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Seasonal Patterns of Carbon, Nitrogen, and Phosphorus Concentration and Speciation in Contrasting River–Lake Networks

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by

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Abstract

In many catchments, lakes and rivers are not isolated from each other but are hydrologically connected as part of integrated freshwater networks which control the transport, fate and impacts of elements, matter and energy. These river–lake networks are potentially important regulators of carbon (C), nitrogen (N) and phosphorus (P) during transport of these critical elements between terrestrial and marine ecosystems. However, despite conceptual development of the river-lake network framework, very little empirical research has examined how natural lakes influence the concentration and speciation of N, P and C in a network context. The research reported in this thesis sought to address this key research gap, focussing on how seasonal change through spring to summer, lake trophic status, and annual average water retention time influenced the impacts of natural lakes on the concentration and speciation of N, P and C in river networks. Based on a programme of coupled field and laboratory research, these questions were explored in exemplar lake-river networks in the English Lake District. Synoptic sampling of inflow river, lake and outflow river sites was conducted within two contrasting river-lake networks between March and July 2025. The resulting data reveal how lakes significantly altered the concentration and speciation of nutrient elements within river networks. Compared to inflow rivers, lakes increased DOC concentrations by an average of 78% (0.52 mg C/L) across both river-lake networks and all sampling dates, whilst also driving changes in spectrophotometric parameters describing the quality of the dissolved organic matter. Within the more eutrophic river-lake network, the natural lake switched between a substantial source (+92% or 0.29 mg N/L) and sink (-78% or 0.34 mg N/L) for nitrate across the spring-summer period, and consistently acted as a sink for soluble reactive phosphorus. Importantly, lake effects on the concentration and speciation of N, P and C persisted for several kilometres in the downstream river of both river-lake networks, demonstrating the potential for natural lakes to impose extensive impacts on river biogeochemistry. These findings highlight the key role that river-lake networks play in the transport of macronutrients through the freshwater interface between terrestrial and marine ecosystems.

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Abbreviations

AMP – adenosine monophosphate

ATP – adenosine triphosphate

BDOC – biodegradable dissolved organic carbon

BOP – bioavailable organic phosphorus

C – carbon

CH_4 – methane

CO_2 – carbon dioxide

CPOM – coarse particulate organic matter

DIC – dissolved inorganic carbon

DIN – dissolved inorganic nitrogen

DNA – deoxyribonucleic acid

DOC – dissolved organic carbon

DOM – dissolved organic matter

DON – dissolved organic nitrogen

DOP – dissolved organic phosphorus

EC – electrical conductivity

ELD – English Lake District

FPOM – fine particulate organic matter

HABs – harmful algal blooms

HCO_3^- – bicarbonate

RNA – ribonucleic acid

LDOC – labile dissolved organic carbon

N, N_2 – nitrogen

NH_3 – ammonia

NH_4^+ – ammonium

NO_3^- – nitrate

NO_2^- – nitrite

NPOC – non-purgeable organic carbon

OC – organic carbon

OP – organic phosphorus

P – phosphorus

P/R – primary production and respiration

RCC – river continuum concept

SDC – serial discontinuity concept

SDOC – semi-labile dissolved organic carbon

SFCA – surfactant free cellulose acetate

SRP – soluble reactive phosphorus

SUP – soluble unreactive phosphorus

$SUVA_{254}$ – specific ultraviolet absorbance at 254 nm

TDN – total dissolved nitrogen

TDP – total dissolved phosphorus

UK – United Kingdom

USEPA – United States Environmental Protection Agency

USGS – United States Geological Survey

UV – ultraviolet

VPDB – Vienna PeeDee Belemnite

WWTP – wastewater treatment plant

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Chapter 1: Introduction, Aims, Objectives and Thesis Structure

1.1. Background

Eutrophication is perhaps the most significant water quality issue facing surface waters worldwide, and is primarily caused by increased loads of the biologically essential nutrients nitrogen (N) and phosphorus (P) entering receiving waters from surrounding catchment areas. Increased N and P loads can drive significant changes in the rate of production and community composition within the autotrophic components of aquatic food webs, principally algae and macrophytes. In turn, these changes can result in a wide range of adverse ecological effects including harmful algal blooms (HABs), reduced water transparency, oxygen depletion or anoxia from organic matter decomposition, increased frequency of fish mortality events, diminished biodiversity, and declines in fishery yields (Correll, 1998; Fink et al., 2018; Qin et al., 2012; Smith & Schindler, 2009). Whilst additional factors such as increasing water temperature under climate change scenarios may play an important role (Kosten et al., 2012), the intensification of eutrophication processes observed in surface waters across recent years has been mainly driven by increased loads of N and P. HABs are one of the primary social and economic concerns associated with nutrient enrichment and associated detrimental impacts within lake and river ecosystems, leading to longstanding and intensive calls for these ecosystems to be actively restored (Gulati et al., 2012; Spears, 2014). Nitrogen and P are typically the primary limiting nutrients for the cyanobacterial growth that underpins the risk of HABs, because these nutrients directly constrain photosynthetic C fixation. Therefore, the sources, cycling and export to receiving waters of N, P and C within catchments are of significant interest, with calls being widely made to better incorporate coupled N and P control within future eutrophication management strategies (Dodds & Smith, 2016).

However, at the same time, C remains much more scarcely studied as a factor contributing to the control of aquatic communities in lakes and rivers, particularly organic carbon (OC) (Bai et al., 2023; Kragh & Sand-Jensen, 2018; Schindler et al., 2016; Seekell et al., 2015; Urban et al., 2005). Organic carbon provides a substrate for heterotrophic bacteria and fungi, supporting secondary production. These heterotrophic processes are also central to ecosystem functioning, for example, by influencing nutrient recycling and oxygen dynamics (Brett et al., 2017). Carbon has multiple roles in aquatic ecosystems: dissolved inorganic carbon (DIC; CO_2/HCO_3^-) is the immediate substrate for photosynthesis, whilst dissolved organic carbon (DOC) mostly affects algae and cyanobacteria indirectly by fuelling heterotrophic microbial production and nutrient recycling. Additionally, some freshwater cyanobacteria and marine picocyanobacteria can employ photoautoheterotrophy and assimilate certain organic substrates (Joset-Espardellier et al., 1978; Partensky et al., 1999; Rippka, 1972). Therefore, the specific control and regulation of C in freshwater also remain key priority areas in working towards understanding and managing sustainable aquatic ecosystems (Arp & Baker, 2007; Jarvie et al., 2018).

