate dosing was reported. Linework was created using the 'usmap' package on R (Di Lorenzo, 2022).

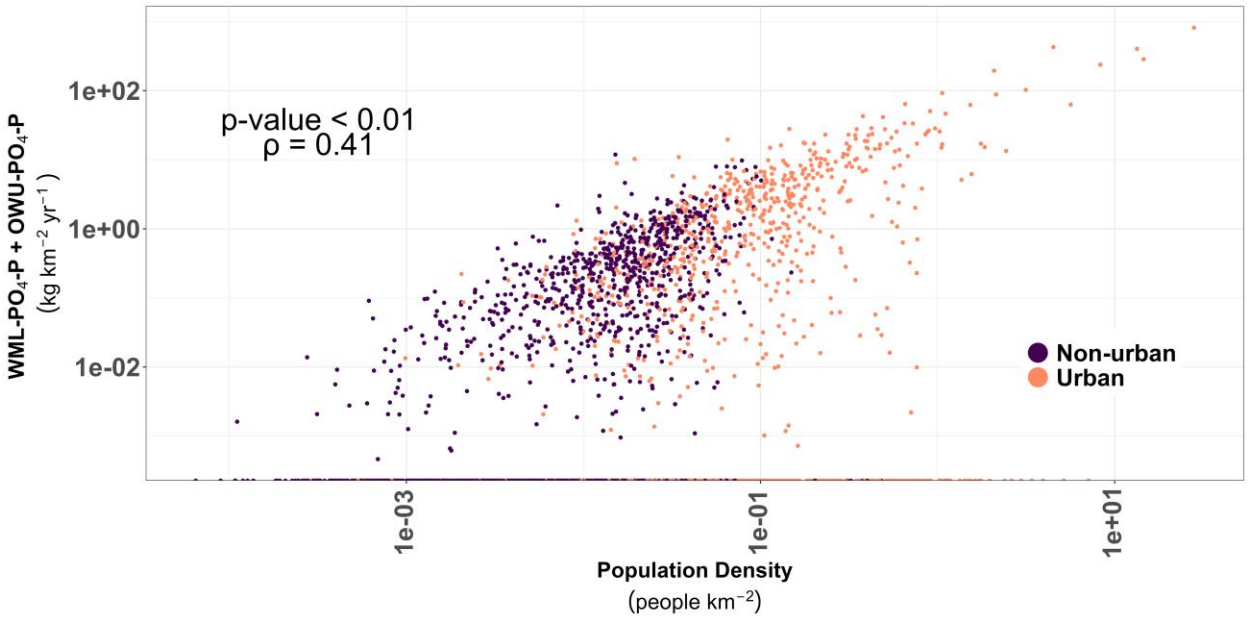

Figure 4.5. Relationship between the sum of combined area-normalised watermains leakage fluxes of phosphate (WML-PO_4-P) and outdoor water use fluxes of phosphate (OWU-PO_4-P) and population density (p-value < 0.01, ρ = 0.41), for both urban and non-urban counties across the United States. Urban counties are those defined as 'metro' and 'nonmetro' within the US Department of Agriculture's Rural Urban Continuum Codes, respectively (USDA, 2020a). Counties with WML-PO_4-P and OWU-PO_4-P fluxes equal to zero are where no phosphate dosing occurred.

4.4 Discussion

4.4.1 Controls on the Extent of Phosphate Dosing for Corrosion Control and Mass Flux of Phosphorus Entering the Water Distribution Network

The methodology and the data reported in this research have allowed, for the first time, P flux estimates associated with PO_4 dosing by public water systems (DOSE-PO_4-P_{pws}), watermains leakage (WML-PO_4-P), domestic outdoor water use (OWU-PO_4-P) and the returns of PO_4 dosed water to wastewater treatment plants (DOSE-PO_4-P_{wwtp}) on a sub-national scale across the US. Results show that the national-level DOSE-PO_4-P_{pws} flux across the US may have been up to 14.9 kt PO_4-P yr^{-1} in the year 2015, with up to 17% of this PO_4 lost to the environment via watermains leakage and 21% input to the environment via domestic outdoor water use. Some upper bound

county-level WML-PO_4-P and OWU-PO_4-P fluxes exceeded other well-constrained P fluxes to the environment, such as point source P inputs. Once WML-PO_4-P and OWU-PO_4-P fluxes had been accounted for, the national DOSE-PO_4-P_{wwtp} flux was estimated to be up to 9.3 kt PO_4-P yr^{-1}. The most recent and comprehensive analysis of the extent of PO_4 dosing, undertaken by the USEPA (2020a), estimates that the number of public water systems (PWS) undertaking dosing nationally is slightly larger than the one presented here (around 8,500, or 5.6%), suggesting that the approach used in this work may have underestimated the number of PWS undertaking dosing, and thus DOSE-PO_4-P_{pws}, WML-PO_4-P and OWU-PO_4-P estimates. Despite this, the analysis presented here provides the first sub-national scale insight into the variance of PO_4 dosing across the country (Figure 4.3a).

The inverse relationship between the number of PWS that undertake PO_4 dosing and the size of population they serve (Table 4.2) is consistent with findings reported by McNeill and Edwards (2002). However, the proportion of PWS dosing was found to be lower for all PWS size categories when compared to previously published research (Arnold et al., 2019; McNeill and Edwards, 2002). Whilst these previous studies investigated the extent of PO_4 dosing across the US (concluding that more than 50% of utilities use PO_4 based corrosion inhibitors), they targeted a limited number of utilities (264 and 60 out of around 50,000, respectively). The disparity between their estimates, the USEPA (2020a) estimate (5.6%), and the one reported here (3%) may also be due to the bias incorporated within past research through only investigating medium to large size utilities, with this analysis suggesting that larger size PWS are more likely to undertake PO_4 dosing.

Although around 7% of the total US population is thought to be served by PWS with lead watermains pipes (Cornwell et al., 2016), this analysis suggests 26% of people served by community water systems were supplied with PO_4 dosed water. This disparity is likely due to precautionary PO_4 dosing by PWS, given the lack of comprehensive lead watermain pipe inventories (USEPA, 2019a), alongside the fact that many remaining lead solder components are

located within property boundaries, and are thus not the responsibility of the utility. PWS may also undertake PO_4 dosing in order to prevent other metals (copper, manganese and iron) found within non-lead pipes to be released into the water distribution network (Comber et al., 2011; Lytle et al., 2018; Lytle and White, 2014; McNeill and Edwards, 2002; USEPA, 2016b). Recent Lead and Copper Rule revisions may drive changes in both the spatial extent of PO_4 dosing practices and the PO_4 concentrations required in the future (USEPA, 2019a; USEPA, 2020a). Estimating the extent of future PO_4 dosing practices across the country, and the effect this might have upon WML-PO_4-P, OWU-PO_4-P and DOSE-PO_4-P_{wwtp} fluxes, should therefore be a priority for future research.

Urbanised counties across Midwestern and Northeastern regions, such as Philadelphia, Chicago and Milwaukee have the largest total and proportional populations served by dosed water (Figure 4.2). The higher proportion of PWS undertaking PO_4 dosing in these areas likely reflects the dense network of lead watermains pipes in these areas (Cornwell et al., 2016; NRDC, 2022), that would have been installed prior to the lead piping ban in 1986 (AWWA, 2012; USEPA, 1989). Higher dosing rates across many urbanised areas have also been linked to the elevated corrosivity of their raw surface waters (Stets et al., 2018). Further, corrosivity of raw groundwater used for public supply is also higher across eastern regions of the US, including the states of New Jersey, Maryland, Delaware and South Carolina (Belitz et al., 2016), where higher dosing rates were observed (Figure 4.2). However, regions of the US with a low prevalence of PO_4 dosing, such as Georgia (Figure 4.2), do not necessarily indicate a lower presence of lead watermains pipes. Many of these areas use alternative corrosion control methods, such as pH adjustment instead (USEPA, 2022b).

Prescribing a fixed lower or upper PO_4 dosing concentration within calculations (0.33 or 1.0 mg PO_4-P L^{-1}, respectively) will have propagated uncertainty to DOSE-PO_4-P_{pws}, WML-PO_4-P, OWU-PO_4-P and DOSE-PO_4-P_{wwtp} estimates. In reality, PWS across the US add PO_4 in varying concentrations both within and outside of the USEPA target range (Comber et al., 2013; The

Cadmus Group Inc., 2004; USEPA, 2016b). When PWS first establish PO_4 dosing regimens, they may add PO_4 at concentrations two to three times higher than the target concentration required at the consumers tap, meaning county-level DOSE-PO_4-P_{pws} values may have been underestimated in the research reported here, at least for any PWS in the early stages of establishing a dosing regimen. Whilst assuming a dosing concentration of 3 mg PO_4-P L^{-1} across the entire US would result in a DOSE-PO_4-P_{pws} flux of 44.7 kt PO_4-P yr^{-1}, opposed to the 14.9 kt PO_4-P yr^{-1} upper estimate reported in this research, these higher doses are often only needed to be applied for a few weeks before they can be reduced back to target maintenance concentrations (Hill and Cantor, 2011; MOE, 2009; USEPA, 2016b). Along with the fact that concentrations of PO_4 can also vary with distance along the distribution pipe network, an improved understanding of how PO_4 concentrations may change at various points along water distribution networks is fundamental to better constrain the uncertainties associated with DOSE-PO_4-P_{pws}, WML-PO_4-P, OWU-PO_4-P and DOSE-PO_4-P_{wwtp} fluxes.

4.4.2 Losses of Phosphate from Water Distribution Networks due to Watermains Leakage and Outdoor Water Use and Implications for Phosphorus Returns to Wastewater Treatment Plants

Whilst a number of previous studies have assumed that residual PO_4 loads within the distribution network will ultimately be returned to WWTPs (Comber et al., 2013; Vaccari, 2011), the research reported here highlights that these residual loads may also be released into the environment and bypass WWTPs. Results suggest that 5-17% and 5-21% of DOSE-PO_4-P_{pws} is either lost from the water distribution network across the US due to watermains leakages or removed due to outdoor water use at domestic residences, respectively. Whilst the USEPA (2020a) incorporated leakage and outdoor water use within their conceptual mass balance model to investigate increases in P loading at WWTPs as a result of dosing for corrosion control, a single rate of water loss was applied to each process across the country. Further, the study did not report the national level, sub-national scale variance or significance of the estimated loss of P to the environment. The use of more locally determined leakage rates within this research, either on a utility-level for the states of California and Georgia, or state-level where possible, allows for greater spatial

resolution in WML-PO_4-P estimates when compared to previous research. Results presented here still do not fully capture the localised variance in leakage rates across the country, however. The proportion of water lost due to leakage ($f_{leakage}$) can vary significantly even within a single state, with Californian utilities having leakage factors varying between <0.01 and 0.75 for the year 2015 (California Department of Water Resources, 2019; DeOreo et al., 2011). It is likely that many counties within the Northwest and Midwestern regions of the US will have locally elevated water leakage rates, due to the ageing condition of infrastructure in these areas (Folkman, 2018). The use of state-average factors will have masked these highly localised differences and have therefore introduced further uncertainty into the resulting WML-PO_4-P flux estimates.

The largest county-level OWU-PO_4-P fluxes were observed across densely populated urban areas in the Northeastern US (Figure 4.3c). These are areas associated with the largest public supply deliveries to domestic users (Appendix 13c), although the proportion of water used outdoors (f_{owu}) at domestic residences is often below the national average (Appendix 13a). The effect of population density upon public supply withdrawals and domestic deliveries, and thus on both WML-PO_4-P and OWU-PO_4-P fluxes, is highlighted in Figure 4.5. Higher f_{owu} values across the Southwestern US (Appendix 14), due to the arid climate in these areas (USEPA, 2017), contribute to the larger OWU-PO_4-P estimates across constituent counties within this region, such as California (Figure 4.3c). Despite this, data disclosing f_{owu} values across the US is limited, with only nine states having values reported either on state environmental department websites or within reports. The use of a nationally averaged f_{owu} value masks the large differences in outdoor water use rates between states. Even the use of a single state reported f_{owu} value will have masked the spatial heterogeneity that persists in the use of water outdoors, even between individual cities and properties (DeOreo et al., 2011; Mini et al., 2014), thus adding uncertainty to OWU-PO_4-P flux estimates. Future work should aim to utilise more localised $f_{leakage}$ and f_{owu} values, as well as to incorporate seasonality in both leakage (Folkman, 2018; Healey et al., 2021) and outdoor water use rates (Opalinski et al., 2020), in order to enhance the accuracy of WML-PO_4-P and OWU-PO_4-P estimates.

Whilst it was assumed that PO_4 would only be present within publicly supplied water if added for corrosion control purposes, low PO_4 concentrations are also found within non-dosed water. This may be associated with both natural processes and other human activities, for example resulting in median concentrations of non-dosed groundwater used for US public supply reaching 0.033 mg PO_4-P L^{-1} (Hem, 1985; Kent et al., 2020). With ubiquitous watermains leakage and outdoor water use across all water systems (USEPA, 2017), low level WML-PO_4-P and OWU-PO_4-P fluxes will occur even in the absence of dosing, and are likely to have resulted in marginally conservative WML-PO_4-P and OWU-PO_4-P flux estimates. As a result of these data limitations, hotspots of WML-PO_4-P and OWU-PO_4-P fluxes are largely determined by differences in public supply withdrawals and domestic water deliveries, respectively (Appendix 13b and c). Higher county-level WML-PO_4-P fluxes, particularly across Midwestern and Eastern regions (Figure 4.3b), not only reflect the higher proportion of PO_4 dosing in these areas (see Section 4.4.1), but also larger $WD_{pws\text{-}total}$ and $f_{leakage}$ values in these areas (Appendix 12 and 13). For example, densely populated urban areas, such as the cities of New York, Chicago and Philadelphia, are underlain by dense networks of watermain pipes (Bonneau et al., 2017). These networks are capable of supplying higher volumetric rates of water for public supply, as reflected in county-level water use estimates made by Dieter et al. (2018a) (Appendix 13b and c).

Once WML-PO_4-P and OWU-PO_4-P fluxes had been accounted for, the national-scale DOSE-PO_4-P_{wwtp} estimate presented here (9.3 kt PO_4-P yr^{-1}) was in broad agreement with the 6 kt PO_4-P yr^{-1} reported by the USEPA (2020a), thereby supporting the robustness of the method developed in this research. This annual DOSE-PO_4-P_{wwtp} flux is equivalent to approximately 2.7% of the total inflow P load to municipal WWTPs estimated by Hallas et al. (2019), and is relatively low when compared to other major contributors, such as human excreta and detergents (Vaccari, 2011). In proportional terms, this is below the 6% estimated for WWTPs in England (Comber et al., 2013). This likely reflects the lower prevalence of PO_4 dosing across the US compared to the UK, with around 95% of water supplies in the UK dosed (CIWEM, 2011;

Environment Agency, 2019) compared to the 25% estimated across the US. The non-ubiquitous nature of dosing across the US means that in the 84% of counties where dosing is undertaken, PO_4 dosed water may represent a larger proportion of the P loads entering their constituent WWTPs than suggested by the national-scale figure (Rodgers, 2014). Assessing the proportional contribution that DOSE-PO_4-P_{wwtp} fluxes make to individual WWTP influent P loads is beyond the scope of this study, although is an important area for future research. Leaking and overflowing sewage infrastructure and septic tanks are commonplace across the US (ASCE, 2017) and can be major sources of nutrients to catchments across the country (Delesantro et al., 2022; Iverson et al., 2018). Omitting losses of drinking water derived PO_4 from sewage infrastructure due to these processes (equation 4.9) may have led to overestimation of DOSE-PO_4-P_{wwtp} values. Improved understanding and quantification of P losses from sewage infrastructure should therefore be a future research priority.

The localised significance of WML-PO_4-P and OWU-PO_4-P fluxes highlights that these fluxes should be included within WWTP mass balances that aim to quantify P loads and financial impacts associated with PO_4 dosing practices (The Cadmus Group Inc., 2004). A nation-wide analysis of these loads to individual WWTPs is imperative, as P treatment is estimated to cost WWTPs around $2.08 per kg of P incrementally added upstream at drinking water treatment plants prior to distribution (USEPA, 2020a). Further, these mass balances would also reveal the extent to which P dosing ultimately contributes to the release of P into the environment from WWTPs.

4.4.3 Significance and Potential Environmental Impacts of Watermains Leakage and Outdoor Water Use Phosphate Fluxes

WML-PO_4-P and OWU-PO_4-P fluxes represent not only a loss of water and P from distribution networks, but also an additional source of P to the environment. Unlike the fluxes of nitrate associated with watermains leakage, where leakage acts to return nitrate that was previously retained via public supply water withdrawals (Flint et al., 2022), WML-PO_4-P fluxes represent a new source of P to the local environment. On a national level, WML-PO_4-P and OWU-PO_4-P fluxes

were small when compared to other major P inputs (Table 4.3). The inclusion of these fluxes within national-level US P source apportionment studies, as they have been in the UK (Environment Agency, 2019; Gooddy et al., 2017), could support more informed P source management strategies (Sabo et al., 2021b; Smith et al., 2019). More importantly, the exceedance of county-level WML-PO_4-P and OWU-PO_4-P fluxes over other major P sources (Figure 4.4) supports calls for more localised nutrient management approaches, that consider these WML-PO_4-P and OWU-PO_4-P fluxes when developing best management practices for individual watersheds (Frei et al., 2021; Hejna and Cutright, 2021; Mooney et al., 2020; Smith et al., 2019). Climate change and an increasing population are growing threats to the quality and availability of drinking water across the US (Brown et al., 2019b) and concerns surrounding watermains leakage and outdoor water as unsustainable uses of water and energy are rising globally (Chini and Stillwell, 2018; Gober et al., 2016; Jarvie et al., 2015; Xu et al., 2014). Watermains leakage reduction and more conservative outdoor water use are established tools for more sustainable water management (Mini et al., 2014; Rupiper et al., 2022). The WML-PO_4-P and OWU-PO_4-P fluxes reported in this work now highlight the need to integrate P and water resource management strategies (Metson et al., 2012).

Although the fate of leakages from watermains is largely unknown (D'Aniello et al., 2021), most leakages are not major burst events that are visible from the surface, but instead occur into the subsurface and go relatively undetected (Rupiper et al., 2022). It is therefore hypothesised that WML-PO_4-P fluxes will largely be released into the shallow sub-surface alongside watermains leakage nitrate fluxes (Flint et al., 2022) and leaking sewage mains (Howard and Gerber, 2018; Lee et al., 2015; Pennino et al., 2016; Sercu et al., 2011). Once released, these fluxes may be transported through the vadose zone and within groundwater flow to surface water environments via base flow (Fillo et al., 2021), potentially contributing to elevated concentrations of P in surface waters (Howard and Gerber, 2018). The fate of WML-PO_4-P fluxes will depend on local watershed hydrology and a range of widely varying environmental conditions. For example, soils rich in calcium carbonate, clays and metal oxides are more likely than sandy soils to reduce the movement of PO_4 due to adsorption (Domagalski and Johnson, 2012; Smith et al., 2019). This

temporary retention of leakage derived PO_4 may then contribute to legacy P that may be released in the future, thus hampering the water quality response time of future of P management practices (Sharpley et al., 2013). Pipe infrastructure can also alter hydrology, such as through the creation of sub-surface fractures, meaning that urbanisation may not only influence the magnitude of WML-PO_4-P and OWU-PO_4-P fluxes (Figure 4.5), but also enhance the transport and alter the fate of these fluxes within the shallow sub-surface (Bonneau et al., 2017; Howard and Gerber, 2018; Kaushal and Belt, 2012). Around half of water used outdoors across the US is for lawn irrigation. Inefficient watering practices across the country means that a proportion of this water will leach into the sub-surface or be lost via runoff (USEPA, 2017). Quantifying the amount of drinking water derived PO_4 that is being applied to lawns will allow for the extent to which this P already contributed to fertilization requirements to be determined, and thus help to address the unsustainable use of P-based fertilizers across many urban watersheds (Hobbie et al., 2017).