Nutrient elements are delivered to surface waters from a wide range of sources within catchments, varying in terms of physical and chemical form and in terms of bioavailability from source to source (Garzon-Garcia et al., 2018; Mayer et al., 1998). Nutrient loads from point sources (dominated by wastewater treatment plants, WWTPs, in many catchments) are typically highly bioavailable and usually contain considerable loads of readily degradable organic material (Mainstone & Parr, 2002). The diffuse nutrient loads from arable and livestock agricultural activities generally represent major nutrient contamination sources in rural catchments, rather than large-scale WWTPs, where high proportions of soluble P and N can occur when livestock excreta or soluble inorganic fertilisers are exported from land, particularly when heavy rainfall occurs soon after application of these materials (Carpenter, 2008; Chen et al., 2008; Mainstone & Parr, 2002). A diverse range of inorganic fertilisers represents key pollutants contributing to nutrient enrichment in freshwaters, with the range of compounds used in fertilisers continually evolving, for example from ammonium (NH_4^+)-nitrate (NO_3^-) to urea in the context of N (Chen et al., 2008; Paerl et al., 2016). The diffuse, or non-point source, nutrient loads exported from agriculture also contribute significantly to eutrophication within freshwaters (Kronvang et al., 1995; Zhang et al., 2014). For example, agricultural runoff is widely recognised as a primary threat to the quality of water in China (Yang et al., 2013) and as a very significant challenge for freshwaters across large parts of Europe and North America (Smith & Schindler, 2009). Nutrient loads identified as responsible for stimulating and intensifying eutrophication within individual freshwaters on a global-scale, including through HABs and toxin generation, are also important for N and P loads delivered via freshwater networks to a range of downstream ecosystems, including rivers, lakes, wetlands, estuaries and, ultimately, coastal marine ecosystems (Belisle et al., 2016; Dodds & Smith, 2016; US EPA, 2008). The importance of this network perspective to the understanding of the fate and impacts of nutrients in freshwaters underpins a significant component of the research reported later in this thesis.

1.2. Sources, mobilisation, transformation and fate of C, N and P

Substantial research in recent decades has characterised lakes and rivers as hot spots of C cycling in the landscape, acting both as conduits for the transport and cycling of inorganic C and as locations for mineralisation and other transformations of terrigenous organic carbon (OC) (Cardille et al., 2007; Cole et al., 2007; Hanson et al., 2004; Hanson et al., 2011). Atmospheric carbon dioxide (CO_2) is absorbed by terrestrial plants during photosynthesis, with a fraction of this CO_2 released back to the atmosphere through respiration (Field et al., 1998). Carbon incorporated by plants within lignin and cellulose can ultimately represent as much as 80% of the OC in forests and 60% in grasslands (Martens et al., 2004; Bose et al., 2009). Litterfall and root OC exudates subsequently contribute to organic matter within soils which is mixed with inorganic sedimentary material, and where plant-derived and petrogenic OC are both stored and transformed by microbial and fungal activity (Ward et al., 2017). As rainfall travels across forest canopies and down stems, it entrains DOC and DIC originating from plants and atmospheric aerosols (Qualls & Haines, 1992, Fig. 1). In the areas without forest cover, such as grassland, DOC and DIC inputs to grassland could arise from plant litter, root exudates and soil organic matter leaching, and when above the threshold of grassland water demand further rainfall may replenish ground water reserves, and subsequently flow into drainage channels and rivers (Ayling et al., 2021). Infiltration may deliver solute-laden water to soil solutions and groundwater, whereas overland flow is generated once soils reach saturation or precipitation exceeds infiltration capacity (Ward et al., 2017), with these surface or subsurface transport pathways ultimately coalescing into rivers and lakes. Inland and coastal aquatic systems play a significant role in the global C cycle by processing both terrestrial and autochthonous OC (Asmala et al., 2018; Liu et al., 2021; McCallister et al., 2018; Xia et al., 2023). Within river networks, microbial and abiotic processes such as photo-oxidation drive the decomposition of OC, resulting in substantial CO_2 emissions to the atmosphere, comparable to terrestrial C sequestration (Raymond et al., 2013). Whilst lakes, reservoirs, and floodplains store large amounts of OC, they are typically net heterotrophic and also emit CO_2 and methane, albeit at lower rates than rivers (Tranvik et al., 2009; Raymond et al., 2013). Estuarine and coastal ecosystems, despite supporting elevated primary production compared to many upstream ecosystems due to increased nutrient availability, often remain net sources of atmospheric CO_2 (Cai, 2011; Cooley et al., 2007; Subramaniam et al., 2008). Coastal marshes contribute to both C sequestration and emission, whereas continental shelves and the open ocean act as CO_2 sinks through long-term burial via the biological pump, a process whereby phytoplankton fix inorganic C (e.g. atmospheric CO_2) into organic matter that is transferred to the deep ocean through sinking particles and subsequent burial (Cai, 2011; Moore et al., 2011; Moran et al., 2016; Odum et al., 1979; Wehrli, 2013).