The PWS responsible for DOSE-PO_4-P_{pws}, WML-PO_4-P and OWU-PO_4-P fluxes, and the downstream WWTPs and agencies responsible for P management, may extend beyond county, watershed and country boundaries. For this reason, understanding the fate of both OWU-PO_4-P and WML-PO_4-P fluxes and the potential for these fluxes to modify DOSE-PO_4-P_{wwtp} fluxes and contribute to elevated P concentrations within freshwater environments, remains an important area of future research. The characterisation of the stable oxygen isotope composition of PO_4 dosed public supply water may provide an important framework and isotopic label through which to explore the fate of these fluxes (Davies et al., 2014; Gooddy et al., 2015). The transferrable methodology developed in this research could help to quantify fluxes of PO_4 associated with leakage and outdoor water use in other locations that use PO_4 based corrosion inhibitors. Minimising OWU-PO_4-P and WML-PO_4-P fluxes is important for reducing the reliance of water and wastewater industries upon sparse and finite P rock reserves. Additionally, reducing these fluxes will increase DOSE-PO_4-P_{wwtp} fluxes and thus enhance potential for more sustainable P recovery and recycling processes at WWTPs (Haque, 2021).

4.5 Conclusions

This work estimates that PO_4 dosing of publicly supplied water for corrosion control purposes across the US added 4-14.9 kt PO_4-P yr^{-1} into the water distribution network in the year 2015. Watermains leakage and outdoor water use across the US were estimated to result in 5-17% and 5-21% of this added PO_4 (0.7-2.6 and 0.8-3.1 kt PO_4-P yr^{-1}) being lost or actively removed from the water distribution network, respectively. These estimates suggest that up to 9.3 kt PO_4-P yr^{-1} of the PO_4 initially added was returned to wastewater treatment plants, representing around 2.7% of the national wastewater treatment plant influent P load estimated for the US. This work demonstrates that county-level PO_4 dosing, watermains leakage and outdoor water use PO_4 fluxes are heterogenous across the US. The greater prevalence of PO_4 dosing across urbanised counties in Midwestern and Eastern regions of the country likely reflects the presence of legacy lead piping in these areas. When combined, regions with the largest area-normalised watermains leakage and outdoor water use PO_4 fluxes were also found across these same regions. This reflects not only the occurrence of PO_4 dosing, but also larger volumes of water required to supply more dense populations in these areas. Estimates reported in this work represent an initial assessment of the significance of dosing-derived PO_4 fluxes in the context of existing US P budgets, with lower and upper estimates of combined watermains leakage and outdoor water use PO_4 fluxes exceeding P loads to surface waterbodies from point sources across 461-541 counties. Future work should use the methodology developed in this research with utility specific data, as a way of more accurately estimating these fluxes. The significance of these fluxes in the context of other major anthropogenic P inputs encourages their inclusion within P source apportionment studies and could help develop more effective P management strategies, particularly within urban areas, both across the US and around the world.

4.6 Acknowledgements

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5. Anthropogenic Water Withdrawals Modify Freshwater Carbon Fluxes Across the United States

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Author contributions are as follows:

Flint conceptualised the research questions and developed the methodology used for data analysis. Flint acquired and analysed data disclosing dissolved inorganic carbon concentrations, freshwater withdrawal rates and the processes associated with estimating net DIC fluxes. Flint undertook modelling of additional freshwater DIC concentrations using the THINCARB model, developed figures and wrote and revised the manuscript. Co-authors Ascott provided support in developing the methodology through the suggestion to use the THINCARB model. Co-authors Ascott, Gooddy, Surridge and Stahl have signed below to confirm that they provided general support for development of conclusions during project meetings and provided several rounds of feedback on manuscript drafts.

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5.1 Introduction

Fresh waters are critical, reactive interfaces that influence the transport and fate of carbon (C) (Cole et al., 2007). 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 (Aufdenkampe et al., 2011; Butman et al., 2016; Cole et al., 2007). 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 (Cole et al., 2007; Li et al., 2017; Mendonça et al., 2017; Raymond et al., 2013; Zhang and Planavsky, 2019) and continental scales (Butman et al., 2016; Clow et al., 2015; Zhang et al., 2022). However, despite growing recognition of fresh waters as critical interfaces that moderate the global C cycle (Tranvik et al., 2018), 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 (Regnier et al., 2013). Whilst some research has focused on developing a more integrated understanding of freshwater C cycling (Vachon et al., 2021), the continued omission of these anthropogenic influences within C budgets can lead to biased estimation and associated uncertainty of other C budget components (Butman et al., 2018; Chaplot and Mutema, 2021; Regnier et al., 2013; Regnier et al., 2022; Zhang and Planavsky, 2019). 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 (Regnier et al., 2022).

Freshwater withdrawals are defined by the USGS as “the total amount of water removed from the water source for a particular use” (Dieter et al., 2018b), with these sources being most commonly either a groundwater or surface water intake. Recent research has identified the anthropogenic withdrawal of fresh water as a potentially significant mechanism perturbing freshwater C cycling. Globally, withdrawals of groundwater were estimated to bring 19 Tg C yr^{-1}

to surface water environments (Downing and Striegl, 2018), 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 (Huo et al., 2022; McCarthy et al., 2020; Mishra et al., 2018; Wood and Hyndman, 2017) and the treatment of organic C within withdrawn fresh water prior to distribution (Finlay et al., 2016) are identified as sources of atmospheric CO_2 around the world. Reservoir drawdown areas, that are hotpots for emissions of CO_2 to the atmosphere, can also be created in part due to anthropogenic water withdrawal (Keller et al., 2021). Freshwater withdrawals have also been found to prevent the downstream export of organic C to the oceans by rivers (Finlay et al., 2016; You et al., 2023). 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 (Steffen et al., 2015). Addressing this gap in understanding is therefore increasingly urgent and the focus of the research reported here.

Fluxes of total dissolved C from US fresh waters to the ocean are predominantly in the form of DIC (Stets and Striegl, 2012) and the country has some of the highest DIC exports to the ocean of anywhere globally (Chaplot and Mutema, 2021; Li et al., 2017). The US also has some of the highest total and per capita withdrawals of fresh water in the world (FAO, 2024). The removal of this water from both groundwaters and surface water environments has been identified as an important inorganic nitrogen retention mechanism (Flint et al., 2022) and a nationally significant CO_2 emissions source (Wood and Hyndman, 2017). In the research reported here, the US is used as an exemplar to develop and apply a new framework that serves to quantify the impacts of both groundwater and surface withdrawals on freshwater DIC fluxes. It was hypothesised that:

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

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

5.2 Methods

5.2.1 Estimating the Gross Impact of Withdrawals of Fresh Water on the Lateral Export of Dissolved Inorganic Carbon

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, sourced from Dieter et al. (2018a), and median county-level groundwater and surface water DIC concentrations (DIC_{gw} and DIC_{sw}, in Tg C L^{-1}, see equations 5.1 and 5.2). Median fresh groundwater and surface water DIC concentrations were adopted in flux calculations due to the skewed (non-normal) distribution of DIC concentration data (Appendix 16).

$$WD\text{-}DIC_{gw} = WD_{gw} \times DIC_{gw} \quad (5.1)$$

$$WD\text{-}DIC_{sw} = WD_{sw} \times DIC_{sw} \quad (5.2)$$

The workflow developed in this research for obtaining DIC_{gw} and DIC_{sw} concentrations is outlined in Figure 5.1. Measured DIC concentrations generally carry less uncertainty than calculated DIC concentrations, predominantly due to the sensitivity of calculations to the accuracy of a measured pH value. Although the use of directly measured freshwater DIC concentrations is therefore preferable, concentrations of DIC within fresh waters are infrequently measured during water quality monitoring. To increase data capture, water quality parameter queries were extended to be between 01.01.2010 and 31.12.2020. Data retrievals from the Water Quality Portal (WQP, 2023) returned no measured DIC data for groundwater sites and measured surface water DIC data for only 79 counties (Figure 5.1). Given this lack of measured DIC concentration

data, THINCARB (Thermodynamic modelling of Inorganic CARBon) was used to model DIC_{gw} and DIC_{sw} concentrations (Jarvie et al., 2017). The THINCARB model builds upon thermodynamic equations developed by Neal et al. (1998). It uses commonly measured freshwater quality parameters (pH, alkalinity, temperature and altitude) to estimate DIC concentration, speciation and excess partial pressures of carbon dioxide in freshwaters. Model inputs were queried using the advanced search tool within the Water Quality Portal (WQP, 2023). More specifically, alkalinity (from filtered samples), pH, water temperature, altitude, and calcium concentrations from groundwater (well) or surface water (stream, lake, reservoir or impoundment) sites were queried as characteristics using parameter codes detailed in Table 5.1. This facilitated the return of values from both EPA and USGS databases, as well as state, federal, tribal and local agencies. This enabled the modelling of DIC_{gw} and DIC_{sw} concentrations across 1,024 and 584 counties, respectively (Figure 5.1). Where possible, modelled DIC_{sw} concentrations were validated against measured DIC_{sw} concentrations that had been determined during the same sampling activity (n = 2,961), with this approach concurrent with other literature (Jarvie et al., 2017). The agreement between modelled and measured DIC_{sw} values was strong ($\rho = 0.98$), with a regression slope close to one (Figure 5.2). Although there is likely to be some degree of bias in the selection of locations for water quality testing across the United States, the use of each of these methods produced a DIC concentration dataset with sites distributed across varying land uses and geologies (Figure 5.3).

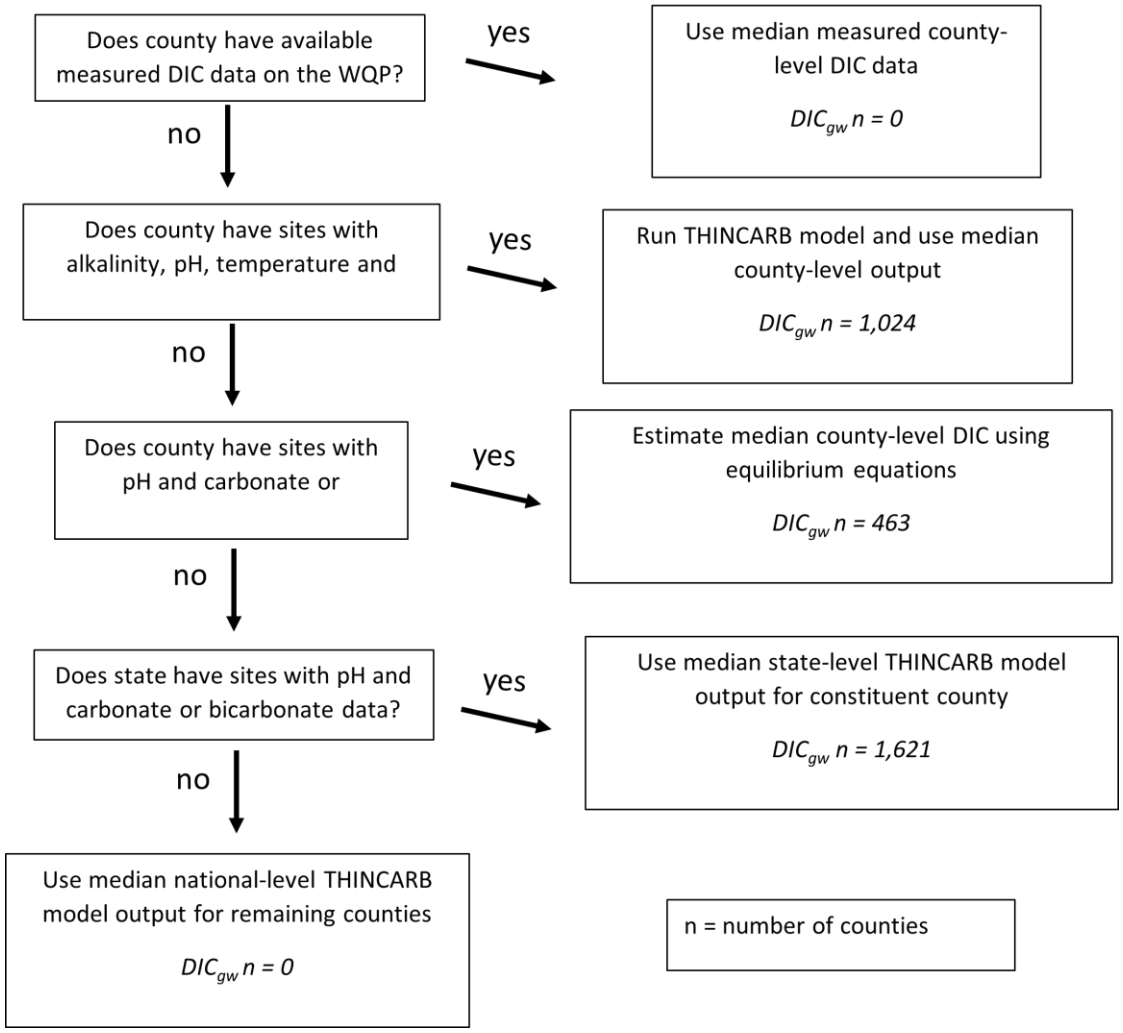

Figure 5.1. Schematic outlining the methodology used to determine county-level freshwater dissolved inorganic carbon concentrations across the United States. Dissolved inorganic carbon (DIC) concentrations are seldom measured and reported on the Water Quality Portal (WQP). To expand the DIC concentration dataset, this research made use of thermodynamic inorganic carbon modelling (THINCARB) and equilibrium equation to estimate additional DIC concentrations. The number of counties (n) that made use of each method to obtain groundwater and surface water DIC concentrations (DIC_{gw} and DIC_{sw}) are detailed in Figure 5.1.

Table 5.1. Table of parameter codes used to obtain parameter inputs for subsequent use in DIC THINCARB modelling and equilibrium calculations. The percentage of returned water quality measurements that have been accepted and percentage of pH values measured in-situ that were used within the analysis are also detailed.

Parameter	Parameter Code	% of Values Accepted	% pH Values Measured in Field
Groundwater (Wells)			
Equilibrium Calculations			
pH	00400, 00403, 00408	-	53
Carbonate and bicarbonate	00452, 29807, 29808, 29809, 63788, 00453, 29804, 29805, 29806, 63786	90	-
THINCARB			
pH	00400, 00403, 00408	-	67
Calcium	00915, 91051	-	-
Alkalinity	00418, 00421, 29801, 29802, 39036, 39086, 39087	74	-
Surface Water (Streams, Lakes, Reservoirs and Impoundments)			
Measured DIC			
DIC	00691	86	-
Equilibrium Calculations			
pH	00400, 00403, 00408	-	<1
Carbonate and bicarbonate	00452, 29807, 29808, 29809, 63788, 00453, 29804, 29805, 29806, 63786	99.9	-
THINCARB			
pH	00400, 00403, 00408	-	84
Calcium	00915, 91051	-	-
Alkalinity	00418, 00421, 29801, 29802, 39036, 39086, 39087	93	-

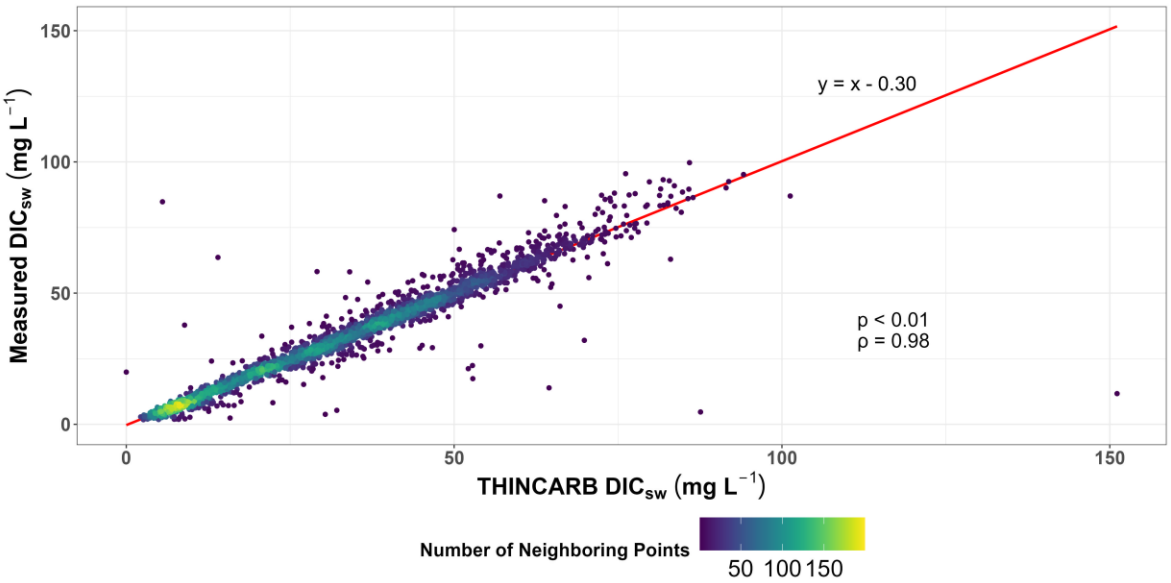

Figure 5.2. Measured surface water DIC concentrations (WQP, 2023) compared to those modelled using THINCARB. The regression line is shown in red, with a Spearman correlation coefficient (ρ) value of 0.98 and p-value < 0.01.

Field measured pH values within THINCARB modelling and DIC equilibrium equations were preferentially used (opposed to laboratory measured pH values), due to the potential for pH values to reduce between sample acquisition and laboratory analysis. This resulted in approximately 67% and 84% of groundwater and surface water pH values used within THINCARB model inputs were explicitly reported as being measured in the field, respectively (Table 5.1). Where a site had both reported field and laboratory pH values, the impact of using laboratory pH values upon DIC_{sw} and DIC_{gw} concentrations (opposed those measured in the field) was investigated. Using laboratory pH values, median DIC_{gw} and DIC_{sw} concentrations across the country were -7% and -1% of the DIC_{gw} and DIC_{sw} concentrations determined using field measured pH values, respectively, and therefore within reasonable uncertainty bounds (i.e. ±10%). With approximately 53% and <1% of groundwater and surface water pH values used within equilibrium calculations explicitly reported as being measured in the field, respectively, DIC_{gw} and DIC_{sw} concentrations using this method may also have been slightly underestimated.

The inherent quality of data from the Water Quality Portal used within this analysis has also been investigated. It was found that the majority of water quality data points used in this analysis have a final status of 'accepted', opposed to 'preliminary' (Table 5.1), suggesting that data used within this work has undergone quality assurance and quality control checks (e.g. acceptable ion balance), and is therefore of reliable and publishable quality. The status of alkalinity, carbonate and bicarbonate results used within this analysis is also shown in more detail within Table 5.1.

Where input data required for modelling DIC concentrations were not available, equilibrium equations (Appelo and Postma, 2005), 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 (Figure 5.1). Measured values of pH, CO_3^{2-} and HCO_3^- were queried using the Water Quality Portal's advanced search tool (WQP, 2023), with specific parameter codes detailed in Table 5.1. For the 1,621 and 2,223 counties without sufficient input data to model or calculate DIC_{gw} and DIC_{sw} values, respectively, median state-level DIC concentrations (derived from THINCARB modelling) were applied to the state's constituent county (Figure 5.1). 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 (Dieter et al., 2018a). The limitations associated with acquiring DIC concentration data using these various approaches are discussed in Section 5.4.1.

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 (Kulongoski and McMahon, 2019) and using 25th and 75th percentile DIC concentrations from equations 5.1 and 5.2 (Helsel et al., 2020). County-level fluxes were also expressed following normalisation for land area, in kg C km^{-2} yr^{-1}.

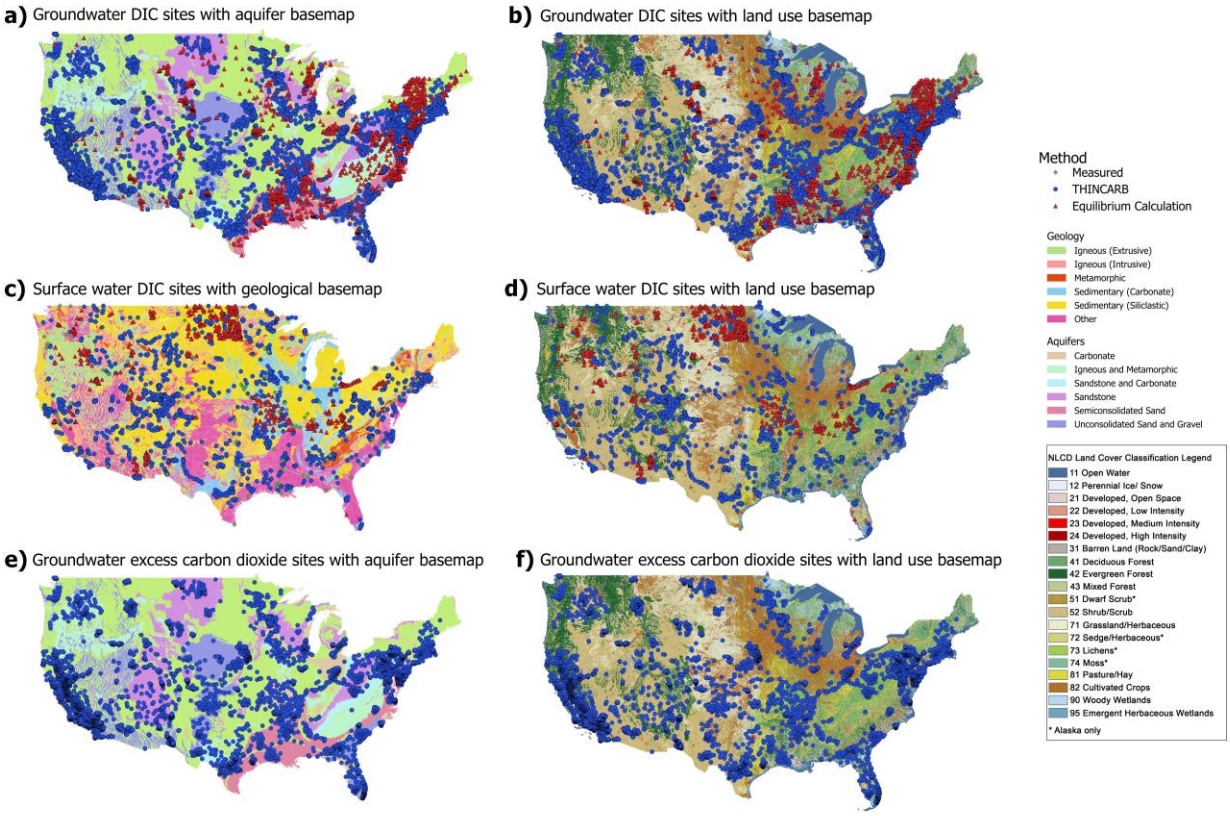

Figure 5.3. Maps showing the distribution of freshwater DIC and E[$CO_{2\ gw\text{-}atm}$] concentration data points estimated using different methods across the United States. Maps showing the distribution of sites where fresh groundwater DIC concentrations were estimated, in the context of a) principal aquifers (U.S. Geological Survey, 2003) and b) land uses (U.S. Geological Survey, 2024) across the United States. Maps showing the distribution of sites where fresh surface water DIC concentrations were estimated, in the context of c) geology (McCafferty, 2023) and d) land use (U.S. Geological Survey, 2024) across the United States. Maps showing the distribution of sites where fresh groundwater E[$CO_{2\ gw\text{-}atm}$] concentrations were estimated, in the context of e) principal aquifers (U.S. Geological Survey, 2003) and b) land uses (U.S. Geological Survey, 2024) across the United States.

5.2.2 Estimating the Net Impact of Withdrawals of Fresh Water on the Lateral Export of Dissolved Inorganic Carbon

Fully understanding the impact of freshwater withdrawals on C cycling requires the fate of withdrawn DIC to be determined. The research reported here attempts to estimate net withdrawal DIC fluxes through assessing the key processes that may affect the speciation and flux of DIC returned to fresh waters following withdrawal. These net fluxes can be defined as the flux of DIC that is permanently prevented from downstream transport on timescales relevant to 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 withdrawals but was then returned entirely to surface water after use via effluent discharge, this would result in a positive net WD-DIC_{gw} flux and a negative net WD-DIC_{sw} flux.

Table 5.2. Table detailing the sources of data and assumptions that were adopted to estimate net freshwater withdrawal dissolved inorganic carbon fluxes (WD-DIC). Note that no assumptions or data were available to estimate any process associated with net mining fluxes.

Assumption/Data	Value (unit)	Reference
Irrigation		
Off-farm withdrawals/leakage of conveyance infrastructure	40%/15%	Hrozencik et al. (2022)
Thermoelectric		
Consumptive use of water in recirculating/once-through plants	100%/0%	Dieter et al. (2018a); Lee et al. (2018)
Proportion of return flows to surface water	100%	Templin et al. (1980)
Public Supply and Domestic		
National average leakage rate	16%	USEPA (2013)
Outdoor water use	33%	USEPA (2017)
Proportion of centralised wastewater treatment plant return flows to surface water	95%	USEPA (2016a)
Industry		
Proportion of return flows to surface water	100%	McCarthy et al. (2022)
Livestock		
Consumptive use	100%	Marston et al. (2018), Döll et al. (2012)
Aquaculture		
Proportion of return flows to surface water	100%	Dieter et al. (2018b)
Average pond depth	2m	Boyd et al. (2008)
Total aquaculture pond surface area	5.74×10^8 m^2	USDA (2019)

The current lack of county-level and state-level data meant that several assumptions were adopted to estimate national-level net WD-DIC fluxes, with these assumptions summarised in Table 5.2. Previous work has assumed that once fresh water has been used (for all water use sectors, including irrigation) it will be returned to downstream surface water bodies (Caldwell et al., 2012; Duan et al., 2018), whilst other water balance studies have assumed all returns of water post irrigation to be to groundwater (de Graaf et al., 2014). Both assumptions represent an oversimplification. Instead, the impacts of freshwater withdrawals for irrigation upon surface water and groundwater interactions and surface-subsurface water budgets across the US are highly localised and depend on factors such as the presence of artificial drainage and efficiency of irrigation method (Döll et al., 2012; Leng et al., 2014). Determining the proportion of irrigation return flows via surface runoff and subsurface recharge has important implications for C cycling

and will require comprehensive, country-wide datasets reporting on irrigation efficiency and the impacts of irrigation on the water balance. Whilst this data is currently lacking, fluxes of DIC returned to groundwater due to leakages from irrigation canals have been estimated through adopting that assumption that 40% of freshwater withdrawals are done so away from the location of use and that 15% of this water is subsequently leaked from irrigation channels during conveyance (Hrozencik et al., 2022).

Similarly to how reservoirs and dams for public supply and irrigation can retain fresh waters (Yang et al., 2018a), the recirculation of water within recirculating thermoelectric cooling plants can retain both fresh water and associated DIC. The consumptive use of water within once-through and recirculating thermoelectric plants were assumed to be 0% and 100%, respectively (Lee et al., 2018). The proportion of total freshwater thermoelectric withdrawals that were used within recirculating plants across the US (Dieter et al., 2018a) was determined and applied to gross county-level thermoelectric WD-DIC_{gw} and WD-DIC_{sw} estimates. Return flows of water used for thermoelectric, industrial and aquaculture sectors were assumed to be exclusively to surface water environments (McCarthy et al., 2022; Templin et al., 1980).

It was hypothesised that the elevated temperatures of once-through cooling plant effluents may result in reduced CO_2 solubility and thus additional CO_2 degassing. To test this hypothesis, the THINCARB model was used to calculate the excess partial pressure of CO_2 ($EpCO_2$) within effluent waters of elevated temperatures. Median county-level thermoelectric plant effluent temperatures, for the year 2015, were calculated using data sourced from the USEPA's online 'Water Pollution Search' tool (USEPA, 2023a). These effluent temperatures were then assigned to any of that county's constituent surface water sites that had corresponding alkalinity, pH, altitude, and where possible calcium concentrations, sourced from the USGS Water Quality Portal (WQP, 2023) (see Section 5.2.1 for more information on the acquisition of these water quality determinants). This assumed that water used within once-through cooling plants was entirely sourced from surface water, based on the fact that over 99.9% of water withdrawals for once-

through cooling are from surface water (Dieter et al., 2018a). Model output $EpCO_2$ values were then used to determine excess CO_2 concentrations within effluents ($E[CO_2]_{eff}$) at each site (see Section 5.2.3). County-level CO_2 emissions from thermoelectric effluent degassing were then determined as the product of median county-level $E[CO_2]_{eff}$ values and county-level volumes of water returned after use within once-through cooling plants (Dieter et al., 2018a).

Most withdrawals of fresh water for aquaculture are used within flow-through aquaculture systems that return water directly to surface water environments with negligible consumption (Dieter et al., 2018b). In contrast, water used within aquaculture ponds was assumed to be consumptive (Gephart et al., 2017). The total volume of water stored in these ponds ($1.14x10^{12}$ L yr^{-1}) was estimated from known pond surface area and average depth across the US (area = $5.72x10^{8}$ m^2, depth = 2 m) (Boyd et al., 2008; USDA, 2019). The proportion of water therefore stored in ponds, in comparison to total freshwater aquaculture withdrawals ($9.83x10^{12}$ L yr^{-1}) (Dieter et al., 2018a), is 12%. Applying this proportion to total gross freshwater aquaculture $WD\text{-}DIC_{gw}$ and $WD\text{-}DIC_{sw}$ fluxes facilitated the estimation of net aquaculture withdrawal DIC fluxes.

After withdrawal, leakage and outdoor water use have been identified as mechanisms returning fresh water and associated dissolved constituents to the subsurface (Flint et al., 2022; Flint et al., 2023). Assuming a nationally averaged leakage rate of 16% (USEPA, 2013), an outdoor water use rate of 33% (USEPA, 2017) and that 95% of the remaining public supply and domestic $WD\text{-}DIC_{gw}$ and $WD\text{-}DIC_{sw}$ fluxes will be returned to wastewater treatment plants and subsequently be released into a surface water environment (USEPA, 2016a), return fluxes of DIC due to watermains leakage and outdoor water use have been estimated. It was assumed that 100% of water used for livestock was consumed (Döll et al., 2012; Marston et al., 2018). Processes such as flowback water and reinjection make determining the fate of freshwater withdrawals used for mining highly complex (Kondash et al., 2017; Veil, 2020). Data disclosing the proportion of mining

water that is stored or returned to surface water and groundwater environments, as well as any associated changes in DIC concentrations, are currently limited across the US.

5.2.3 Estimating Carbon Dioxide 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 ($E[CO_{2\ gw\text{-}atm}]$; equation 5.3). $E[CO_{2\ gw\text{-}atm}]$ concentrations were estimated using excess CO_2 partial pressures ($EpCO_2$) modelled by THINCARB using inputs described in Section 5.2.1. $EpCO_2$ is the ratio of the partial pressure of CO_2 in the groundwater sample ($pCO_{2\ gw}$) to the partial pressure of CO_2 in the atmosphere ($pCO_{2\ atm}$), which was assumed to be 0.0003994 atm for the year 2015 (equation 5.4).

$$WD\text{-}CO_{2\ gw} = WD_{gw} \times E[CO_{2\ gw\text{-}atm}] \tag{5.3}$$

$$EpCO_2 = \frac{pCO_{2\ gw}}{pCO_{2\ atm}} \tag{5.4}$$

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 (Deirmendjian et al., 2018; Macpherson, 2009), as well as the full equilibration of $pCO_{2\ gw}$ with $pCO_{2\ atm}$ (Cole et al., 2007). $EpCO_2$ values were subsequently used to determine $E[CO_{2\ gw\text{-}atm}]$ concentrations using equations 5.5-5.8. Use of the Van't Hoff equation allowed changes in temperature (T) to be related to changes in equilibrium constant (K_H; equation 5.5). $pCO_{2\ atm}$ values were then corrected using K_H to give the partial pressure of groundwater when in equilibrium with the atmosphere ($pCO_{2\ gw\text{-}atm}$; equation 5.6). $pCO_{2\ gw}$ was then estimated as the product of $EpCO_2$ and $pCO_{2\ gw\text{-}atm}$ (equation 5.7).

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 $pCO_{2\ gw\text{-}atm}$ (equation 5.8). Median state-level $E[CO_{2\ gw\text{-}atm}]$ concentrations were applied to the 2,084 counties without a modelled $EpCO_2$ value.

$$K_H = 0.034e^{-(2400\left(\frac{1}{289}\left(\frac{1}{273+T}\right)\right))} \quad (5.5)$$

$$pCO_{2\ gw\text{-}atm} = K_H \times pCO_{2\ atm} \quad (5.6)$$

$$pCO_{2\ gw} = EpCO_2 \times pCO_{2\ gw\text{-}atm} \quad (5.7)$$

$$E[CO_{2\ gw\text{-}atm}] = (pCO_{2\ gw} - pCO_{2\ gw\text{-}atm}) \times 1000 \times 44.01 \quad (5.8)$$

Where $EpCO_2$ is the excess CO_2 partial pressure of groundwater with respect to the atmosphere (expressed as a ratio), K_H is the equilibrium constant, T is the temperature of the water sample in degrees Celsius, sourced from the WQP (2023). $pCO_{2\ gw\text{-}atm}$ is the partial pressure of the groundwater sample when in equilibrium with the atmosphere, $pCO_{2\ atm}$ is the partial pressure of the atmosphere, $pCO_{2\ gw}$ is the partial pressure of the groundwater sample and $E[CO_{2\ gw\text{-}atm}]$ is the excess concentration of CO_2 in the groundwater sample, with respect to the atmosphere.

It is known that a lack of accurately reported field pH values may lead to underestimated $E[CO_{2\ gw\text{-}atm}]$ concentrations and thus WD-$CO_{2\ gw}$ fluxes (Macpherson, 2009). The impact of using laboratory pH values upon $E[CO_{2\ gw\text{-}atm}]$ concentrations (opposed those measured in the field) was investigated using data from sites with both reported field and laboratory pH values. The median difference between calculating $E[CO_{2\ gw\text{-}atm}]$ concentrations using lab versus field pH values was -70%. Despite this, the majority (67%) of groundwater pH values used within this analysis were measured in the field (in-situ).

The impact of assuming both groundwater's full equilibration with the atmosphere and rapid rate of CO_2 degassing upon WD-$CO_{2\ gw}$ fluxes was also investigated. This additional analysis assumed groundwater CO_2 would degas until it reached an equivalent CO_2 supersaturation level of fresh surface water. County-level emissions of CO_2 due to the degassing of CO_2 supersaturated groundwater withdrawals until reaching equilibrium with surface waters (WD-$CO_{2\ gw\text{-}sw}$, 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 surface water ($E[CO_{2\ gw\text{-}sw}]$; equation 5.9). County-level $E[CO_{2\ gw\text{-}sw}]$ concentrations, in mg CO_2 L^{-1}, were determined as the difference between $CO_{2\ gw}$ concentrations and median state-level surface water CO_2 concentrations ($CO_{2\ sw}$) (Toavs et al., 2023) (equation 5.10). $CO_{2\ gw}$ values were estimated using $pCO_{2\ [gw]}$ values (equation 5.11 and 5.7). Median state-level $E[CO_{2\ gw\text{-}sw}]$ concentrations were assigned to any constituent counties without a county-level concentration (n = 2,084 counties). The national-level $WD\text{-}CO_{2\ gw\text{-}sw}$ emission was determined through the summation of county-level estimates.

$$WD\text{-}CO_{2\ gw\text{-}sw} = WD_{gw} \times E[CO_{2\ gw\text{-}sw}] \quad (5.9)$$

$$E[CO_{2\ gw\text{-}sw}] = CO_{2\ gw} - CO_{2\ sw} \quad (5.10)$$

$$CO_{2\ [gw]} = pCO_{2\ [gw]} \times 1000 \times 44.01 \quad (5.11)$$

5.2.4 Contextualising the Magnitude of Gross Freshwater Withdrawal Dissolved Inorganic Carbon Fluxes and Groundwater Withdrawal Carbon Dioxide Emissions

The magnitude of the gross national-level $WD\text{-}DIC_{sw}$ flux was contextualised 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 (Butman et al., 2016). 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 5.1). The DIC_{SGD} flux (0.7 Tg C yr^{-1}) was estimated as the product of the annual US fresh subterranean groundwater discharge volume ($1.5x10^{13}$ L yr^{-1}) (Sawyer et al., 2016), 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-$CO_{2\,gw}$ flux was evaluated through comparison with the estimated CO_2 emissions from rivers and lakes across the US (Butman et al., 2016). WD-$CO_{2\,gw}$ 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 (USEPA, 2023c), electricity generation both for pumping groundwater for irrigation (Driscoll et al., 2024) and for the operation of drinking water systems (Zib et al., 2021). Counties with significant WD-$CO_{2\,gw}$ emissions were identified through the comparison of county-level WD-$CO_{2\,gw}$ estimates to the county's total CO_2 emissions from major sources (USEPA, 2023b), specifically, those sources obliged to report to the US Environmental Protection Agency's (USEPA) Greenhouse Gas Reporting Program (GHGRP-CO_2). These detailed emissions data are collected from approximately 7,300 greenhouse gas emitting facilities across the US that emit over 25,000 t CO_2 yr^{-1}, either via combustion or process emissions. When combined, these emissions account for around 50% of total US greenhouse gas emissions (USEPA, 2023d).

5.3 Results

5.3.1 Gross Dissolved Inorganic 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 – 31.12.2020 were modelled (using THINCARB) to be 48.2 and 29.7 mg C L^{-1}, respectively. 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 5.3), with values in parentheses representing lower and upper estimates (see Section 5.2.1). Irrigation and public supply withdrawals contribute 92% of the total national-level WD-DIC_{gw} flux, and irrigation and thermoelectric withdrawals contribute 81% of the total national-level WD-DIC_{sw} flux (Figure 5.4a). Counties with largest area-normalised WD-DIC_{gw} and WD-DIC_{sw} fluxes were concentrated within the states of Nebraska (NE), Florida (FL) and California (CA; Figure 5.4b), and Montana (MT) and Wyoming (WY; Figure 5.4c), 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 5.4d, with the irrigation

and public supply sectors being the largest contributors to counties across 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 5.3). 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 5.3). 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 5.3).

Table 5.3. Gross freshwater withdrawal dissolved inorganic carbon fluxes for groundwater and surface water (WD-DIC_{gw} and WD-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 DIC export 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-DIC_{sw} (6.7-9.9)	7.9-11.6	23.1-34.1	5.9-8.7	-	-
WD-DIC_{gw} (5.3-8.8)	-	-	-	757-1,257	-
WD-DIC_{total} (12.0-18.7)					40.4-63.0

[a] Butman et al. (2016)

[b] Estimated using the total subterranean groundwater discharge estimate made by Sawyer et al. (2016) and the median DIC concentration of groundwater determined in this study (48.2 mg C L^{-1})

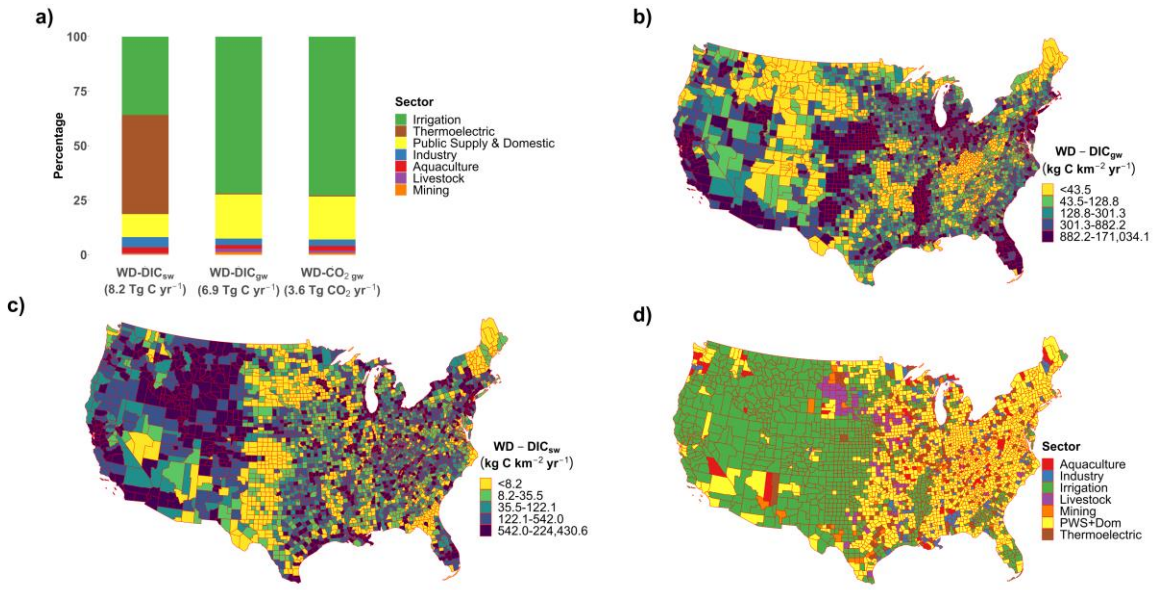

Figure 5.4. a) Contribution of water use sector withdrawals to gross national-level surface water and groundwater withdrawal DIC fluxes (WD-DIC$_{sw}$ and WD-DIC$_{gw}$), and the national-level emissions of CO_2 due to degassing groundwater withdrawals (WD-$CO_{2\ gw}$) across the United States. b) Total area-normalised county-level groundwater withdrawal DIC fluxes (WD-DIC$_{gw}$) across the United States. c) Total area-normalised county-level surface water withdrawal DIC fluxes (WD-DIC$_{sw}$) across the United States. Scales represent quintile groups. d) The water use sector that makes the largest contribution to the gross total withdrawal DIC flux (WD-DIC$_{total}$) for each county across the United States. Linework created using the 'usmap' package in R (Di Lorenzo, 2022).