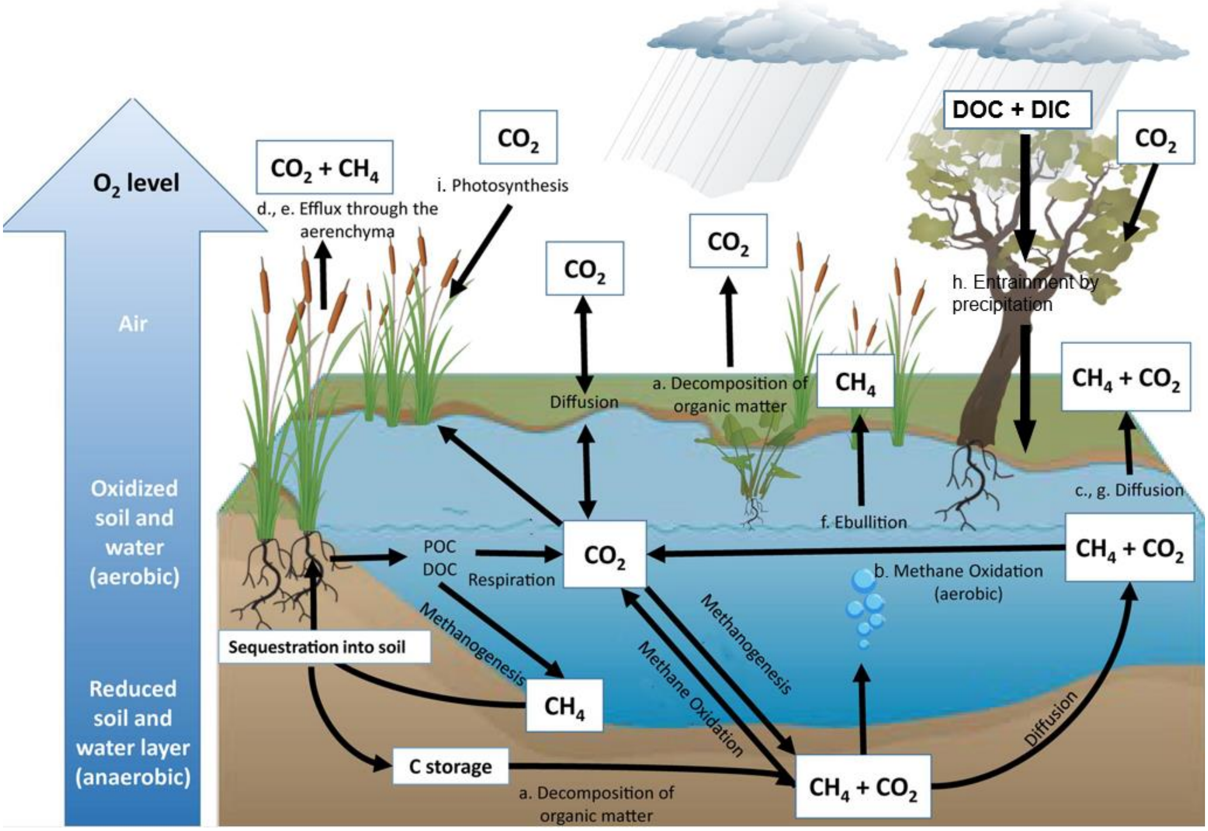

Fig. 1. Representation of the inland C cycle, adapted from Limpert et al. (2020). Major pathways of CO_2 emissions include respiration during decomposition of organic matter (a), oxidation of methane (CH_4) (b), diffusion (c), and release of greenhouse gases through plant aerenchyma (d). Major pathways of CH_4 emissions include methanogenesis via efflux through plant aerenchyma (e), ebullition (f), and diffusion

(g). Major pathways of carbon deposition include entrainment by precipitation (g) and photosynthesis (i).

Phosphorus (P) is an essential element that controls metabolic processes within all life, being integral to the structure and function of key biomolecules including DNA, RNA, adenosine triphosphate and phospholipids (Pasek et al., 2014; White & Metcalf, 2007). With the exception of trace emissions of phosphine from volcanoes, the P compounds found on the surface of the Earth are not volatile and transport through the atmosphere is primarily in dust or aerosols (Correll, 1998). Phosphorus only occurs in the pentavalent form and is delivered to aquatic systems as a mixture of dissolved and particulate inputs, each of which is a complex mixture of different molecular forms of pentavalent P. Examples are orthophosphate, pyrophosphate, longer-chain polyphosphates, organic phosphate esters and phosphodiesters, and organic phosphonates.

Human society has profoundly altered the global P cycle, primarily by mining phosphate rock to support the synthesis of inorganic fertilisers and widespread application to agricultural land, and by significantly changing the pathways of P losses from land to water (Yuan et al., 2018). Modern agriculture is now heavily dependent on regular applications of phosphate fertilisers produced from mined phosphate rock, which replenish the P removed from soils during crop growth and harvesting (Cordell et al., 2009). This large scale mobilisation of P has led to a dramatic increase in the availability of reactive P in the environment, with significant quantities ultimately lost to freshwater ecosystems through diffuse agricultural runoff and wastewater discharges (Elser & Bennett, 2011).

Urbanisation has further intensified these fluxes, where the global population excretes around 3 million tonnes of P annually, and with over half of humanity now living in cities, sewage has become a major source of P to rivers and lakes (FAO, 2007). Nutrients in human excreta were historically tightly recycled back to agricultural land, but today are more commonly discharged into waterways or are buried in landfills (Cordell et al., 2009).

Over-fertilisation of agricultural soils, particularly in the northern hemisphere has also contributed to widespread increases in P losses, with close to 25% of the 1 billion tonnes of P mined since 1950 estimated to have been transferred to aquatic systems or disposed of in landfills (Cordell et al., 2009; Rosmarin, 2004). In addition, a striking dual challenge or paradox surrounds P: whilst P scarcity raises concerns about long-term fertiliser security, excessive P leakage continues to drive eutrophication, HABs, and water quality deterioration worldwide (Cordell et al., 2009). Surface waters receive most of their P via surface runoff pathways, rather than via subsurface flow within deeper groundwater pathways, due to the capacity for many soils and sediments to bind significant quantities of phosphate (Yuan et al., 2018). Once P is delivered to rivers, lakes, reservoirs and estuaries, it may be efficiently assimilated by biota or adsorbed to inorganic sediments, subsequently being deposited within bed sediments in these aquatic ecosystems and creating a legacy of P enrichment that means these systems remain sensitive to pollution with excess P over the long-term.

Organic phosphorus (OP) compounds, those containing both C and P atoms, exist in dissolved and particulate forms in aquatic ecosystems, with multiple hydrolysis pathways able to transform these compounds into orthophosphate that is bioavailable to aquatic organisms (Correll, 1998). In aquatic ecosystems, P dynamics are closely dependent on ecosystem trophic status. For example, in oligotrophic lakes, P stocks within bed sediments are largely retained due to persistent oxygenation of bottom waters. However, seasonal or diurnal bottom-water deoxygenation within more eutrophic lake ecosystems can trigger the release of sediment-bound P back into the water column, potentially exacerbating nutrient enrichment and eutrophication (Correll, 1998).