5.3.2 Net Dissolved Inorganic Carbon Fluxes Associated with Withdrawals of Fresh Water

The net national-level WD-DIC fluxes that could be estimated in this thesis are summarised in Figure 5.5. It was estimated that 0.18 Tg C yr^{-1} and 0.30 Tg C yr^{-1} of the irrigation $WD\text{-}DIC_{sw}$ and $WD\text{-}DIC_{gw}$ flux 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 5.4.2). Thermoelectric plants utilising water recirculating technologies result in net $WD\text{-}DIC_{gw}$ and $WD\text{-}DIC_{sw}$ 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 $WD\text{-}DIC_{gw}$ and $WD\text{-}DIC_{sw}$ 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 CO_2 yr^{-1}.

The return of $WD\text{-}DIC_{sw}$ to groundwater due to leakage from public supply distribution pipes and outdoor water use at domestic residences resulted in a net public supply $WD\text{-}DIC_{sw}$ flux of 0.43 Tg C yr^{-1}. Approximately 95% of the remaining public supply and domestic $WD\text{-}DIC_{gw}$ and $WD\text{-}DIC_{sw}$ fluxes will be returned to wastewater treatment plants and subsequently be released into a surface water environment (USEPA, 2016a), resulting in a combined net public supply and domestic $WD\text{-}DIC_{gw}$ 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 $WD\text{-}DIC_{gw}$ flux of 0.21 Tg C yr^{-1}. The consumption of water for livestock results in net $WD\text{-}DIC_{sw}$ and $WD\text{-}DIC_{gw}$ fluxes of 0.033 Tg C yr^{-1} and 0.11 Tg C yr^{-1}, respectively. The storage of fresh water within aquaculture ponds was estimated to temporarily retain 0.010 Tg C yr^{-1} and 0.025 Tg C yr^{-1} from groundwaters 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 $WD\text{-}DIC_{gw}$ flux of 0.11 Tg C yr^{-1} (Figure 5.5).

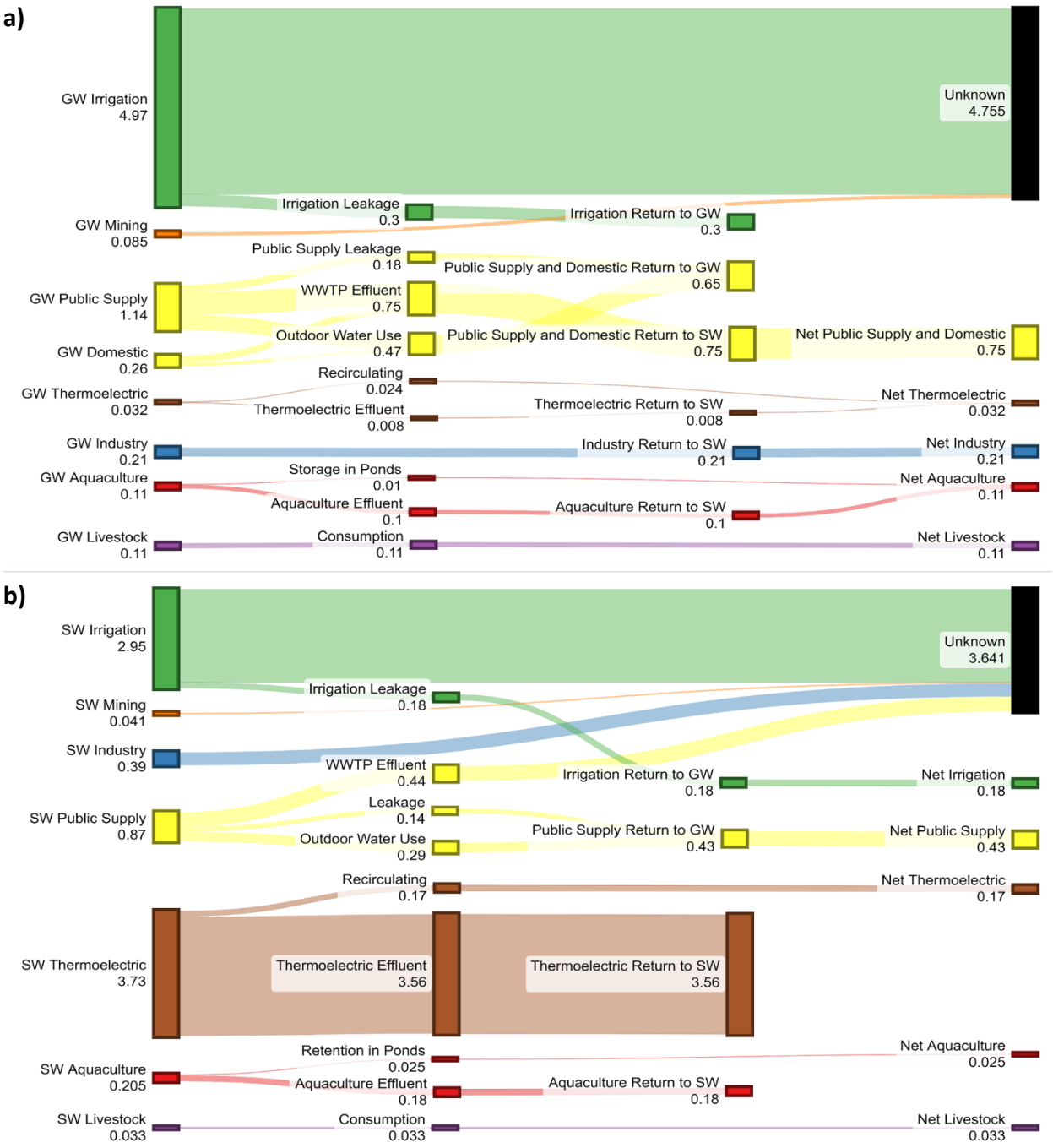

Figure 5.5. a) Sankey diagram showing median gross and net freshwater withdrawal DIC fluxes for each major water use sector across the United States due to groundwater withdrawals. b) Sankey diagram showing median gross and net freshwater withdrawal DIC fluxes for each major water use sector across the United States due to surface water withdrawals.

5.3.3 Impact of Degassing Fresh Groundwater Withdrawals on Carbon Dioxide 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 CO_2 L^{-1}. The national-level emission of CO_2 due to the degassing of CO_2 supersaturated groundwater withdrawals ($WD\text{-}CO_{2\ gw}$) across the US was estimated to be 3.6 (2.2-5.5) Tg CO_2 yr^{-1} (Table 5.4), with irrigation and public supply withdrawals contributing 93% of this total (Figure 5.4a). Counties with the largest area-normalised $WD\text{-}CO_{2\ gw}$ fluxes were generally concentrated within the states of Nebraska (NE) and North Carolina (NC; Figure 5.6a).

The national-level $WD\text{-}CO_{2\ gw}$ flux (2.5-5.5 Tg CO_2 yr^{-1}) was estimated to be equivalent to between 0.7-1.8% 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 USEPA's Greenhouse Gas Reporting Program ($GHGRP\text{-}CO_2$; Table 5.4). The national-level $WD\text{-}CO_{2\ gw}$ 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 14.9-36.4% of the CO_2 emissions associated with electricity generation for pumping groundwater for irrigation use. The national-level $WD\text{-}CO_{2\ gw}$ flux due to public supply and self-supplied domestic withdrawals (0.5-1.1 Tg CO_2 yr^{-1}) was equivalent to between 1.8-4.1% of the CO_2 emissions associated with electricity generation for the operation of US drinking water systems (Table 5.4). Approximately 45% of all US counties (1,401) were estimated to have median $WD\text{-}CO_{2\ gw}$ fluxes that exceeded county-level $GHGRP\text{-}CO_2$ emissions, with these counties concentrated in the states of Montana, South Dakota (SD), Nebraska and Idaho (Figure 5.6b).

Table 5.4. National-level carbon dioxide (CO_2) emissions associated with the degassing of withdrawn groundwaters (WD-$CO_{2\ gw}$), expressed as a percentage, when 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) (2,640) [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						
WD-$CO_{2\ gw}$ (2.2-5.5)	0.7-1.8	0.08-0.2	-			-
Irrigation						
WD-$CO_{2\ gw}$ (1.6-3.9)			42.1-102.6	14.9-36.4	112-273	
Public Supply & Domestic						
WD-$CO_{2\ gw}$ (0.5-1.1)						1.8-4.1

[a] Butman et al. (2016)
[b] USEPA (2023b)
[c] USEPA (2023c)
[d] Driscoll et al. (2024)
[e] Qin et al. (2024)
[f] Zib et al. (2021)

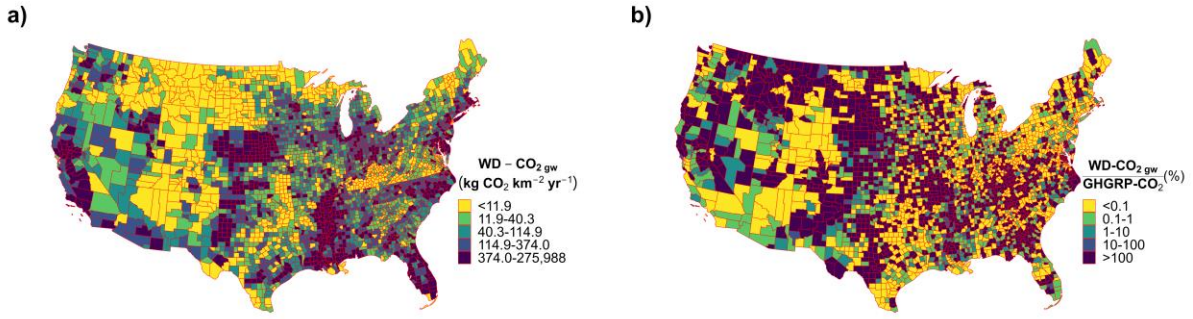

Figure 5.6. a) Total area-normalised emissions of carbon dioxide due to groundwater withdrawals (WD-$CO_{2\ gw}$) for each county across the United States. b) The percentage equivalence of carbon dioxide emissions due to degassing groundwater withdrawals (WD-$CO_{2\ gw}$), to the carbon dioxide emissions from the facilities required to report to the Greenhouse Gas Reporting Program (GHGRP-CO_2), for each county across the United States. GHGRP-CO_2 data was sourced from the USEPA (2023b). Linework created using the 'usmap' package in R (Di Lorenzo, 2022).

Assuming equilibrium between groundwater and surface water (Section 5.2.3) resulted in a national-level WD-$CO_{2\ gw}$ emission of 3.3 Tg CO_2 yr^{-1}, which is 8% lower than the initial estimate made using the assumption of full equilibrium with the atmosphere (3.6 Tg CO_2 yr^{-1}). Whilst neither of the methodologies presented in this work can utilise data that capture the complexity of localised conditions controlling CO_2 degassing from groundwater (such as turbulent mixing), the similarity of the national-level WD-$CO_{2\ gw}$ emissions flux (i.e. within 10% of each other) suggests that this methodology is robust and provides a good opportunity to begin estimating the sub-national scale patterns in this emissions source.

5.4 Discussion

5.4.1 Anthropogenic Withdrawals of Fresh Water Perturb the Lateral Transport of Dissolved Inorganic Carbon

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 withdrawals may cause important perturbations to overall national-level DIC cycling (Table 5.3). Carbon budgets are often determined using a mass balance approach. These findings therefore emphasise the importance of incorporating WD-DIC fluxes into national-scale C cycling budgets as a way of more accurately determining other budget components (Butman et al., 2018; Butman et al., 2016; Regnier et al., 2013; Regnier et al., 2022). Uncertainties associated with gross WD-DIC fluxes, largely due to the scarcity of measured DIC concentration data, should be reduced as more temporally and spatially resolved water use and DIC concentration data become available (Luukkonen, 2023).

The most recent release of water use data by the USGS discloses annual total water use for each defined major water use sector across each county of the United States (Dieter et al., 2018a). As

a result, annual freshwater withdrawal DIC fluxes were estimated, where possible, using annually averaged (median) county-level freshwater DIC concentration values. Due to limited availability of a county-level freshwater DIC concentration value, 1,621 and 2,233 counties had to adopt state-level median fresh groundwater and surface water DIC concentrations within flux calculations, respectively (Figure 5.1). Freshwater DIC concentrations are spatially heterogeneous (Stets et al., 2023). The state-level aggregation of DIC concentration data within county-level flux calculations will have therefore given rise to an increase in the uncertainty associated with flux estimates, as expressed by lower and upper estimates made using 25th and 75th percentile DIC concentrations. It should be noted that even the use of an annual median county-level DIC concentration neglects the inherent local and seasonal variability in freshwater DIC concentrations (Potter and Xu, 2022; Stets et al., 2023). Despite this, the use of a single state or county-level median DIC concentration provides an appropriate starting point for estimating these fluxes on a spatial scale as large as the contiguous United States.

5.4.2 Future Priorities for Estimating Gross Dissolved Inorganic Carbon Fluxes

Estimating freshwater withdrawal DIC fluxes with greater temporal (e.g. monthly) and spatial (e.g. for individual intakes and wells) resolution, initially focusing on WD-DIC flux hotspots identified in this work, will facilitate a more accurate assessment of freshwater withdrawal DIC fluxes. It would also provide more insight into heterogeneity of anthropogenic influences, natural controls and ecological impacts of these fluxes, which could feed into the development of more tailored and effective water management decisions. Increasing the spatial and temporal resolution of freshwater withdrawal DIC flux estimates should therefore be a future research priority, once required data becomes available. For example, data disclosing freshwater withdrawal volumes and DIC concentrations associated with individual US reservoirs are currently lacking, with reservoir withdrawals currently making an unknown contribution to surface water withdrawals (Dieter et al., 2018a). Reservoirs for water supply purposes are widespread across the US, with approximately 15% of US dams being constructed for municipal and irrigation water supply purposes (Song et al., 2018; Steyaert et al., 2022). Processes

controlling DIC concentrations within the lentic environment of a reservoir will often differ substantially from those within the wider lotic network of a river or stream (Tranvik et al., 2009). The physical, biological and chemical characteristics of individual reservoirs are also highly variable, which in turn may have a substantial influence on the DIC concentrations found within them (Li et al., 2024). Although contribution of withdrawals from individual reservoirs to overall US WD-DIC_{sw} fluxes and downstream DIC export is beyond the scope of this study, future research should focus on this area of work, when relevant data become available.

5.4.3 Sector Dependent Controls on Net Dissolved Inorganic Carbon Fluxes

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 their net WD-DIC flux counterparts. Comparing gross WD-DIC fluxes with other freshwater DIC retention fluxes therefore only serves to help assess the potential maximum magnitude and importance of WD-DIC fluxes in the broader context of freshwater DIC cycling, and to justify future determination of more accurate net WD-DIC fluxes.

The retention of DIC through the consumption and storage of water varies across the country and between different water use sectors (Marston et al., 2018). The storage and consumption of water within industrial water use sector is largely unknown and complex to estimate (McCall et al., 2021; McCarthy et al., 2022; Miranda and Sauer, 2010), contributing to unresolved net industry WD-DIC flux estimates. The consumption and storage of water within mining derived products and tailings is a major component of the mining sectors hydrological impact across the US. The amount of water consumed and stored at mining sites is localised and relevant data is scant (Northey et al., 2016), meaning the potential for deducing US-wide DIC retention through this process is currently limited. The capacity for recirculating thermoelectric plants to temporarily store DIC is small compared to other naturally freshwater DIC retention mechanisms

(Table 5.1), however this capacity may increase in the future given the predicted transition to recirculating technologies across the US (Peer and Sanders, 2018).

Return flows of withdrawn water can also redistribute water and associated DIC between groundwater and surface water environments (de Graaf et al., 2014; Voisin et al., 2017). The flowback and reinjection of produced water associated with mining activities will result in a complex and site-specific reapportioning of DIC between surface water and groundwater environments (Kondash et al., 2017; Veil, 2020). Industrial, thermoelectric, public supply and aquaculture sectors return both withdrawn groundwaters and surface waters almost exclusively to surface water environments via effluents, resulting in the net removal of DIC from groundwaters (Figure 5.5a). Conversely, the leakage of water from mains distribution pipes and the return of water during outdoor water use can return biologically important nutrients to subsurface environments (Flint et al., 2022; Flint et al., 2023), thus resulting in the net removal of DIC from surface waters (Figure 5.5b).

The use of water for irrigation and mining will also result in the complex and localised movement of water and associated DIC between groundwater, surface water and atmospheric environments (Caldwell et al., 2012; de Graaf et al., 2014; Haddeland et al., 2006; Leng et al., 2014; Veil, 2020). However, there are no comprehensive national-level datasets 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 modelled to decrease fresh surface water discharge to the ocean by 4.2% (Haddeland et al., 2006). 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 a 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 the irrigation WD-DIC_{sw} flux estimated here. Applying a proportional decrease to the reported river DIC export flux estimated by Butman et al. (2016) (29 Tg C yr^{-1}) 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 the gross WD-DIC_{sw} flux estimate presented in this work (2.95 Tg C yr^{-1}).

This research has also estimated the impact of increased thermoelectric plant effluent temperatures upon national-level CO_2 emissions. More localised assessments could be undertaken to reveal hotspots of these emissions, particularly across eastern regions of the country, where once-through technologies responsible for thermal pollution are more common (Chini et al., 2020). 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 (Raptis et al., 2016). The use of water for irrigation, public supply, industrial and mining sectors will also lead to changes in DIC speciation and concentration. For example, after freshwater irrigation, the precipitation of carbonate minerals within soils, CO_2 emissions and the utilisation of DIC for primary production, can act to decrease DIC concentrations and the amount of DIC that can be leached to groundwaters or transported via runoff to surface waters (Ortiz et al., 2022). Fresh water used for public supply and industry is also likely to undergo a vast range of chemical or physical processes that that may impact DIC speciation and retention, such as the deliberate adjustment of the pH of publicly supplied water (Arnold et al., 2019). Similarly, in-pipe processes such as the precipitation of carbonates within municipal and industrial water supply pipes may retain DIC and prevent it from being further transported downstream (Tang et al., 2021b; Tang et al., 2021a). However, data relating to these speciation and concentration changes remain spatially limited, 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 5.5a), and net WD-DIC_{sw} fluxes for irrigation, industrial, mining and public supply sectors remain unknown (Figure 5.5b). Research priorities and data needed to resolve these issues are highlighted in Section 5.4.4.

5.4.4 Future Priorities for Estimating Net Dissolved Inorganic Carbon Fluxes

Determining the proportion of irrigation return flows via surface runoff and subsurface infiltration has important implications for C cycling (You et al., 2023). Along with the physiochemical changes associated with this redistribution of water (Vachon et al., 2021), estimating net US irrigation WD-DIC fluxes is highly complex and beyond the scope of this thesis. With irrigation being the largest sector contributing to the gross national-level WD-DIC_{total} 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 datasets quantifying the impact of irrigation on the water balance, crop uptake of DIC and the extent of carbonate precipitation within soils, followed by the integration of results into overall DIC export models (Ren et al., 2015).

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, limits the ability to accurately determine a net WD-DIC_{sw} flux at this time (Figure 5.5b). It has been estimated that municipal WWTPs process around 6.06×10^{13} L wastewater yr^{-1} (Arabi et al., 2021). This volume exceeds the volume of water initially withdrawn for public supply and domestic uses and is likely due to processes including inflow of groundwater and precipitation into potable and wastewater distribution networks and inter-basin water transfers (McCarthy et al., 2022). WWTP effluents are returned to surface water environments with elevated DIC concentrations (Ator et al., 2022; Regnier et al., 2013) that can contribute to increased DIC exports and acidification downstream (Alshboul et al., 2016; Barnes and Raymond, 2009; Hossler and Bauer, 2013; Yang et al., 2018b). Assuming bicarbonate concentrations from US WWTP discharges are analogous to DIC concentrations (USEPA, 2023a), a median WWTP effluent DIC concentration of 48 mg C L^{-1} was estimated to result in a total WWTP effluent DIC flux of 2.9 Tg C yr^{-1}. The input of DIC via public supply return flows (WWTP effluent) therefore 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 estimate DIC retention within the water distribution system and the degree to which freshwater withdrawals can moderate the downstream export of potentially environmentally damaging DIC inputs from municipal wastewater effluents (Yang et al., 2018b).

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 localised scales. In addition, these sectors often withdraw water within environmentally sensitive locations (Miranda and Sauer, 2010), 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 (Marston et al., 2018; Veil, 2020), as well as any associated DIC concentration changes, are currently limited on a national scale. Net WD-DIC fluxes for these water use sectors should be estimated as more comprehensive datasets emerge. With 10% of counties responsible for over 70% of total freshwater consumption across the country (Marston et al., 2018), efforts to determine net WD-DIC fluxes could also be prioritised in these areas.

5.4.5 Degassing of Carbon Dioxide from Groundwater Withdrawals

The degassing of CO_2 supersaturated groundwater withdrawals across the US are known to contribute to the country's atmospheric CO_2 emissions (McCarthy et al., 2020; Wood and Hyndman, 2017). The research reported here develops a more robust methodology to estimate the sub-national and sectoral contributions to an updated national-level CO_2 emission estimate of 3.6 Tg CO_2 yr^{-1} (Figure 5.4a). This value is over two times greater than the 1.7 Tg CO_2 yr^{-1} previously reported (Wood and Hyndman, 2017). This is primarily due to the use of total groundwater withdrawal volumes within the calculations presented here, as opposed to the lower volumes that represent groundwater depletion, or net withdrawals used by Wood and Hyndman (2017). Although this research uses larger (gross) withdrawal volumes for estimating

WD-$CO_{2\,gw}$ emissions, as opposed to net withdrawal (depletion) volumes, the excess groundwater CO_2 concentrations (E[$CO_{2\,gw\text{-}atm}$]) determined and used within this research are on average lower than those adopted in previous work (Wood and Hyndman, 2017). This work advocates that the approach reported here 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 (Deirmendjian et al., 2018; Macpherson, 2009), and that the use of THINCARB has modelled 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 have led to an underestimate of CO_2 emissions from groundwater (Section 5.2.3).

Ninety-six percent of the 1,401 counties that have WD-$CO_{2\,gw}$ emissions exceeding those from major emitting facilities (Figure 5.6b) have no emissions reported as part of the GHGRP (USEPA, 2023b), which is assumed to largely reflect the fact that any emissions from facilities within those counties are below the reporting threshold (USEPA, 2023d). Despite this, the identification of regions where WD-$CO_{2\,gw}$ emissions are important in relation to other major CO_2 emission sources (Figure 5.6b) 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 (Liu and Mauter, 2022).

Previous work has generally focused on quantifying the CO_2 emissions associated with degassing groundwater withdrawals for irrigation use (Huo et al., 2022; McCarthy et al., 2020). A more comprehensive assessment of the sectoral withdrawals that can contribute to total withdrawal CO_2 emissions has been made in this 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 5.4a). With the

volume of groundwater withdrawals anticipated to increase across many regions of the US (Warziniack et al., 2022), WD-$CO_{2\ gw}$ emissions are likely to persist or even increase into the future. Whilst beyond the scope of this research, the E[$CO_{2\ gw\text{-}atm}$] dataset and methodology developed in this thesis 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 (Kellner et al., 2015; McDonough et al., 2020) and hydrogeological setting (Klaus, 2023) (Figure 5.3e and f). 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 reducing atmospheric CO_2 emissions through the regulation of irrigation method, for example (McCarthy et al., 2020). Whilst this work highlights the localised 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 (Macpherson, 2009). Future research should also 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.

5.4.6 A Global Perspective on the Impacts of Water Withdrawals on Freshwater Carbon Fluxes

Whilst 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 (Döll et al., 2012) and adopting median US DIC_{gw} and DIC_{sw} concentrations determined in this study, this thesis estimates net global WD-DIC_{gw} and WD-DIC_{sw} fluxes to be 12.4 and 35.0 Tg C yr^{-1}, respectively. These net global WD-DIC_{gw} and WD-DIC_{sw} fluxes may therefore be equivalent to approximately 82.6% of the global DIC_{SGD} flux (15 Tg DIC yr^{-1}) and 6.7% of global riverine DIC export (520 Tg DIC yr^{-1}), respectively (Liu et al., 2024). 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) (United Nations, 2022) and the median excess groundwater CO_2 concentration

estimated in this study (13.7 mg CO_2 L^{-1}), the global WD-$CO_{2\ gw}$ flux is estimated 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 (2017), an artefact of the simultaneously higher gross WD_{gw} volume but lower E[$CO_{2\ gw\text{-}atm}$] concentration adopted in the research reported here. This estimate is much lower than the 36.7-110 Tg CO_2 yr^{-1} estimated by Macpherson (2009) due to the lower E[$CO_{2\ gw\text{-}atm}$] concentration adopted in this study. Emerging global datasets estimating sectoral water use and consumption should be used to resolve similar fluxes elsewhere around the world (Khan et al., 2023), with priority given to countries undertaking globally significant withdrawals of fresh water.

5.5 Acknowledgements

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6. Concluding Discussion

6.1 Contributions of this Research to Scientific Knowledge in Relation to Thesis Objectives

The main aim of this thesis was to develop an understanding of how water supply processes can impact C, N and P cycling across the US. Unknown fluxes of N, C and P identified at the beginning of this thesis (Figure 2.2) have been estimated and are detailed in Figure 6.1. Through addressing the research objectives in Section 1.2, this thesis has made the following major contributions to scientific knowledge:

- Withdrawals of fresh surface water and groundwater have been identified as a fresh water NO_3 retention mechanism, for the first time across the US. On a national level, fresh surface water and groundwater withdrawals for the year 2015 have been estimated to result in median retention fluxes of 189 and 228 kt NO_3-N yr^{-1}, respectively. Together, these freshwater NO_3 retention fluxes were equivalent to 57% of in-stream denitrification and 21% of N uptake by pasturelands. For the first time anywhere globally, this research has determined the contribution that withdrawals for each major water use sector make to total withdrawal NO_3 fluxes, with irrigation, thermoelectric and public supply sectors contributing to 86% of this total. These results highlight the importance of freshwater withdrawals as an influence on N cycling across the US and therefore support the inclusion of freshwater withdrawals within the development of N budgets across the country (objective 2).

- Withdrawals of fresh surface water and groundwater have been identified as a fresh water DIC retention mechanism across the US. On a national level, fresh surface water and groundwater withdrawals in the year 2015 have been estimated, for the first time anywhere globally, to result in median retention fluxes of 8.2 and 6.9 Tg DIC yr^{-1}, respectively. These fluxes are equivalent to 28% of the total export of DIC to the oceans from US rivers and nearly ten times the magnitude of the DIC export to the oceans by US subterranean groundwater discharge, respectively. These results have implications for the accurate determination of other components of the US freshwater C budget, such as

terrestrial inputs of C to fresh waters, net ecosystem productivity and CO_2 emissions from fresh waters (objective 2).

- Upon withdrawal, degassing fresh CO_2 supersaturated groundwaters across the US are a source of CO_2 to the atmosphere. This research has re-estimated national-level CO_2 emissions from degassing fresh groundwater withdrawals, through the development and use of a more robust methodology than previous work, to be 3.6 Tg CO_2 yr^{-1} (over two times greater than a previous estimate). For the first time, this research identifies the relative contribution that each major water use sector makes to this national-level CO_2 emissions value, with irrigation and public supply contributing to 93% of the total. This analysis therefore highlights the importance of estimating groundwater degassing CO_2 emissions beyond those caused by irrigation withdrawals alone. This research makes a novel contribution by revealing the local significance of these emissions on a county-level across the country, with CO_2 emissions from degassing groundwater withdrawals exceeding total county-level CO_2 emissions from major emitting facilities across 1,401 counties (objective *2*).

- On a national-level, PO_4 dosing of potable US water supplies in the year 2015, for the purpose of minimising lead and copper corrosion and release, was estimated to add up to 14.9 kt PO_4-P yr^{-1} into the US water distribution network (objective 3).

- For the first time, the dosing of potable water with PO_4 and subsequent leakage of dosed water from watermains and its use outdoors at domestic residences have been identified as inputs of P to the environment across the US. On a national level, watermains leakage and outdoor water use were responsible for the release of up to 2.6 and 3.1 kt PO_4-P yr^{-1}, respectively. When combined, upper county-level estimates of watermains leakage and outdoor water use P inputs exceeded P loads from documented point sources across 541 counties. The localised significance of watermains leakage and outdoor water use P inputs, in the context of overall anthropogenic cycling of P, promotes their inclusion

within the development of P budgets and have novel implications for the sustainable use management of P. For example, the potential environmental impact and economic loss that leaked PO_4 might induce when lost from the water supply system might support the replacement of both aged and lead service lines, particularly across the northeast region of the country (objective 3).

- For the first time, watermains leakage of NO_3 from distribution pipes has been identified as an important mechanism that can return N back to the environment across the US. On a national level, watermains leakage was estimated to return a median flux of 7 kt NO_3-N yr^{-1} to the environment, which was equivalent to 13% of the NO_3-N initially retained due to freshwater withdrawals for public supply. Watermains leakage fluxes estimated on a county level across the US have also revealed the localised importance of watermains leakage as a mechanism returning N across urban environments, with 265 counties having watermains leakage N inputs that were equivalent to 10% or more of N inputs from agricultural fertilizer. These results support the inclusion of treated water transfers and watermains leakage N fluxes within the future development of US N budgets (objective 3).

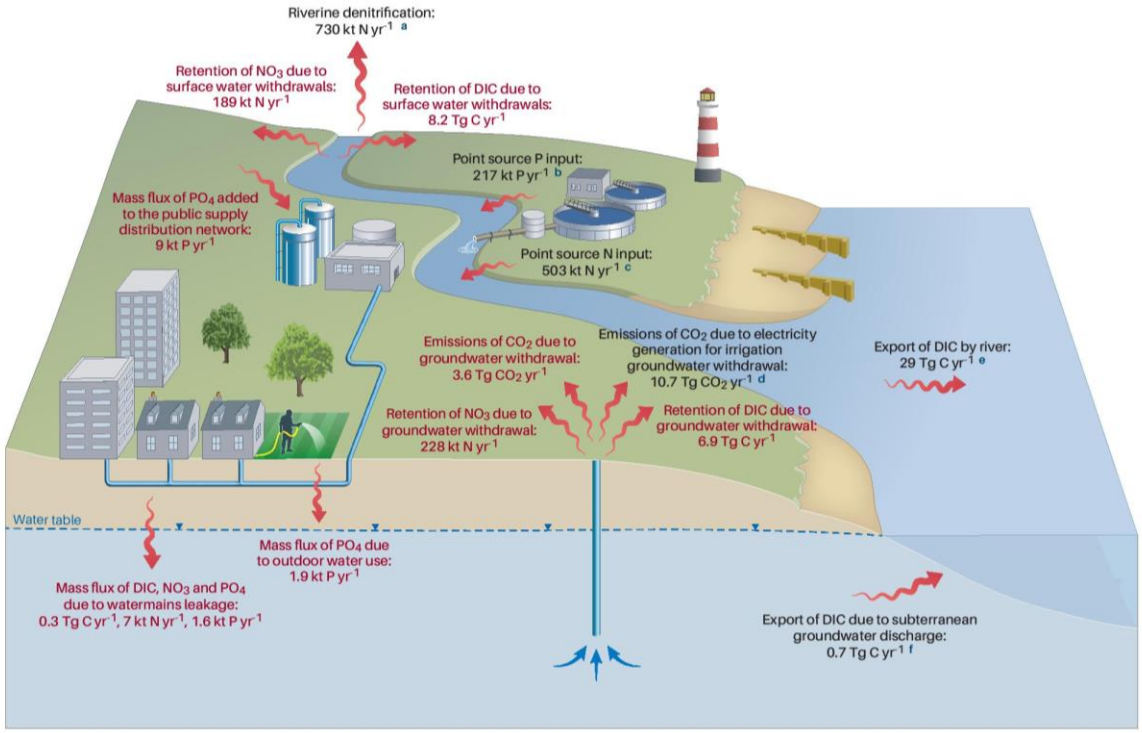


Figure 6.1 Schematic showing the contribution that this research makes to understanding the impact of water supply processes upon macronutrient cycling across the United States. Major nitrogen, carbon and phosphorus fluxes determined in previous work are shown in black ([a] Baron et al. (2012), [b] USEPA (2023a), [c] Skinner and Wise (2019), [d] Driscoll et al. (2024), [e] Butman et al. (2016), [f] Estimated using the total subterranean groundwater discharge estimate made by Sawyer et al. (2016) and the median DIC concentration of groundwater (48 mg C L^{-1}) determined in this study. Median fluxes estimated in this thesis are shown in red. Corresponding research objectives as follows: [g] objective 2, [h] objective 3.

6.2 Implications for Integrated Nitrogen, Carbon and Phosphorus Budgets

Ultimately, the balance between N, P and C input and retention processes along the freshwater continuum will control the downstream export of these nutrients to the ocean and the gaseous exchange of N and C between fresh waters and the atmosphere. As a result, omission of any component within these balances can lead to biased estimation of other components, with implications for the subsequent development of effective nutrient management practices. Ensuring all inputs, transformations and retention processes are incorporated within N, C and P

budgets is therefore required as part of an integrated approach (Casas-Ruiz et al., 2023; Grizzetti et al., 2015; Wu and Ma, 2015). Whilst water supply processes have been identified as mechanisms impacting fluxes of N, C and P around the world, these fluxes have largely been estimated as part of small-scale studies and omitted from nutrient budgets. The research presented in this thesis therefore has important implications for the development of integrated N, C and P budgets, both across the US and around the world.

The omission of freshwater withdrawal and watermains leakage NO_3 fluxes within N budgets and models used by policymakers in their attempts to manage N may invalidate budget and model outputs. Integrating these fluxes into budgets is particularly important when the budget in question is deduced using a mass balance methodology, such as when undertaking net anthropogenic N input assessments (Hong et al., 2011). Similarly, incorporating freshwater withdrawal retention fluxes of DIC into the hydrological components of net ecosystem and watershed C balance assessments, particularly those using a bottom-up approach, is fundamental to accurately determine other components of the inland water C budget, as well as wider terrestrial and atmospheric components of the C cycle (Casas-Ruiz et al., 2023; Vachon et al., 2021). The importance of watermains leakage PO_4 fluxes across the UK was impetus for their incorporation into national-level source apportionment studies by the country's environmental regulator (Environment Agency, 2019). Acknowledgement of both watermains leakage and outdoor water use derived N and P inputs should now be made within source apportionment studies undertaken by the USEPA and the country's individual state agencies (Sabo et al., 2021b; Tomich et al., 2016). The localised significance of county-level fluxes estimated within this work, in the context of other N, C and P budget components, has particularly strong implications for developing accurate nutrient budgets on more localised scales. Leakage and outdoor water use have been identified as important sources of N and P across urban areas of the US, and as such will be important to include within urban watershed nutrient budget studies across the country (Hobbie et al., 2017; Small et al., 2023). A conceptual mass balance model has published estimated annual P loads to WWTPs and the environment due to PO_4 dosing practices on a national level (USEPA, 2020a). The heterogeneity in county-level dosing, watermains leakage,

outdoor water use and WWTP return PO_4 fluxes now calls for the publication of these estimates on more localised and management-relevant scales (e.g. for individual watersheds and utilities). This in turn will facilitate more targeted nutrient management strategies. Similarly, the localised importance of CO_2 emissions from degassing groundwater withdrawals is an impetus for incorporating this mechanism into sectoral, city or water supply system level net greenhouse gas emission assessments (Liu and Mauter, 2022; McGill et al., 2018; Sowby and Capener, 2022).

6.3 Implications for Nutrient and Water Management

A lack in observed water quality improvements following the implementation of nutrient management strategies across the US has partially been attributed to the need for more locally targeted and tailored nutrient management strategies (Frei et al., 2021; Kirk et al., 2024; Sabo et al., 2021a; USDA, 2020b). The source apportionment of nutrients on a national level is often unsuitable for informing these more targeted nutrient and water management strategies, with locally important sources and sinks of nutrients often not identified or robustly quantified. Whilst this research does not aim to make prescriptive policy suggestions, the advancement in understanding that this research provides should inform the development of more integrated nutrient budgets that can inform more effective nutrient management strategies on a range of spatial scales.

Specifically, county-level fluxes estimated within this research may have greater implications for more accurate source apportionment and the implementation of effective and targeted nutrient management practices. County-level hotspots of P inputs via watermains leakage and outdoor water use that have been identified as part of this work could provide some basis for understanding why reductions to other anthropogenic P inputs, such as wastewater treatment plant effluents, may not have resulted in expected improvements in water quality and aquatic ecology. They may also be used as impetus for prioritising the removal of ageing and lead pipe networks within these hotspot areas (DEC, 2022; USEPA, 2019b). The economic and environmental costs associated with N and P loss from the US public water supply network may

result in the water supply industry incorporating these fluxes into sustainable economic level of leakage assessments (California State Water Resources Control Board, 2021; Rupiper et al., 2022), whereby the economic cost of mains pipe replacement would be evaluated against the costs of water loss, phosphate loss (and thus unrecoverable nature of P at downstream WWTPs) and environmental impacts associated with WML-PO_4-P fluxes. The amount of P unintentionally applied to domestic lawns through using PO_4 dosed water for lawn irrigation may also have implications for P fertilizer requirements at domestic residences within states where its use remains permissible (Carey et al., 2012). Further, a number of states have passed laws banning the use of lawn P fertilizer (Lee and McCann, 2018) and OWU-PO_4-P fluxes estimated in this work might support the development of similar policies across other states.

Similarly, irrigation withdrawal N fluxes have already been highlighted as a mechanism that can contribute to state-level fertilizer N requirements (Stahl, 2019). This work now provides county-level irrigation withdrawal NO_3 flux estimates to which more localised (and regulatorily enforceable) assessments could be made. This research reveals the potential impact that treated water transfers and watermains leakage may have on the N balance of the receiving location. These impacts may now be a consideration in the future regulation of water transfer permits both across the US and around the world (Stormwater Report, 2015). The CO_2 emissions from degassing fresh groundwater withdrawals may also have implications for policy development surrounding sustainable groundwater withdrawals and use (Kovacs and West, 2016). For example, the propagation of groundwater withdrawal wells to deeper depths in the future may result in the withdrawal of groundwaters with greater $E[CO_2]_{gw}$ concentrations (Macpherson, 2009; Perrone and Jasechko, 2019). With these deeper withdrawals potentially leading to greater CO_2 degassing, the results presented in this work are additional rationale supporting the narrative that deeper well drilling in inherently unsustainable (Perrone and Jasechko, 2019). Future policy may also strive to both limit well propagation in areas likely to have notably high $E[CO_2]_{gw}$ concentrations, as well as to take degassing groundwater withdrawal CO_2 emissions into account when developing and enforcing optimum irrigation practices (McCarthy et al., 2020).

6.4 Further Research

Whilst this research has made significant strides in increasing understanding of how water supply processes can impact macronutrient cycling across the US, it has also identified a range of knowledge gaps. Several future research areas are therefore suggested:

- Transfers of water from areas of surplus to those of stress can affect nutrient cycling (Zeng et al., 2015; Zhuang, 2016). A comprehensive investigation into the impacts of raw and treated water transfers upon input and output fluxes of nutrients (e.g. N), from both source and recipient catchments across the US, should be undertaken. This work could prioritise large-scale 'mega' transfers, defined as those transferring water a distance of more than 190 km or a volume of water greater than 0.23 $km^3\ yr^{-1}$ (Shumilova et al., 2018). Data relating to water transfers across the US (Siddik et al., 2023; Young and Brozovik, 2019) could also be used to verify that transfers may be a cause of the watermains leakage NO_3 fluxes that exceed retention fluxes of NO_3 due to public supply withdrawals (see Section 3.4.2).