In aquatic environments, OP occurs in diverse chemical forms, including nucleic acids, nucleotides, inositol phosphates, phospholipids and phosphonates (Baldwin, 2013). Nucleic acids (DNA and RNA), mainly derived from algae and bacteria, may contribute to relatively stable OP pools through interactions with particles (Bravo et al., 2010; Shinohara et al., 2012). Nucleotides such as 5’-triphosphate (5’-ATP) and adenosine 5’-monophosphate (5’-AMP), typically present at low concentrations, but can be highly dynamic and represent a rapidly cycling source of P, particularly in oligotrophic systems (Azam & Hodson, 1977). These compounds may also participate in microbial communication processes such as quorum sensing (Bruns et al., 2003). Inositol phosphates originate largely from plant and agricultural sources (e.g. manure and plant-derived feed) and may also be produced in situ by aquatic plants including

Spirodela sp. (Brearley & Hanke, 1996) and Azolla sp. (Benaroya et al., 2004). However, their bioavailability remains uncertain and varies among organisms (Baldwin, 2013). Phospholipids can be transported with humic materials within lotic systems and may serve as an important P source, especially in oligotrophic environments (Mills et al., 1996; Van Mooy, B. A. et al., 2008). Phosphonates remain less well known, though evidence suggests they could represent an overlooked contributor to aquatic P cycling (Baldwin, 2013; Benitez-Nelson et al., 2004).

In terrestrial N cycling, N is fixed by biologically mediated processes and released back to the atmosphere primarily through denitrification with a smaller contribution from nitrous oxide losses during nitrification (Gruber & Galloway, 2008). Nitrogen is transferred from land to the oceans primarily via riverine runoff and atmospheric deposition, where it supports marine productivity and is eventually transformed into gaseous compounds through denitrification (Field et al., 1998). However, human activities (i.e. synthetic fertiliser production, fossil fuel combustion, and cultivation) have significantly altered the N cycle by introducing large inputs of reactive N compounds to terrestrial ecosystems (Batjes, 1996; Fixen & West, 2002). These anthropogenic sources amplify N fluxes to aquatic environments, disrupting natural feedbacks and intensifying downstream effects such as eutrophication and greenhouse gas emissions. In lakes and rivers, N can be influenced via multiple processes including fixation, nitrification, denitrification and assimilation by aquatic organisms (Burgin & Hamilton, 2007). These processes can transform the physical and/or chemical form of N, for example across multiple inorganic compounds from ammonia through nitrite to NO_3^-, or between inorganic compounds and the wide range of N-bearing organic compounds, or between dissolved and gaseous forms of N (Fig. 2).

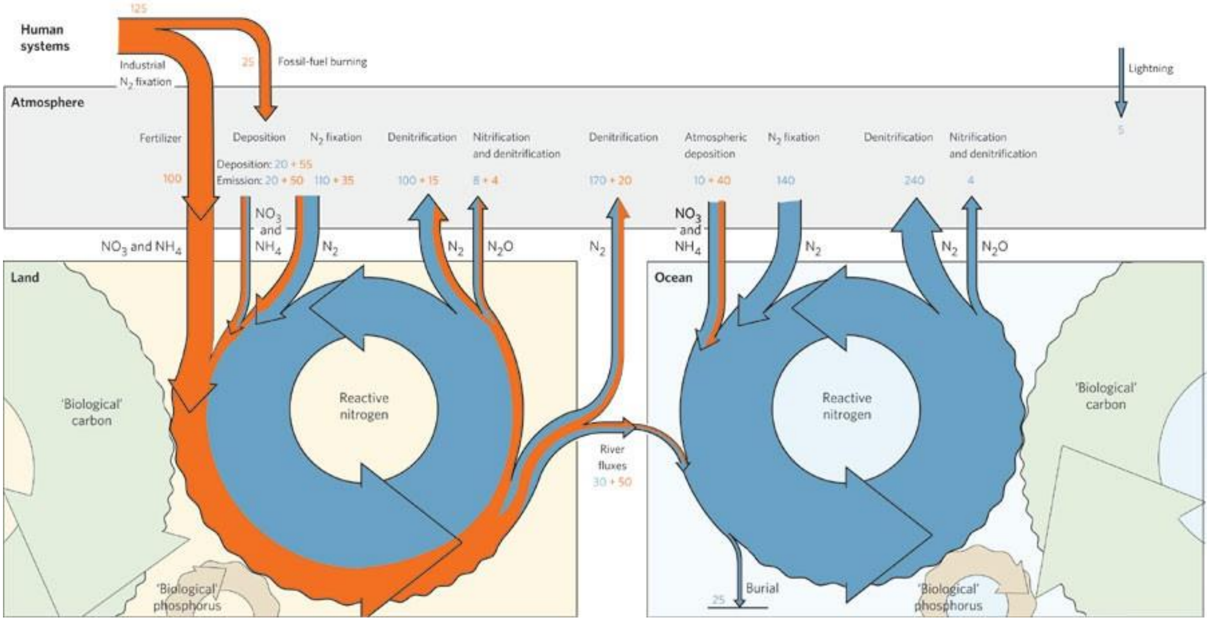

Fig. 2. Depiction of the global N cycle (adapted from Gruber and Galloway, 2008). Major processes that transform molecular N into reactive N, and back, are shown. Also shown is the tight coupling between the N cycles on land and in the ocean. Blue fluxes indicate 'natural' fluxes; orange fluxes indicate anthropogenic perturbation.

1.3. Nutrients in river-lake networks at the freshwater interface

This thesis is concerned with the role of freshwater ecosystems in the transport of N, P and C within the Earth system. In this context, freshwater ecosystems are increasingly recognised as being located at the critical interface between terrestrial and marine systems (Bouwman et al. 2013; Beusen et al. 2016). Global riverine N and P transport to the oceans through this interface has increased during the 20th century, despite increased retention of these nutrient elements along the aquatic continuum (Beusen et al., 2016). Historically understood to conservatively transport allochthonous inputs from terrestrial environments towards downstream ecosystems, more recent research has emphasised the highly biogeochemically reactive nature of the freshwater interface (e.g. Cheng & Basu 2017; Marcé et al., 2018).