- The magnitude and importance of water supply processes upon N, C and P fluxes across the US in the future should be determined. This could include the impacts of both future water treatment regulation changes, including increased prevalence and concentration of PO_4 dosed for corrosion control (USEPA, 2020a), as well as potential future increases in freshwater withdrawal, transfers and use across the US (Shumilova et al., 2018; Warziniack et al., 2022) upon N, C and P fluxes.

- Future work should continue to resolve net freshwater withdrawal fluxes of DIC and NO_3 across the US, that account for speciation changes, return flows, consumption and transfers. This must include a robust rationale as to how to apportion withdrawal fluxes as being either gross or net, which in term will require the permanency or transiency of withdrawal fluxes to be defined, in the context of both ecologically and policy relevant timescales. Data required for this will be specific to each major water use sector, and will

reflect the contrasting withdrawal, treatment and end use processes that are characteristic for each of them.

- Determining the impact of in-pipe processes on the retention of N, C and P will have implications on accurately determining the fate of these nutrients once in public supply systems and thus assessing the sustainability of nutrient use within the water supply industry. For example, differing pipe materials, climate change, urbanisation, and changing water use patterns will have a complex effect on both the biotic (Liu et al., 2019; Rhoads et al., 2015) and abiotic environment within water distribution networks (Agudelo-Vera et al., 2020; Pelletier et al., 2017; Tang et al., 2021b).

- The fate of watermains leakage and outdoor water use N and P within the environment should be determined across the US. This could involve building upon research that has begun isotopically labelling dosing derived PO_4 (Davies et al., 2014; Gooddy et al., 2015). Determining the fate of these fluxes, particularly within urban areas, has important implications as to whether the released N and P is retained within groundwaters and sub-surface sediment to become potential sources of legacy pollution, released directly into surface waters via surface run-off, or incorporated back into the wastewater system via run-off into drains, where N and P can then undergo treatment before being released into surface waters (Carey et al., 2013).

- The impact of freshwater withdrawal, treatment and use upon fluxes of other C and N species (e.g. organic N and C and NH_4) should be investigated and incorporated into nutrient budgets across the US. This includes impact of freshwater withdrawals on the riverine export of both particulate and dissolved organic C (Casas-Ruiz et al., 2023; You et al., 2023).

- Research should assess the net impact that degassing groundwater withdrawals can have on the release of CH_4 and N_2O to the atmosphere, as part of a wider greenhouse gas assessment (McGill et al., 2018; Trost et al., 2013).

- Fluxes presented in this research should be continually re-examined and estimated as more comprehensive water use, water quality and leakage data become available across the US, with particular focus on the hotspot areas identified in this thesis. Fluxes should be integrated within numerical modelling efforts that seek to quantify the impacts of anthropogenic water supply upon nutrient cycling (Pennino et al., 2023; Zhu et al., 2020). The reprojection or modelling of these fluxes on a watershed scale may also be beneficial, given that many nutrient budgets and management strategies are estimated and implemented on this spatial scale (Swaney et al., 2012; USEPA, 2010; Van Meter et al., 2021).

- Uncertainties associated with fluxes estimated in this thesis are expressed as lower and upper estimates, through applying ±10% on terms relating to volumetric flow rates of water and the use of lower and upper quartile concentrations. The uncertainty associated with water use data remains difficult to constrain, due to the vast range of data sources and assumptions used in its compilation (Bradley, 2017). However, future work should explore uncertainties more robustly through implementation of a bootstrapping method. Here, freshwater NO_3 and DIC concentrations, as well as values within the recommended range for PO_4 dosing, along with freshwater withdrawal volumes between ±10% of reported values, would be randomly resampled to allow for a distribution of flux values to be estimated and interpreted.

- This research has estimated the magnitude of perturbations that water supply processes can have upon separate N, C and P cycles. Developing integrated nutrient management practices, that can successfully address the impacts of anthropogenically altered nutrient cycles, will require the impacts of water supply processes upon the stoichiometry of

freshwater N, C and P to be investigated (Maranger et al., 2018; Shousha et al., 2023; Whitehead and Crossman, 2012). For example, the enrichment of fresh waterbodies with respect to N and P is known to significantly alter C cycling on a range of spatial scales (Cross et al., 2022; Mackenzie et al., 2002). However, the impact of N import into a watershed via water transfers upon the C mineralisation and CO_2 emissions from the receiving waterbody remains to be investigated.

- An understanding of what other water supply processes may impact N, C and P cycles across countries, with both similar and contrasting development pathways, water management practices and climates, is limited. The transferable methodology presented in this research should therefore motivate similar assessments to be undertaken around the world. Implementing this methodology will require data relating to the volumetric flow rate of freshwater use, nutrient concentrations within raw fresh waters, the treatment of fresh water for various end uses and freshwater transfers. Therefore, this work also serves to promote for the collection and open reporting of these related datasets, with the ultimate goal being to contribute to a globally comprehensive assessment of the impacts that water supply processes can have upon macronutrient cycling.

6.5 Conclusion

Anthropogenic activity continues to significantly disrupt natural cycles of N, C and P. Despite long-standing efforts to regulate inputs of N and P in the environment, human perturbations continue to persist and contribute to the extensive eutrophication of both freshwater bodies and downstream coastal areas. The importance of fresh waters as moderators of the wider C cycle has only recently been acknowledged. This has resulted in many natural and anthropogenic freshwater C fluxes being poorly constrained or omitted entirely from C budgets, with implications for the accurate determination of terrestrial and atmospheric C, the management of C and ultimately the effective tackling of climate change. Successfully mitigating the impacts

of human caused eutrophication and climate change requires the development of integrated nutrient budgets, that identify and accurately quantify all nutrient inputs, transformations, and outputs to a given system. These budgets will then inform more locally tailored and effective nutrient management strategies.

The primary aim of this thesis was to advance an understanding of how water supply processes can impact C, N and P cycles across the US. This research has undertaken an up-to-date review the current state of science related to the impacts of water supply processes upon N, C and P cycles around the world and across the US (objective 1). This review identified that, although there has been progress in understanding how human use of fresh water can affect N, C and P cycles, research in this field remains limited and estimates of associated fluxes across the US and around the globe are either unavailable or poorly defined (objective 1). Given the globally significant use of fresh water across the US, the persistence of nutrient pollution and greenhouse gas emissions across the country and the fact that many US water supply challenges reflect those of other countries with globally significant freshwater use, it serves as a pertinent case study for further investigating the influence of water supply processes on N, C and P cycles.

For the first time, this thesis has shown that withdrawals of fresh water across the US are a fresh water NO_3 and DIC retention mechanism, with median national-level flux estimates equivalent to 57% of N retention due to denitrification and 51% of the DIC exported to the ocean via rivers and subterranean groundwater discharge, respectively (objective 2). The degassing of CO_2 supersaturated fresh groundwaters upon withdrawal were also identified to be important source of CO_2 emissions across the US, with the median estimate presented in this research (3.6 Tg CO_2 yr^{-1}) being over two times larger than a previous estimate. For the first time, this research details the contribution that groundwater withdrawals for each major water use sector make to this national-level total. Results also highlight degassing groundwater withdrawals as a locally important source of atmospheric CO_2, with CO_2 emissions from degassing groundwater

withdrawals exceeding total county-level CO_2 emissions from major emitting facilities across 1,401 counties (objective 2).

For the first time, watermains leakage of NO_3 from distribution pipes across the US has been identified as a mechanism returning up to 7.7 kt NO_3-N yr^{-1} back to the environment, with 265 counties having watermains leakage N inputs that were equivalent to 10% or more of N inputs from agricultural fertilizer (objective 2). The dosing of potable water with PO_4 and subsequent leakage of dosed water from watermains and its use outdoors at domestic residences have also been identified as novel inputs that can release up to 2.6 and 3.1 kt PO_4-P yr^{-1} into the environment across the US, respectively (objective 3). The local significance of these inputs have been highlighted, with upper county-level estimates of watermains leakage and outdoor water use P inputs exceeding P loads from documented point sources across 541 counties. Conclusions from this research have also made a range of suggestions for priority areas of future work (objective 4).

The knowledge developed through this research should contribute to the creation of more integrated nutrient budgets. Specifically, the importance of withdrawal, treatment, leakage and outdoor water use induced N, C and P fluxes estimated within this work, on both a national and local level, demonstrates the importance of incorporating these water supply processes within N, C and P budgets, as well as within more spatially detailed process-based modelling approaches. The improved accuracy of these budgets and models can then better inform the development of targeted N, C and P management strategies that work towards curbing the impacts of eutrophication and climate change, as well as expectations about the timeliness and effectiveness of associated water quality improvements. This could include the incorporation of WML-PO_4 -P fluxes within US water system assessments of economic levels of leakage and the sustainability of P use, as well as future developments to the Lead and Copper Rule. Similarly, the localised importance of OWU-PO_4-P fluxes estimated in this work may help support the development of state-level policies that seek to regulate the use of P based lawn fertilizers at

domestic residences. The contribution of irrigation and public supply WD-$CO_{2\ gw}$ emissions may have implications for the sustainable use of groundwater, the development of policies guiding irrigation methods (for example flood vs. drip irrigation) and the ability for water systems to achieve net-zero targets.

Both the global significance of water use across the US and transferrable methodology developed within this research have implications for advancing understanding of the impacts that water supply processes can have on macronutrient cycling around the globe. This understanding is imperative, given the future predictions of a planet dominated by population growth, economic development and climate change.

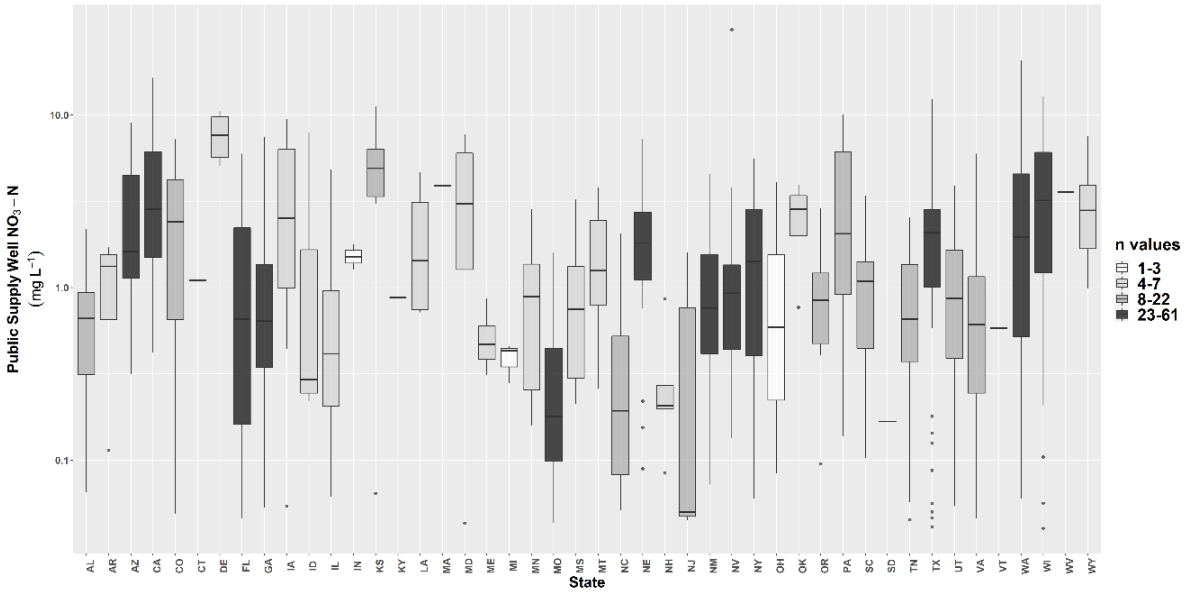
6.6 Research Dissemination

Table 6.1. Dissemination of the research presented in this thesis.

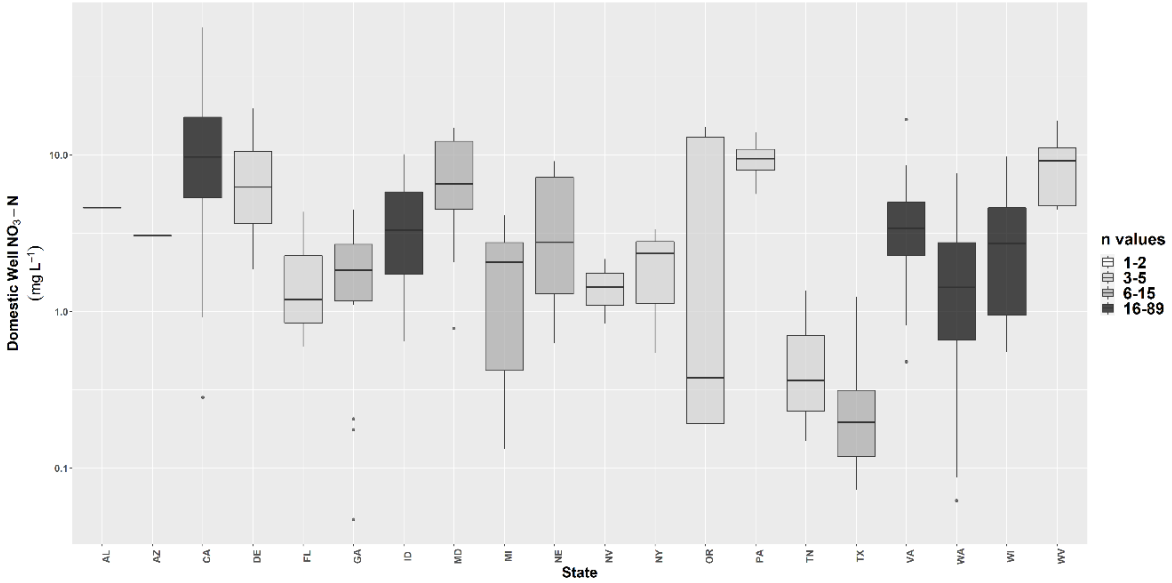
News and Reviews	Paper Title	URL/DOI
Nature Reviews Earth & Environment	Water supply processes are responsible for significant nitrogen fluxes across the United States	https://doi.org/10.1038/s43017-022-00352-2
EoS Research Highlight	Watermains leakage and outdoor water use are responsible for significant phosphorus fluxes to the environment across the United States	https://eos.org/research-spotlights/u-s-public-water-supply-is-a-local-source-of-phosphorus-pollution
One Water News	Watermains leakage and outdoor water use are responsible for significant phosphorus fluxes to the environment across the United States	https://www.onewaternews.com/phosphate-in-drinking-water-can-contribute-to-nutrient-pollution-study-says
BGS Communications	Water supply processes are responsible for significant nitrogen fluxes across the United States	https://www.bgs.ac.uk/news/missing-components-of-nitrogen-cycling-budgets-across-the-united-states/
	Watermains leakage and outdoor water use are responsible for significant phosphorus fluxes to the environment across the United States	https://www.bgs.ac.uk/news/how-does-public-water-use-influence-the-amount-of-phosphorus-in-the-environment/
Conference Presentations		
Flint, EM, Ascott, MJ, Gooddy, DC, Surridge, BWJ., and Stahl, MO: *Carbon dioxide emissions associated with fresh groundwater withdrawals across the United States*, AGU Fall Meeting 2023, San Francisco, 2023 (oral)		
Flint, EM, Ascott, MJ, Gooddy, DC, Surridge, BWJ, and Stahl, MO: *Anthropogenic water withdrawals impact freshwater inorganic carbon fluxes across the United States,* AGU Fall Meeting 2023, San Francisco, 2023 (poster)		
Flint, EM, Ascott, MJ, Gooddy, DC, Surridge, BWJ., and Stahl, MO: *Losses of phosphate from water distribution networks have a significant impact on phosphorus cycling across urban areas of the United States*, AGU Fall Meeting 2022, Chicago, 2022 (oral)		
Flint, EM, Ascott, MJ, Gooddy, DC, Surridge, BWJ., and Stahl, MO: *Water supply processes are responsible for significant nitrogen fluxes across the United States*, AGU Fall Meeting 2022, Chicago, 2022 (poster)		
Flint, EM, Ascott, MJ, Gooddy, DC, Surridge, BWJ., and Stahl, MO: *Losses of phosphate from water distribution networks have a significant impact on phosphorus cycling across urban areas of the United States*, American Water Resources Association Conference, Seattle, 2022 (oral)		
Flint, EM, Ascott, MJ, Gooddy, DC, Surridge, BWJ., and Stahl, MO: *Water supply processes are responsible for significant nitrogen fluxes across the United States*, American Water Resources Association Conference, Seattle, 2022 (poster)		
Flint, EM, Ascott, MJ, Gooddy, DC, Surridge, BWJ, and Stahl, MO: *Leakage of water from public supply distribution networks is responsible for significant phosphorus fluxes within many urban catchments across the United States*, EGU General Assembly 2022, Vienna, Austria, 23–27 May 2022, EGU22-6063, https://doi.org/10.5194/egusphere-egu22-6063, 2022 (oral, virtual)		
Flint, EM, Ascott, MJ, Gooddy, DC, Surridge, BWJ, and Stahl, MO: *Understanding current and future impacts of public water supply on global nitrogen cycling*, EGU General Assembly 2021, online, 19–30 Apr 2021, EGU21-15033, https://doi.org/10.5194/egusphere-egu21-15033, 2021 (oral, virtual – vOSPA Winner)		

7. Appendices

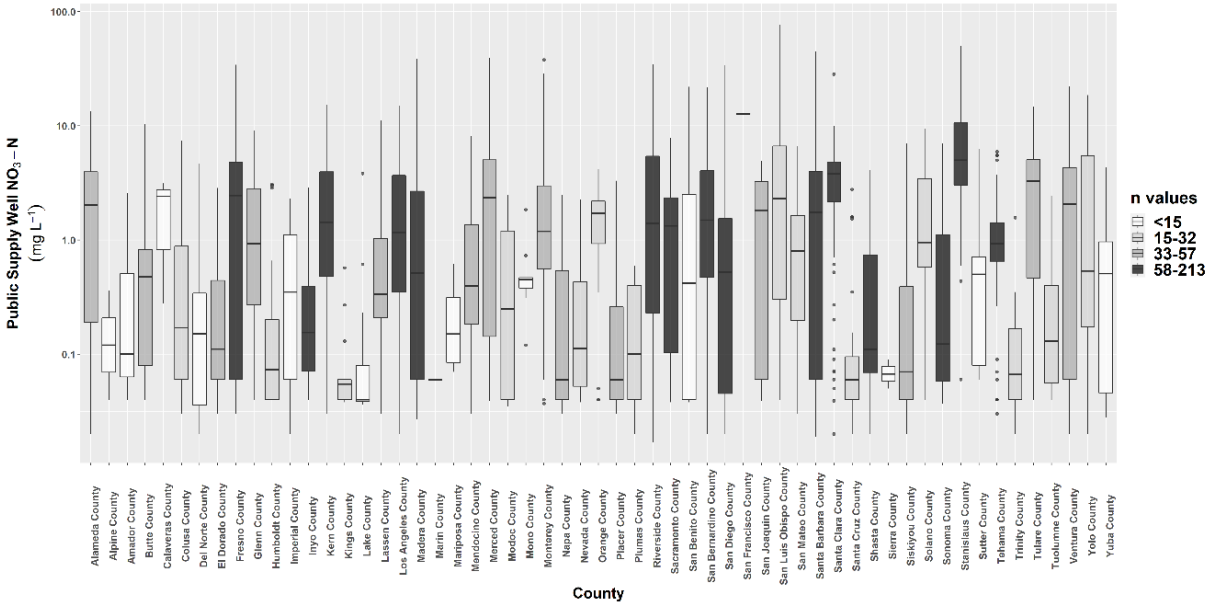
Appendix 1. The number and spread of raw groundwater NO_3-N concentration values from public supply wells for each state across the United States. These concentrations were used to estimate withdrawal NO_3 fluxes for the public water supply sector.