However, although research focussed on eutrophication and nutrient biogeochemistry in lakes and rivers is pervasive, this work to date has largely viewed lakes and rivers as separate, disconnected systems. An integrated perspective which seeks to understand and synthesise the combined effects of lakes and rivers has not been given nearly enough attention. In many freshwaters, lake and river ecosystems are not isolated from each other, but are instead hydrologically connected within integrated river-lake networks. Lakes potentially introduce environmental changes to the continuum of the river network, resulting in differences between parameters and processes upstream and downstream of these discontinuities. However, very little empirical research has adopted a network perspective to examine how natural lake discontinuities control the fate of nutrients within interconnected freshwaters. This thesis seeks to address this issue, by explicitly adopting a river-lake network perspective to examine key aspects of C, N and P transfer through the freshwater interface.

The river continuum concept (RCC) was first developed by Vannote et al. (1980) building on a substantial body of background research (Fig. 3). The RCC provided a groundbreaking concept through which stream ecosystems could be understood as a cohesive sequence of physical gradients and corresponding adjustments in the stream's biotic, physical and chemical composition (Vannote et al., 1980). The RCC was subsequently further developed by Minshall et al. (1985), and Vannote and Minshall (1982), integrating broader spatial and temporal dimensions, covering climate and geology, tributaries, location-specific lithology and geomorphology, and long-term changes introduced by human activity. However, as a framework the RCC is constrained to be relevant only in rivers that have a strong longitudinal connection, such as within lakeless streams in forested catchments that can exhibit continuous downstream trends. In contrast, the RCC is not appropriate for unconstrained reaches (Poole, 2002), or river systems that exhibit other discontinuities within the upstream to downstream network.

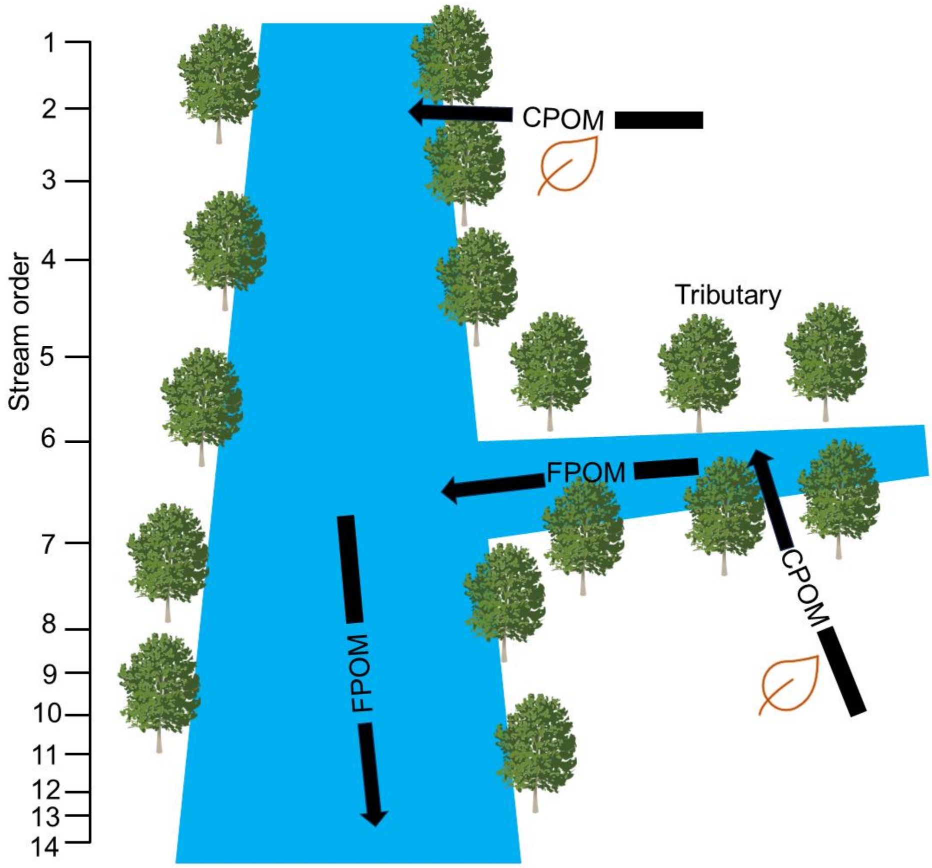

Fig. 3. Illustration of the River Continuum Concept (adapted from Doretto et al., 2020). Headwaters are narrow, shaded, and fuelled by coarse particulate organic matter (CPOM), supporting heterotrophic food webs (primary production and respiration (P/R) < 1) with shredders that generate fine particulate organic matter (FPOM) for collectors. Mid-order streams receive more light, shifting to autotrophy (P/R > 1) with abundant periphyton grazers (scrapers), whilst FPOM still supports collectors. In large rivers, depth and turbidity limit primary production, making them heterotrophic again (P/R < 1), with food webs dominated by FPOM collectors and filter feeders.

Subsequently, Stanford and Ward (1983, 1995) discussed the serial discontinuity concept (SDC) in order to emphasise the need for a perspective on biotic communities and ecosystem processes within rivers that was less strongly based on a single continuum that progressed from headwaters to the oceans. Specifically, the SDC began to consider how discontinuities introduced by human action disturbed the river continuum, with a particular focus on the role of artificial impoundments along river networks (Ward & Stanford, 1995). These artificial discontinuities were understood to be able to 'reset' the river continuum, introducing significant change in multiple physical, chemical and biological properties within river networks, including to processes controlling nutrient biogeochemistry (Ward & Stanford, 1995).

However, Jones (2010) was the first to explicitly develop a conceptual framework for coupling rivers/streams and natural lakes within an integrated stream-lake network perspective. The stream-lake network can be conceptualised using a schematic figure (Fig. 4). Lake-effect streams have one or more lakes on their drainage network (for example Lake 1 receives inputs from two rivers flowing through one inlet; Lake 2 receives input from one inlet, which is also the outflow from Lake 1, etc. Lake 3 receives input not only from the outlet of Lake 2, but also the outlet of Lake 4, which originates from a tributary. Fig. 4).

Lake effects have the potential to impact multiple physical, chemical or biological attributes of outlet streams compared to inlet streams. The influences of a lake within the network will differ depending on drainage patterns. For example, a single lake in the midreach of a trellis network may alter ecological characteristics for a substantial distance downstream, because these lake effects are ‘protected’ for a certain distance downstream from other network branches that may cause dilution of the lake effects (Jones, 2010). In contrast, the same lake effects located in a dendritic basin will likely be more rapidly diluted by tributaries compared to the trellis network (Jones, 2010). The configuration of inlet and outlet streams may also influence the extent to which lake effects are introduced within the river network (Fig. 5). For example, a lake with inlets and outlets at positions shown in Fig. 5a may provide greater opportunity for lake effects to be exerted compared to the situation in Fig. 5c, because the latter configuration offers the chance for short circuiting of lake effects (Jones, 2010). Further, more significant lake effects may be expected when a low flux stream discharges into a large lake, generating a low flushing rate (Fig. 5b), compared to a large stream discharging into a small lake with a smaller flushing rate (Fig. 5d). Finally, the extent of lake effects on downstream river ecosystems generally decreases as water discharge within the downstream river increases, and as distance downstream of the lake increases, both reflecting the opportunity for groundwater and tributary inflow to reduce the lake effect signal (Jones, 2010).

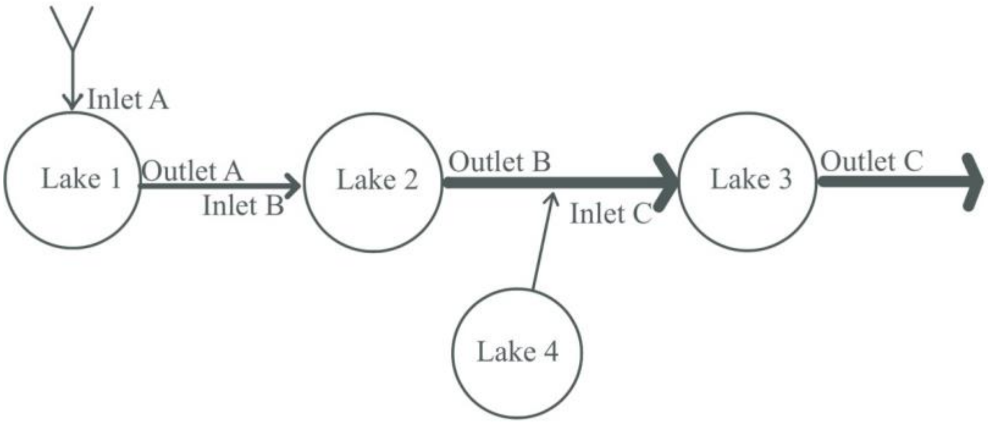

Fig. 4. Stream-lake network schematic image (adapted from Jones, 2010).

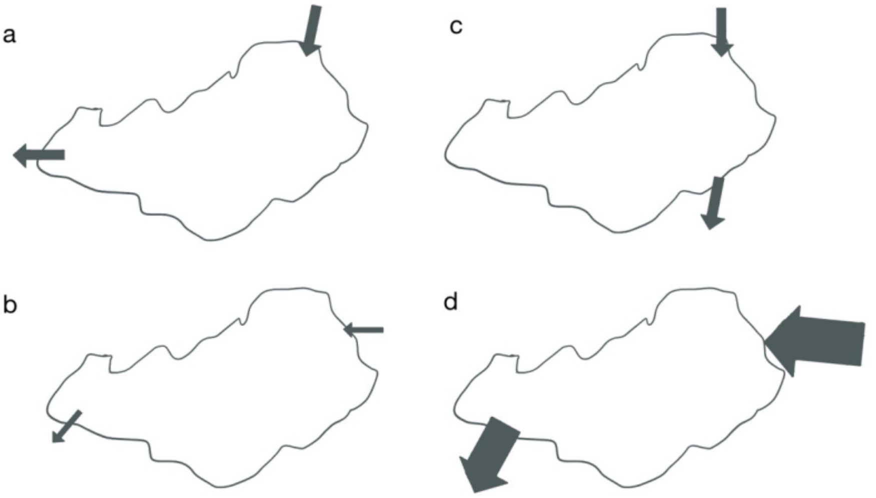

Fig. 5. Effects of inlet and outlet stream configuration on lake effects. Arrows indicate the direction and magnitude of river flow (adapted from Jones, 2010).

Despite the development of conceptual frameworks such as the river–lake network theory of Jones (2010), empirical research explicitly examining how natural lake discontinuities regulate the fate of nutrients in connected freshwaters remains scarce. The limited studies available suggested that nutrient concentrations and limitation patterns can vary significantly along stream–lake networks. For example, downstream declines in primary productivity and particulate N, P and C concentrations have been observed below natural lake discontinuities (Kling et al., 2000), whilst NO_3^- and NH_4^+ dynamics indicate only partial satisfaction of inorganic N demand and moderate uptake rates downstream of natural lakes (Koch, 2005). Further research has suggested contrasting patterns of nutrient limitation between inlets, which are often P-limited, and outlets, which tend to be N-limited, across river-lake networks (Arp & Baker, 2007). Broader syntheses further emphasise the importance of nutrient enrichment, with evidence of significant increases in both N and P across river networks globally (Dodds & Smith, 2016; Jarvie et al., 2018), but organic matter dynamics within this network context remain comparatively understudied (Jones, 2010). Whilst some past research suggests that river–lake transitions may alter nutrient availability and patterns of nutrient limitation, most existing work has focussed narrowly on inorganic N and P. In contrast, scarce attention has been paid to DOC concentrations, the quality of dissolved organic matter (DOM) as may be characterised using optical properties such as SUVA_{254} or $\alpha_{250}:\alpha_{250}$, or the role of natural lakes in controlling particulate organic matter cycling rather than cycling of dissolved nutrient fractions, leaving substantial gaps in understanding. Addressing a number of these gaps, the present study investigates how these carbon-related parameters, alongside fractions of N and P, vary across stream–lake discontinuities, thereby providing novel insights into the biogeochemical functioning of river–lake networks.

Substantial research evidence focussed on nutrient biogeochemistry within freshwaters has underpinned significant advances in the management of nutrient elements, including C, P and N, in order to protect and restore freshwaters at risk of eutrophication. Despite this, significant gaps in understanding N, P and C biogeochemistry within the reactive freshwater interface remain. In particular, rather than considering processes within lakes or rivers separately, an integrated river-lake network framework has not been extensively applied to nutrient biogeochemistry within freshwaters (Jarvie et al., 2018). In this context, this thesis contributes new knowledge to the field of nutrient biogeochemistry within coupled river-lake networks, with particular attention paid to the role of seasonal changes and lake trophic status in these freshwater networks. It is envisaged that the research reported within this thesis may contribute to a more comprehensive and integrated understanding of nutrient cycling within aquatic ecosystems, potentially leading to more sustainable management of these ecosystems in the future.