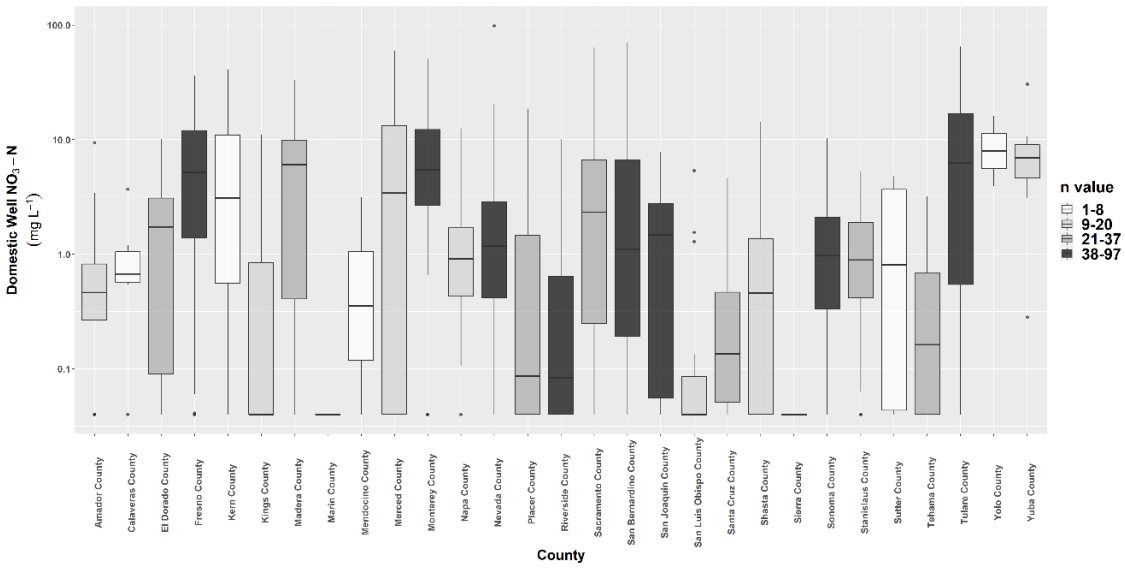
Appendix 2. The number and spread of raw groundwater NO_3-N concentration values from domestic wells for each state across the United States. These concentrations were used to determine withdrawal NO_3 fluxes for the domestic water supply sector.



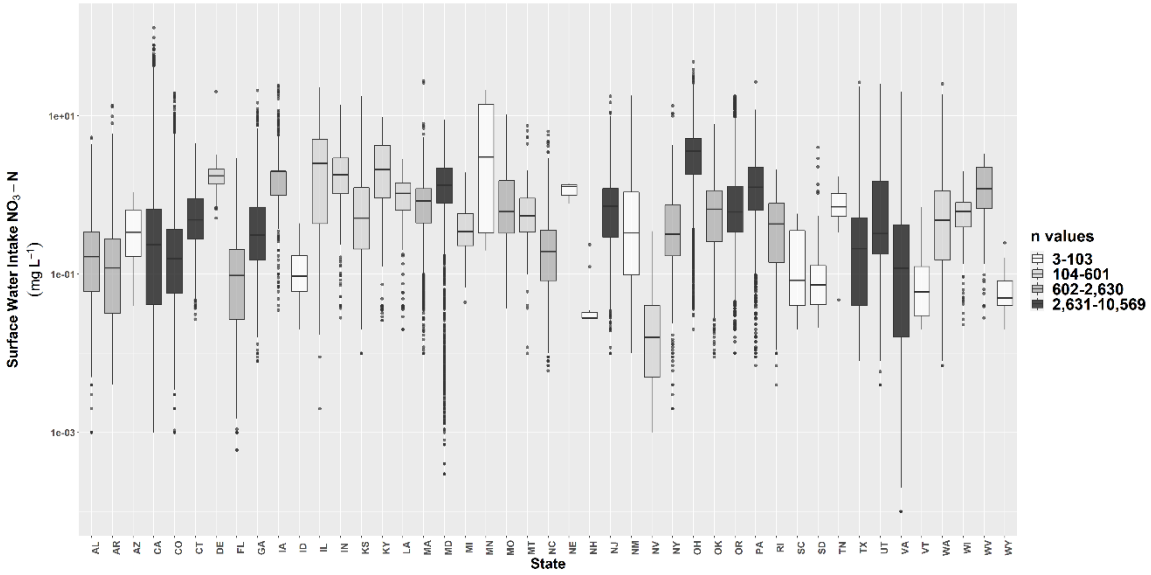
Appendix 3. The number and spread of raw groundwater NO_3-N concentration values from public supply wells within each county across the state of California. Concentrations were used to determine withdrawal NO_3 fluxes for public water supply sector.



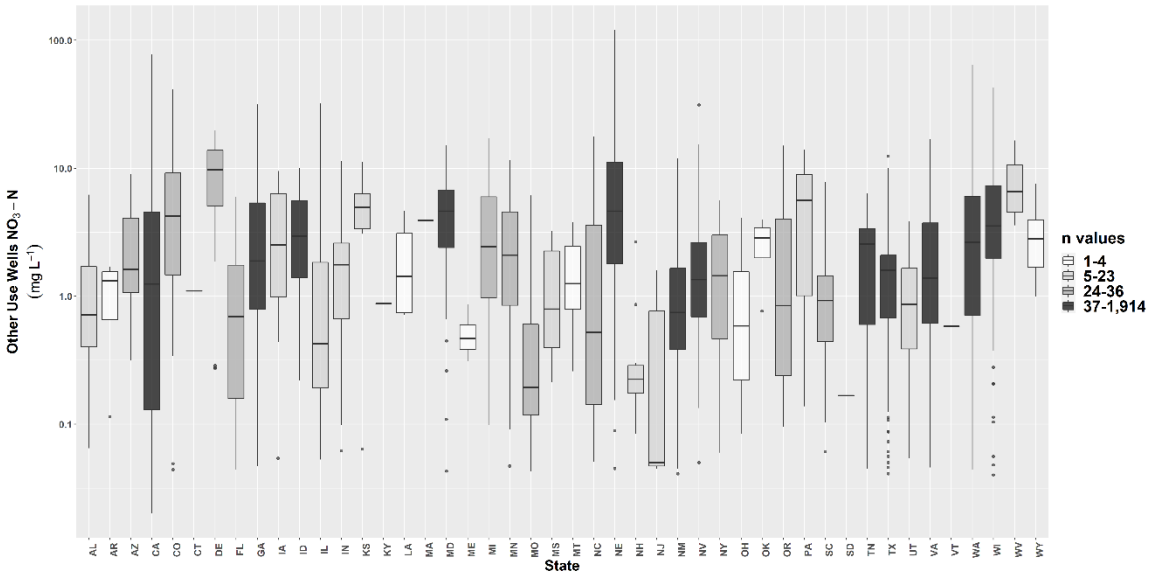
Appendix 4. The number and spread of raw groundwater NO_3-N concentration values from domestic wells within each county across the state of California. Concentrations were used to determine withdrawal NO_3 fluxes for domestic water supply sector.



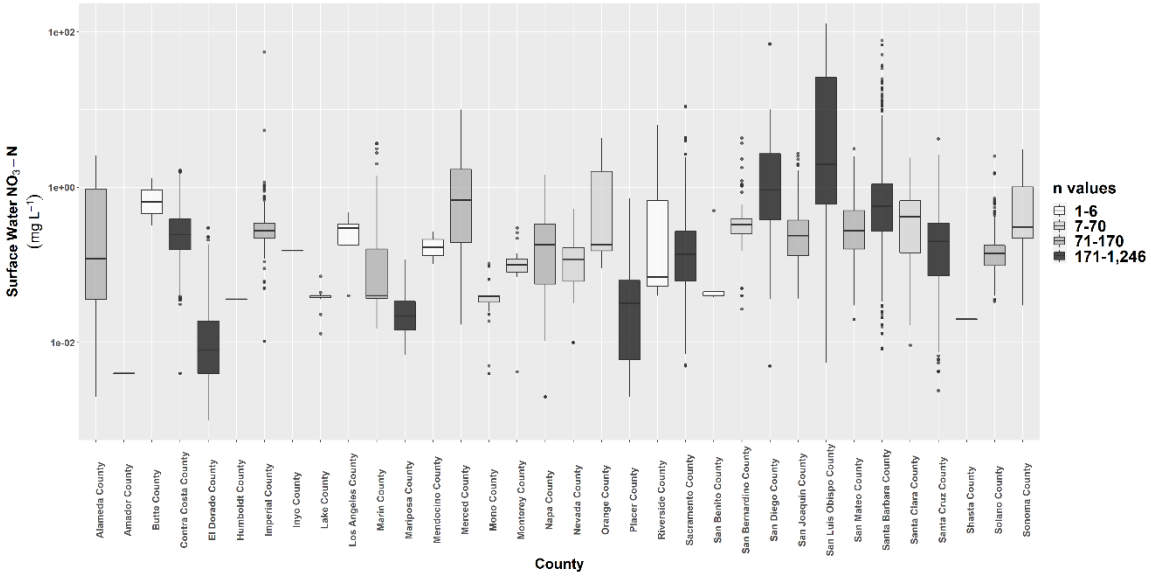
Appendix 5. The number and spread of raw surface water NO_3-N concentration values for each state across the United States. Concentrations were used to determine surface water withdrawal NO_3 fluxes for all water use sectors.



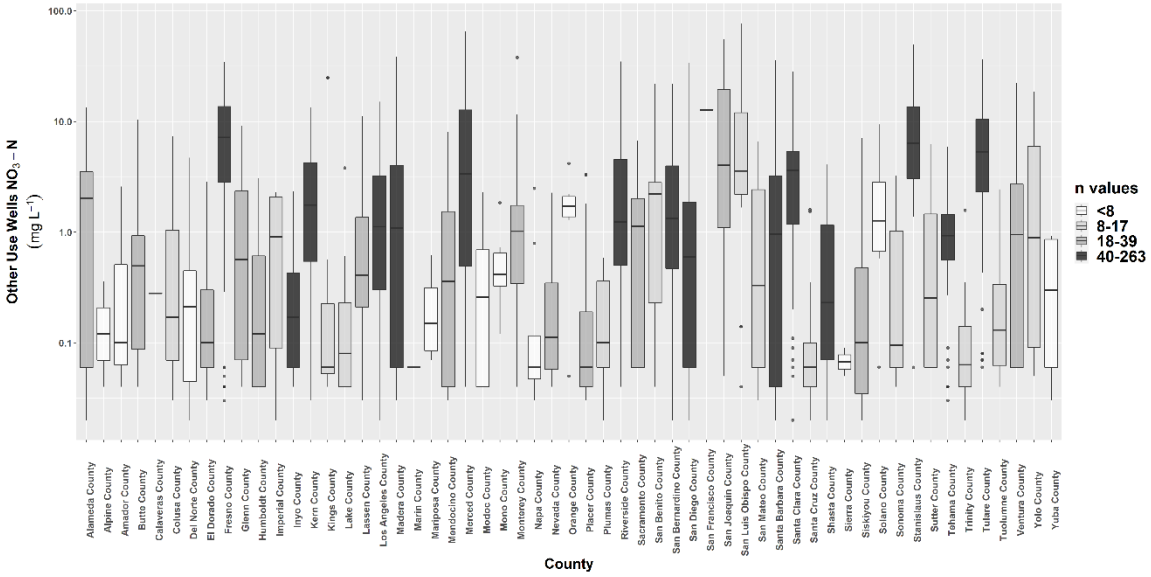
Appendix 6. The number and spread of raw groundwater NO_3-N concentration values for each state across the United States. These concentrations were used to determine withdrawal NO_3 fluxes for the irrigation, thermoelectric, industrial, mining, aquaculture and livestock water use sectors.



Appendix 7. The number and spread of raw surface water NO_3-N concentration values for each county across the state of California. Concentrations were used to determine withdrawal NO_3 fluxes for all major water use sectors across California.



Appendix 8. The number and spread of raw groundwater NO_3-N concentration values within each county across the state of California. Concentrations were used to determine withdrawal NO_3 fluxes for irrigation, thermoelectric, industrial, mining, aquaculture and livestock water use sectors.



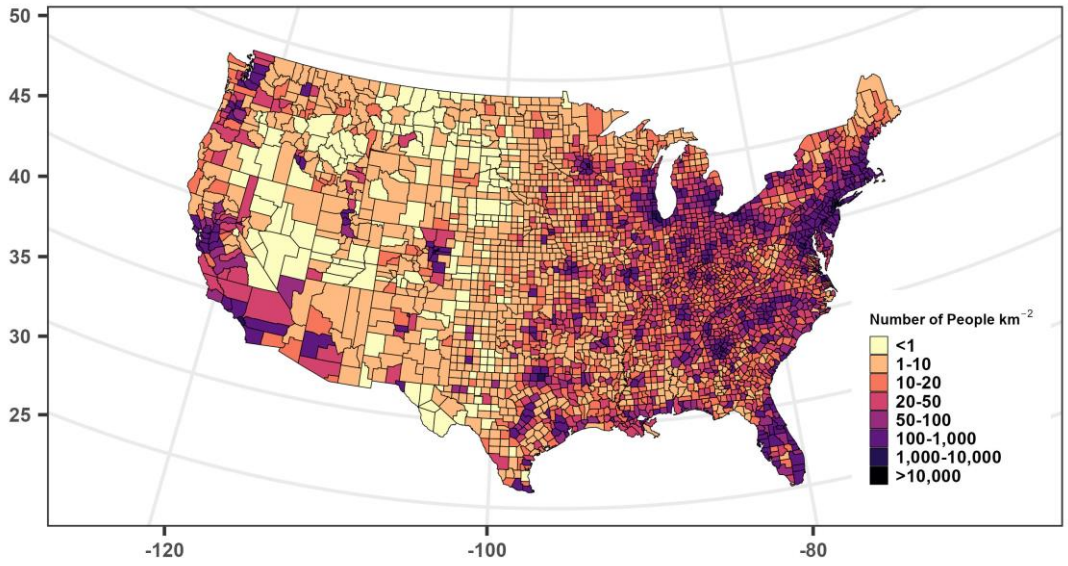
Appendix 9. Table disclosing the value and source of state-level leakage factors ($f_{leakage}$), and watermains leakage fluxes (WML-NO_3-N) for each state across the United States, in units of kg NO_3-N yr^{-1}.

State	$f_{leakage}$	Source of $f_{leakage}$	WML-NO_3-N
Alabama	33	American Water Works Association (2021)	0.196
Arizona	10.3	Jernigan et al. (2018)	0.425
Arkansas	16	National average - USEPA (2013)	0.029
California	6.44	California Department of Water Resources (2019)	0.758
Colorado	4.24	American Water Works Association (2021)	0.018
Connecticut	16	National average - USEPA (2013)	0.043
Delaware	28.9	American Water Works Association (2021)	0.106
Florida	4.1	American Water Works Association (2021)	0.036
Georgia	18.8	Georgia EPD (2016)	0.108
Idaho	16	National average - USEPA (2013)	0.084
Illinois	15.9	Illinois Department of Natural Resources (2015)	0.248
Indiana	16	Indiana Finance Authority (2016)	0.127
Iowa	16	National average - USEPA (2013)	0.182
Kansas	9.81	American Water Works Association (2021)	0.067
Kentucky	10.1	American Water Works Association (2021)	0.055
Louisiana	16	National average - USEPA (2013)	0.058
Maine	16	National average - USEPA (2013)	0.004
Maryland	15.6	Maryland Department of the Environment (2015)	0.242
Massachusetts	16	National average - USEPA (2013)	0.076
Michigan	16	National average - USEPA (2013)	0.074
Minnesota	16	Minnesota Department of Natural Resources (2019)	0.052
Mississippi	16	National average - USEPA (2013)	0.008
Missouri	34	American Water Works Association (2021)	0.453
Montana	16	National average - USEPA (2013)	0.018
Nebraska	16	National average - USEPA (2013)	0.132
Nevada	4.07	American Water Works Association (2021)	0.040
New Hampshire	16	National average - USEPA (2013)	0.009
New Jersey	12.2	National average Kunkel Water Efficiency Consulting (2017)	0.221
New Mexico	9.66	American Water Works Association (2021)	0.031
New York	16	National average - USEPA (2013)	0.304
North Carolina	26	American Water Works Association (2021)	0.037
North Dakota	16	National average - USEPA (2013)	0.005
Ohio	20	American Water Works Association (2021)	0.346
Oklahoma	22	American Water Works Association (2021)	0.146
Oregon	16	National average - USEPA (2013)	0.038
Pennsylvania	32.4	American Water Works Association (2021)	1.114
Rhode Island	16	National average - USEPA (2013)	0.015
South Carolina	18.5	American Water Works Association (2021)	0.101
South Dakota	16	National average - USEPA (2013)	0.006
Tennessee	16.7	American Water Works Association (2021)	0.095
Texas	13.9	American Water Works Association (2021)	0.311
Utah	16	National average - USEPA (2013)	0.166
Vermont	16	National average - USEPA (2013)	0.002
Virginia	16	National average - USEPA (2013)	0.091
Washington	8.2	AQUEOUS / Amy Vickers & Associates (2016)	0.087
West Virginia	16	National average - USEPA (2013)	0.030
Wisconsin	15.3	American Water Works Association (2021)	0.106
Wyoming	16	National average - USEPA (2013)	0.011
United States	-	-	7.0

Appendix 10. Sectoral contributions to total withdrawal NO_3 fluxes (WD-NO_3-N) for each state across the United States, in units of kt NO_3-N yr^{-1}.