1.4. Thesis Aims and Objectives

The overall aim of this thesis is to advance understanding of how integrated river-lake networks control nutrient (C, N and P) cycling at the freshwater interface, with particular attention paid to the role of lake trophic state and season in determining the nature of this control. Two specific thesis objectives lead from this aim:

1. Synthesise and review nutrient biogeochemistry literature within lakes and rivers, as well as the emerging river-lake network literature, to establish key research questions related to the fate of C, P and N within river-lake networks, focussed particularly on the role of lake trophic status and of season;
2. Develop and implement a programme of field and laboratory research to address the key research questions developed under 1. above, evaluating spatiotemporal patterns in C, N, and P cycling within exemplar river-lake networks.

1.5. Thesis Structure

This thesis is presented in the form of three chapters. The current chapter (Chapter 1) provides an introduction to the broader context and background for the research reported within this thesis, including a summary of the overarching aims, objectives and structure of the thesis. In Chapter 2, a literature review is presented that examines the key processes and controlling factors that influence C, N and P cycles within lakes and rivers. This review focusses particularly on the role of lake trophic status and season, in order to develop key research questions for the thesis related to the potential influence of natural lakes on N, P and C cycles within river-lake networks. These key research questions are reported at the end of Chapter 2, leading into Chapter 3 which reports a novel programme of coupled field and laboratory research designed to address these research questions. Working within two exemplar, contrasting river-lake networks in the English Lake District, Chapter 3 examines the impact of natural lakes on the concentration and speciation of C, N and P within river networks through the biologically critical spring-summer period of 2025.

Chapter 2: Literature Review

2.1. Introduction

Freshwater ecosystems play a disproportionately large role in the global C cycle because lakes and reservoirs do not merely passively transmit terrestrial organic matter, but instead serve as sites where multiple processes including the transformation, respiration, burial and export of OC operate, with important consequences for regional C balances and atmospheric CO_2 exchange (Evans et al., 2017; Tranvik et al., 2009). The reactivity of DOC, and whether a water body behaves as a net DOC source or sink, depend strongly on water residence time and trophic status. For example, short-residence time systems are often dominated by rapid light-driven removal of DOC, whereas longer-residence time systems are governed more strongly by slower biotic production and mineralisation of DOC (Hanson et al., 2014). Despite a potentially critical role for inland waters, C cycling within freshwater networks, and specifically within natural lake-river networks, remains relatively understudied. Therefore, the present study addresses gaps in understanding of the C cycle within river-lake networks by measuring DOC, DOM optical properties and $\delta^{13}C$ across river–lake networks, to better resolve how lake discontinuities influence C sources, transformations and fate in river-lake networks.

Total organic carbon (TOC) refers to the total amount of organic C present in a water sample, encompassing both DOC and particulate organic carbon (POC). DOC is usually the dominant fraction of organic C in freshwater ecosystems, and can be an order of magnitude higher than that of POC in some freshwater lakes (Minor & Oyler, 2021). In addition to OC, inorganic C is present either as DIC, including carbon dioxide (CO_2) and bicarbonate (HCO_3^-) or as particulate inorganic carbon (PIC), such as carbonate minerals. Biotic processes within freshwater networks are important controls on DIC cycling. For example, the actual concentration of DIC is lowered by photosynthesis, drawing down CO_2 to undersaturation, whilst coupled photosynthesis and respiration alter pH potentially to extents that can vary the principal molecular hosts of dissolved inorganic carbon (DIC) between CO_2 and HCO_3^- (Balmer et al., 2011; Verschoor et al., 2013). Therefore, although this thesis focuses on OC, it is recognised that inorganic C dynamics are integral to the overall C cycle in freshwaters, influencing processes such as CO_2 evasion, buffering capacity, and long-term C storage.

2.2. Dissolved organic carbon sources and transport within freshwater ecosystems

Major DOC sources to freshwaters are generally considered to be allochthonous inputs from terrestrial catchments and autochthonous production by phytoplankton, benthic algae, and aquatic macrophytes within lakes or rivers (Bertilsson & Jones, 2003; Qualls & Haines, 1992; Ward et al., 2017). Allochthonous DOC mainly originates from soils and terrestrial vegetation, which act as large organic matter pools, and can be mobilised into streams and lakes through surface runoff, groundwater flow, or atmospheric deposition (Godin et al., 2017; Minor & Olyer, 2021; Sobek et al., 2007). In addition, wastewater effluents, agricultural runoff, and other human activities may also serve as important catchment-derived sources of DOC (Wu et al., 2023). Autochthonous DOC is mainly produced within freshwaters by decomposition of aquatic organisms (e.g. phytoplankton, benthic algae, and aquatic macrophytes) and can also be released from sediments (Sobek et al., 2007; Wu et al., 2023). DOC from surrounding catchments is shaped by factors such as land use, geology, climate, and human activity, which act as significant controls on both DOC concentration and composition in freshwaters. Therefore, allochthonous DOC represents a critical linkage in the C cycle between terrestrial and aquatic systems, as subsequently among aquatic ecosystems themselves.

The transport of allochthonous DOC from terrestrial to aquatic environments is often enhanced by increases in precipitation and hydrological connectivity, which facilitate the export of DOC from soils (Mulholland, 2003). Many studies have shown that the export of DOC from terrestrial soils to freshwaters increases with higher precipitation, surface, or subsurface runoff (Mulholland, 2003). However, Sobek (2007) demonstrated the opposite correlation, where higher runoff volume was strongly negatively related to lake DOC concentration. This has been attributed to reduced contact time between rapidly transported runoff and soil organic pools, limiting the dissolution and mobilisation of DOC into receiving waters. Precipitation itself may also exert variable effects, as it does not consistently influence DOC concentrations in either net-heterotrophic or net-autotrophic lakes (Kritzberg et al., 2006). In the study of the budget and cycle for DOC in Lake Superior, precipitation contributed 0.1 Tg C yr^{-1} (10%) inputs, indicating its impact is relatively limited (Urban et al., 2005). Once released into aquatic systems, DOC can undergo mineralisation to CO_2, be assimilated into microbial biomass (e.g. algae and bacteria), or become incorporated into more persistent C pools, including long-lived dissolved, particulate, and sedimentary forms through biological and photochemical processes (Godin et al., 2017; Minor & Oyler, 2021; Sobek et al., 2007).