State	IRR-NO_3-N	THERM-NO_3-N	PWS-NO_3-N	IND--NO_3-N	DOM-NO_3-N	AQUA-NO_3-N	LIVE-NO_3-N	MINE-NO_3-N	WD-NO_3-N_{total}
Alabama	0.126	1.530	0.362	0.139	0.234	0.032	0.015	0.023	2.461
Arizona	5.610	0.141	1.570	0.014	0.101	0.058	0.087	0.153	7.734
Arkansas	17.500	0.245	0.218	0.076	0.074	0.298	0.029	0.001	18.440
California	25.500	0.039	9.990	0.684	1.700	0.581	0.174	0.057	38.725
Colorado	9.280	0.025	0.521	0.042	0.204	0.146	0.135	0.031	10.384
Connecticut	0.010	0.085	0.197	0.155	0.178	0.023	0.002	0.004	0.653
Delaware	1.330	0.036	0.594	0.844	0.131	0.027	0.018	0.005	2.985
Florida	1.270	0.081	1.780	0.182	0.291	0.012	0.025	0.091	3.731
Georgia	1.540	0.325	0.564	0.623	0.266	0.068	0.079	0.043	3.509
Idaho	21.300	0.007	0.104	0.184	0.321	0.439	0.169	0.008	22.533
Illinois	0.178	28.100	4.050	1.110	0.532	0.022	0.021	0.148	34.161
Indiana	0.326	9.560	1.440	5.710	0.736	0.036	0.096	0.315	18.219
Iowa	0.112	0.094	1.100	0.324	0.185	0.026	0.433	0.004	2.278
Kansas	17.500	0.623	1.040	0.213	0.102	0.024	0.582	0.037	20.121
Kentucky	0.110	5.400	1.460	0.522	0.128	0.139	0.115	0.088	7.962
Louisiana	2.200	5.860	1.360	3.330	0.227	1.030	0.012	0.011	14.030
Maine	0.013	0.004	0.058	0.126	0.183	0.037	0.001	0.004	0.425
Maryland	0.337	0.412	1.590	0.140	1.030	0.042	0.041	0.093	3.685
Massachusetts	0.646	0.063	1.600	0.097	0.203	0.046	0.004	0.035	2.693
Michigan	0.913	3.770	0.519	0.435	0.536	0.039	0.073	0.087	6.372
Minnesota	0.846	8.420	1.170	1.020	0.475	0.067	0.171	0.034	12.203
Mississippi	1.890	0.095	0.397	0.155	0.278	0.123	0.015	0.010	2.962
Missouri	0.414	4.970	0.508	0.048	0.332	0.136	0.045	0.013	6.466
Montana	7.240	0.058	0.197	0.012	0.137	0.016	0.044	0.017	7.723
Nebraska	35.800	5.240	0.646	0.272	0.073	0.096	0.609	0.017	42.753
Nevada	1.840	0.013	0.189	0.002	0.071	0.022	0.009	0.350	2.496
New Hampshire	0.000	0.003	0.012	0.002	0.172	0.002	0.000	0.001	0.193
New Jersey	0.043	0.357	0.820	0.066	0.524	0.001	0.000	0.057	1.867
New Mexico	1.680	0.019	0.229	0.003	0.142	0.022	0.032	0.048	2.175
New York	0.051	0.995	2.010	0.184	0.606	0.044	0.037	0.027	3.954
North Carolina	0.125	1.660	0.251	0.059	0.973	0.275	0.041	0.024	3.408
North Dakota	0.312	0.680	0.087	0.023	0.021	0.004	0.033	0.060	1.219
Ohio	0.234	22.000	5.510	1.430	0.805	0.166	0.105	0.449	30.699
Oklahoma	3.220	0.070	0.865	0.069	0.175	0.003	0.147	0.047	4.596
Oregon	4.750	0.010	0.526	0.090	0.039	0.546	0.015	0.012	5.987
Pennsylvania	0.165	6.220	2.680	1.390	2.720	0.461	0.287	0.264	14.187
Rhode Island	0.008	0.001	0.070	0.002	0.038	0.015	0.000	0.004	0.138
South Carolina	0.117	0.583	0.233	0.064	0.683	0.001	0.006	0.011	1.698
South Dakota	0.039	0.000	0.013	0.005	0.032	0.003	0.007	0.001	0.102
Tennessee	0.155	4.530	0.813	0.850	0.021	0.086	0.053	0.074	6.583
Texas	10.100	2.870	3.820	0.284	0.038	0.029	0.343	0.258	17.742
Utah	1.760	0.044	0.545	0.052	0.060	0.100	0.013	0.003	2.577
Vermont	0.001	0.000	0.014	0.002	0.063	0.004	0.004	0.001	0.089
Virginia	0.022	0.445	0.154	0.172	0.587	0.018	0.016	0.015	1.428
Washington	3.830	0.058	1.640	0.525	0.216	0.315	0.082	0.052	6.718
West Virginia	0.010	2.630	0.432	0.911	0.398	0.130	0.022	0.278	4.811
Wisconsin	1.550	3.630	1.350	0.517	0.286	0.144	0.333	0.027	7.837
Wyoming	2.580	0.009	0.214	0.023	0.052	0.021	0.025	0.129	3.051
United States	184.6	122.01	55.5	23.2	17.4	5.97	4.60	3.52	416.8

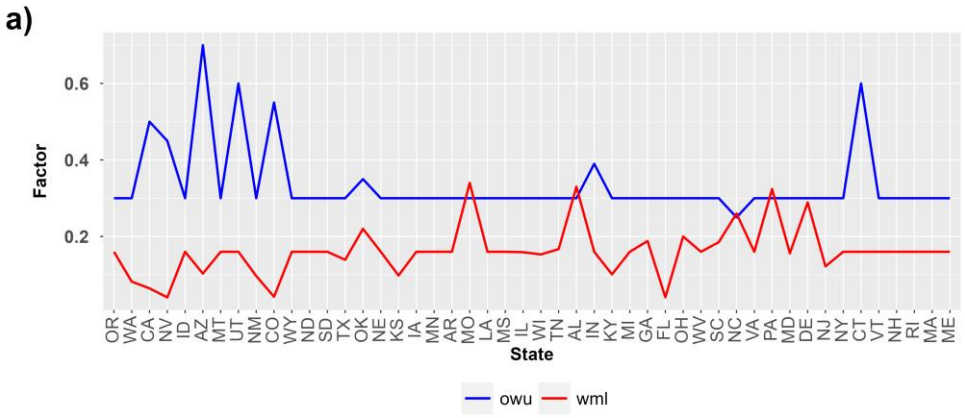
Appendix 11. The population density for counties across the United States, in units of people km^{-2}.

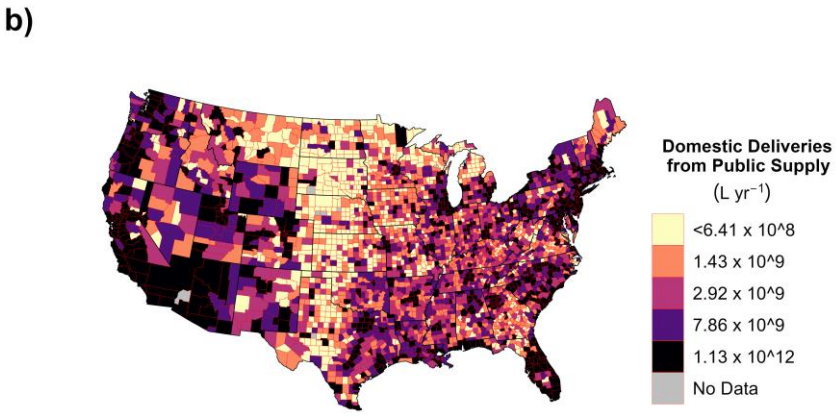


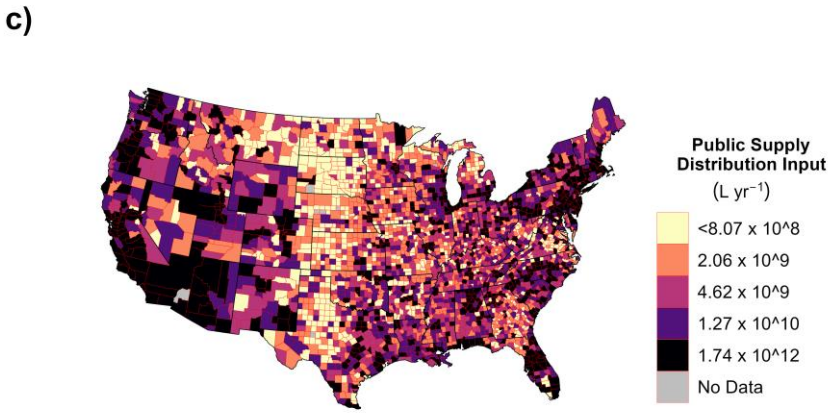
Appendix 12. Value and source of state-level leakage factors ($f_{leakage}$) and watermains leakage PO_4 fluxes (WML-PO_4-P) for each state across the United States, in units of kt PO_4-P yr^{-1}.

State	$f_{leakage}$	Source of $f_{leakage}$	WML-PO_4-P		
			Lower	Median	Upper
Alabama	0.33	American Water Works Association (2021)	0.041	0.091	0.150
Arizona	0.103	Jernigan et al. (2018)	0.017	0.039	0.064
Arkansas	0.16	National average - USEPA (2013)	0.006	0.013	0.022
California	0.0644	California Department of Water Resources (2019)	0.022	0.044	0.067
Colorado	0.0424	American Water Works Association (2021)	0.001	0.002	0.003
Connecticut	0.16	National average - USEPA (2013)	0.013	0.029	0.048
Delaware	0.289	American Water Works Association (2021)	0.007	0.017	0.028
Florida	0.041	American Water Works Association (2021)	0	0	0
Georgia	0.188	Georgia EPD (2016)	$1.57x10^{-4}$	$3.16x10^{-4}$	$4.76x10^{-4}$
Idaho	0.16	National average - USEPA (2013)	$1.72x10^{-5}$	$3.89x10^{-5}$	$6.39x10^{-5}$
Illinois	0.159	Illinois Department of Natural Resources (2015)	0.048	0.108	0.178
Indiana	0.16	Indiana Finance Authority (2016)	0.007	0.017	0.027
Iowa	0.16	National average - USEPA (2013)	0.016	0.004	0.006
Kansas	0.0981	American Water Works Association (2021)	0.003	0.002	0.003
Kentucky	0.101	American Water Works Association (2021)	0.004	0.016	0.026
Louisiana	0.16	National average - USEPA (2013)	0.013	0.036	0.06
Maine	0.16	National average - USEPA (2013)	0.019	0.007	0.012
Maryland	0.156	Maryland Department of the Environment (2015)	0.020	0.008	0.013
Massachusetts	0.16	National average - USEPA (2013)	0.008	0.029	0.047
Michigan	0.16	National average - USEPA (2013)	0.019	0.042	0.07
Minnesota	0.16	Nelson and Steidel (2019)	0.020	0.045	0.074
Mississippi	0.16	National average - USEPA (2013)	0.008	0.018	0.029
Missouri	0.34	American Water Works Association (2021)	0.003	0.007	0.011
Montana	0.16	National average - USEPA (2013)	0.001	0.002	0.004
Nebraska	0.16	National average - USEPA (2013)		0.001	0.001
Nevada	0.0407	American Water Works Association (2021)	0.001	0.002	0.004
New Hampshire	0.16	National average - USEPA (2013)	0.002	0.005	0.008
New Jersey	0.122	Kunkel Water Efficiency Consulting (2017)	0.033	0.074	0.122
New Mexico	0.0966	American Water Works Association (2021)	$6.36x10^{-5}$	$1.43x10^{-5}$	$2.35x10^{-4}$
New York	0.16	National average - USEPA (2013)	0.043	0.098	0.161
North Carolina	0.26	American Water Works Association (2021)	0.068	0.154	0.254
North Dakota	0.16	National average - USEPA (2013)	0.004	0.009	0.014
Ohio	0.2	American Water Works Association (2021)	0.055	0.123	0.203
Oklahoma	0.22	American Water Works Association (2021)	0.010	0.023	0.038
Oregon	0.16	National average - USEPA (2013)	0.001	0.001	0.002
Pennsylvania	0.324	American Water Works Association (2021)	0.142	0.321	0.528
Rhode Island	0.16	National average - USEPA (2013)	0.002	0.004	0.006
South Carolina	0.185	American Water Works Association (2021)	0.021	0.046	0.0766
South Dakota	0.16	National average - USEPA (2013)	0.002	0.005	0.009
Tennessee	0.167	American Water Works Association (2021)	0.014	0.032	0.053
Texas	0.139	American Water Works Association (2021)	0.021	0.047	0.077
Utah	0.16	National average - USEPA (2013)	$5.23x10^{-5}$	$1.18x10^{-4}$	$1.94x10^{-4}$
Vermont	0.16	National average - USEPA (2013)	0.001	0.002	0.003
Virginia	0.16	National average - USEPA (2013)	0.007	0.016	0.026
Washington	0.082	AQUEOUS / Amy Vickers & Associates (2016)	0.001	0.002	0.003
West Virginia	0.16	National average - USEPA (2013)	0.004	0.008	0.014
Wisconsin	0.153	American Water Works Association (2021)	0.012	0.028	0.046
Wyoming	0.16	National average - USEPA (2013)	$3.96x10^{-5}$	$8.94x10^{-5}$	$1.47x10^{-4}$
United States	-	-	0.695	1.59	2.56

Appendix 13. a) Value of state-level outdoor water use and leakage factors (f_{owu} and $f_{leakage}$) across the United States from west to east. b) County-level volumetric rate of domestic water deliveries from public supply, sourced from Dieter et al. (2018) and courtesy of the US Geological Survey c) County-level volumetric rate of public supply distribution inputs, sourced from Dieter et al. (2018) and courtesy of the US Geological Survey.







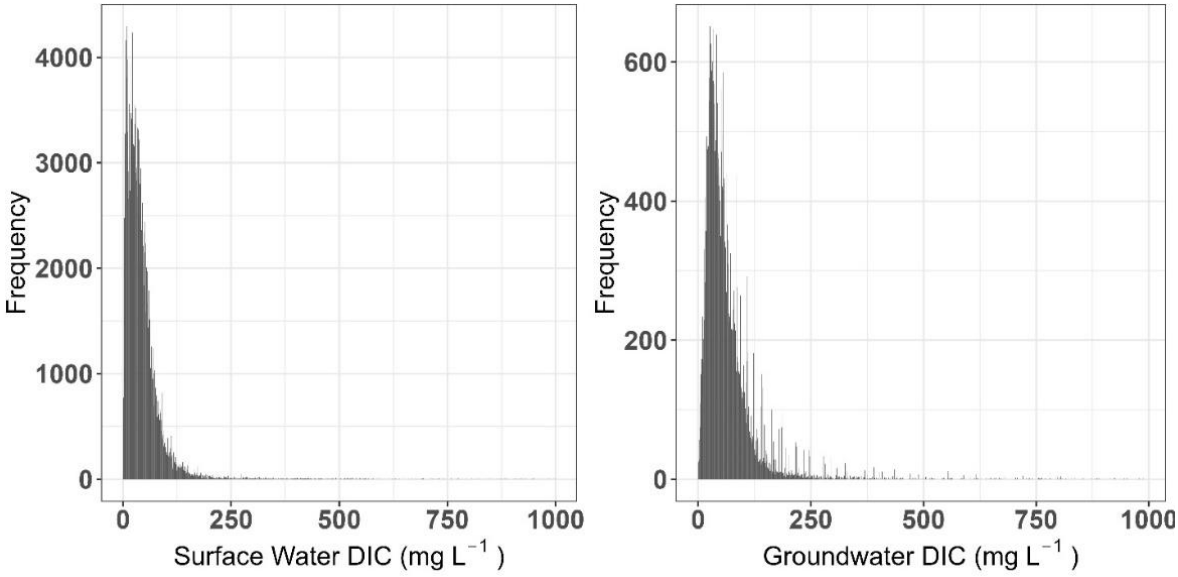
Appendix 14. Source and value of state-level outdoor water use factors (f_{owu}) and outdoor water use fluxes (OWU-PO_4-P) for each state across the United States, in units of kt PO_4-P yr^{-1}.

State	f_{owu}	Source of f_{owu}	OWU-PO_4-P		
			Lower	Median	Upper
Alabama	0.3	USEPA (2017)	0.014	0.031	0.051
Arizona	0.7	Arizona Department of Water Resources (2022)	0.097	0.218	0.358
Arkansas	0.3	USEPA (2017)	0.007	0.016	0.027
California	0.5	Hodel and Pittenger (2015)	0.135	0.304	0.498
Colorado	0.55	Waskom and Neibauer (2014)	0.009	0.021	0.034
Connecticut	0.6	Wallace and Siegel-Miles (2017)	0.019	0.042	0.069
Delaware	0.3	USEPA (2017)	0.005	0.012	0.020
Florida	0.3	USEPA (2017)	0	0	0
Georgia	0.3	USEPA (2017)	0.001	0.002	0.003
Idaho	0.3	USEPA (2017)	$2.53x10^{-5}$	$5.70x10^{-5}$	$9.36x10^{-5}$
Illinois	0.3	Schneemann (2014)	0.053	0.119	0.196
Indiana	0.3	USEPA (2017)	0.008	0.018	0.030
Iowa	0.3	USEPA (2017)	0.001	0.003	0.005
Kansas	0.3	USEPA (2017)	0.001	0.003	0.005
Kentucky	0.3	USEPA (2017)	0.012	0.027	0.044
Louisiana	0.3	USEPA (2017)	0.025	0.026	0.092
Maine	0.3	USEPA (2017)	0.003	0.006	0.009
Maryland	0.3	USEPA (2017)	0.004	0.009	0.015
Massachusetts	0.3	USEPA (2017)	0.011	0.026	0.043
Michigan	0.3	USEPA (2017)	0.015	0.034	0.055
Minnesota	0.3	USEPA (2017)	0.017	0.039	0.065
Mississippi	0.3	USEPA (2017)	0.010	0.022	0.035
Missouri	0.3	USEPA (2017)	0.001	0.003	0.004
Montana	0.3	USEPA (2017)	0.001	0.002	0.004
Nebraska	0.3	USEPA (2017)	$4.48 x10^{-4}$	0.001	0.002
Nevada	0.45	Nevada Irrigation District (2022)	0.007	0.015	0.024
New Hampshire	0.3	USEPA (2017)	0.002	0.005	0.009
New Jersey	0.3	USEPA (2017)	0.035	0.080	0.131
New Mexico	0.3	USEPA (2017)	$1.19x10^{-4}$	$2.67x10^{-4}$	$4.39x10^{-4}$
New York	0.3	USEPA (2017)	0.090	0.202	0.332
North Carolina	0.25	North Carolina Division of Pollution Prevention and Environmental Assistance (2009)	0.035	0.079	0.130
North Dakota	0.3	USEPA (2017)	0.004	0.010	0.017
Ohio	0.3	USEPA (2017)	0.036	0.082	0.135
Oklahoma	0.35	Moore et al. (2020)	0.007	0.017	0.028
Oregon	0.3	USEPA (2017)	0.001	0.002	0.003
Pennsylvania	0.3	USEPA (2017)	0.049	0.110	0.180
Rhode Island	0.3	USEPA (2017)	0.002	0.004	0.006
South Carolina	0.3	USEPA (2017)	0.025	0.056	0.093
South Dakota	0.3	USEPA (2017)	0.003	0.006	0.010
Tennessee	0.3	USEPA (2017)	0.014	0.032	0.053
Texas	0.3	USEPA (2017)	0.037	0.084	0.138
Utah	0.6	Utah State University (2022)	$1.57x10^{-4}$	$3.55x10^{-4}$	$5.82x10^{-4}$
Vermont	0.3	USEPA (2017)	0.001	0.001	0.002
Virginia	0.3	USEPA (2017)	0.009	0.021	0.034
Washington	0.3	USEPA (2017)	0.002	0.004	0.007
West Virginia	0.3	USEPA (2017)	0.004	0.008	0.013
Wisconsin	0.3	USEPA (2017)	0.012	0.026	0.043
Wyoming	0.3	USEPA (2017)	$7.06x10^{-5}$	$1.59x10^{-4}$	$2.62x10^{-4}$
United States	-	-	0.825	1.86	3.1

Appendix 15. The mass flux of PO_4 added by public water systems to distribution networks for the purpose of corrosion control (DOSE-PO_4-P_{pws}) for each state across the United States, in units of kt PO_4-P yr^{-1}.

State	DOSE-PO_4-P_{pws}		
	Lower	Value	Higher
Alabama	0.123	0.275	0.455
Arizona	0.169	0.377	0.624
Arkansas	0.036	0.082	0.135
California	0.421	0.944	1.56
Colorado	0.022	0.048	0.080
Connecticut	0.081	0.181	0.300
Delaware	0.026	0.058	0.095
Florida	0	0	0
Georgia	0.005	0.011	0.019
Idaho	$1.08x10^{-4}$	$2.41x10^{-4}$	$3.99x10^{-4}$
Illinois	0.302	0.676	1.12
Indiana	0.046	0.103	0.170
Iowa	0.010	0.022	0.037
Kansas	0.009	0.020	0.034
Kentucky	0.070	0.158	0.261
Louisiana	0.101	0.225	0.373
Maine	0.020	0.044	0.073
Maryland	0.023	0.052	0.086
Massachusetts	0.080	0.178	0.294
Michigan	0.118	0.263	0.436
Minnesota	0.125	0.281	0.465
Mississippi	0.049	0.109	0.181
Missouri	0.009	0.020	0.033
Montana	0.006	0.014	0.024
Nebraska	0.002	0.004	0.007
Nevada	0.024	0.054	0.090
New Hampshire	0.014	0.032	0.053
New Jersey	0.270	0.604	1.00
New Mexico	0.001	0.001	0.002
New York	0.271	0.607	1.00
North Carolina	0.263	0.590	0.975
North Dakota	0.024	0.053	0.088
Ohio	0.273	0.612	1.01
Oklahoma	0.047	0.105	0.174
Oregon	0.003	0.008	0.013
Pennsylvania	0.440	0.985	1.63
Rhode Island	0.010	0.022	0.037
South Carolina	0.111	0.249	0.412
South Dakota	0.015	0.033	0.055
Tennessee	0.085	0.191	0.317
Texas	0.150	0.337	0.557
Utah	$3.27x10^{-4}$	$7.32x10^{-4}$	0.001
Vermont	0.006	0.013	0.021
Virginia	0.043	0.097	0.161
Washington	0.010	0.022	0.037
West Virginia	0.023	0.052	0.085
Wisconsin	0.081	0.182	0.302
Wyoming	$2.48x10^{-4}$	$5.55x10^{-4}$	$9.18x10^{-4}$
United States	4.00	9.00	14.9

Appendix 16. Histograms showing the distribution of fresh surface water and groundwater dissolved inorganic carbon concentration data points used within this thesis. The non-normal distribution (right skewness) of measured and modelled DIC concentration data provided justification for adopting median county-level DIC concentrations within DIC flux calculations. These plots support results of a Kolmogorov-Smirnov test (p-value < 0.05), that also indicates the non-normal distribution of DIC concentrations.



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