2.3. Particulate organic carbon sources

Dissolved and particulate organic carbon are operationally separated by filtration, with particulate organic carbon (POC) defined as material retained on a filter with a pore size of 0.45 μm, and DOC as material passing through the filter. POC is a key component of the lake OC cycle and has a significant regulatory effect on organic and inorganic C pools. It also plays a crucial role in the transport and cycles of macronutrients, such as N and P, metal and organic contaminants that are incorporated within the particulate material (Adams et al., 2015; Foster et al., 2000). In a similar manner as described above for DOC, POC can be separated into autochthonous and allochthonous sources. The contribution of autochthonous POC within lakes is mainly influenced by photosynthesis and respiration from phytoplankton, benthic algae and macrophytes, with dissolved oxygen concentration, secchi depth (and therefore light availability), and water temperature acting as key controlling factors for photosynthesis and therefore autochthonous POC production within the epilimnion of lakes (Wang et al., 2022). Moving from the epilimnion to the hypolimnion of lakes, allochthonous POC increasingly dominates in the proportion of POC, as can be inferred by the diminishing density of phytoplankton cells (Wang et al., 2022). In eutrophic lakes, phytoplankton-induced primary productivity contributes to the major allochthonous POC input to the hypolimnion (Jones et al., 2012).

2.4. Organic carbon fate and ecological impacts

Within river networks, terrestrial OC together with OC derived from autochthonous primary production is decomposed by microbial communities and by abiotic processes such as photo-oxidation, producing CO_2 emissions from rivers to the atmosphere that are comparable to the annual C uptake of the terrestrial biosphere (Cole et al., 2007; Raymond et al., 2013). Large terrestrial macromolecules such as lignin, are progressively cleaved into smaller fractions and monomers, eventually being respired to CO_2, assimilated into microbial biomass, or transformed into metabolic intermediates (Myers-Pigg et al., 2015). For example, a recent study elevated temperature enhanced both lignin/vanillin decomposition and CO_2 production (Li et al., 2025). Although lakes, reservoirs and floodplains store a considerable amount of OC and sediment, water columns are typically net heterotrophic, yielding atmospheric CO_2 fluxes approximately one order of magnitude lower than those of rivers (Tranvik et al., 2009; Raymond et al., 2013). The anoxic sediments of these systems also sustain elevated methane production (Bastviken et al., 2004). Despite enhanced primary production in river plumes driven by nutrient export, estuarine systems continue to act as a global source of atmospheric CO_2 (Cai, 2011; Cooley et al., 2007; Subramaniam et al., 2008). Coastal marshes both sequester and export "blue carbon" and likely emit CO_2 at rates comparable to rivers on a global scale (Dittmar et al., 2001; Moore et al., 2011; Odum et al., 1979; Wehrli, 2013). By contrast, continental shelves and the open ocean generally play a role as atmospheric CO_2 sinks, with a small fraction of the absorbed C ultimately buried as organic matter in marine sediments via the biological pump (Cai, 2011; Moran et al., 2016).

Carbon rarely serves as a constraint on primary production in rivers or streams due to sufficient DIC from carbonate rocks and the weathering of soils (Jarvie et al., 1997, 2017). However, it should be noted that cyanobacteria possess the ability to access additional inorganic C pools (e.g. HCO_3^-), if CO_2 becomes depleted during blooms (Miller et al., 1990; Price et al., 2008). Carbon cycling is possibly affected by cyanobacteria as they constitute a disproportionately large part of the total biomass of primary producers in eutrophic lakes. Dissolved organic carbon influences several properties in aquatic ecosystems, such as the heterotrophic production of fungi and bacteria, affecting epilimnetic and hypolimnetic respiration (Carpenter et al., 1998; Hanson et al., 2003; Houser et al., 2003). Coloured DOC can protect aquatic plants and animals from harmful ultraviolet (UV) radiation (Bade et al., 2007; Blanchet et al., 2022). Moreover, DOC may affect the thermal structure and mixing depth of lakes. For example, high DOC concentration may reduce radiation penetrating the surface, influencing primary productivity and heat transfer, due to the dark colour of many DOC compounds, which affects the concentrations of DOC in turn (Fee et al., 1996; Song et al., 2018).

Dissolved organic carbon also plays a key role in mediating the fate of heavy metals (i.e. cadmium, mercury) and persistent organic pollutants (POPs) by constituting complexes or participating in redox reactions and photoreactions, thereby affecting the bioavailability and transport of these elements and compounds in aquatic systems. Refractory DOC (RDOC) can form multiple complexes with heavy metals by soluble metal–organic complexes, increasing the solubility, mobility and affecting the bioavailability, toxicity and fate of metals (Jiang et al., 2017; Li & Zhou, 2010). Essential amino acids tend to interact with phenolic compounds rich in carbonyl groups, a process that can enhance the preservation of the amino acids in aquatic environments (Sammond et al., 2014). Quantification and identification of the DOC, as well as elucidation of its complex interactions with other organic and inorganic compounds, are required for further research.

2.5. Labile organic C and stable organic C

The definitions of labile and refractory organic C are somewhat ambiguous, as the specific timescales associated with "short-term" and "long-term" degradation can vary across different studies, ranging from hours to centuries (Ostapenia et al., 2009). Labile OC components in DOC and POC can be degraded in a relatively short time (days to weeks) by free-living or attached bacteria and protists; the decomposition of refractory (stable) organic C may take longer (Wetzel, 2001). The overall recalcitrance of any OC load, especially in terms of the biological availability of the OC, is very difficult to quantify. Some studies have applied biological oxygen demand (BOD) determinations in aquatic research to quantify OC lability (Fallon & Brock, 1979; Jonas & Tuttle, 1990; Ostapenia et al., 2009).

The composition of OC strongly influences its fate and impacts within aquatic environments (He et al., 2020). Labile compounds with low molecular weight, such as sugars, peptides, and amino acids can be easily degraded or assimilated by heterotrophic bacteria and rapidly recycled through microbial pathways within the aquatic food web (Doney, 2010). Similarly, non-humic organic matter with a high molecular weight (e.g. polysaccharides and proteins) is also considered relatively bioavailable and prone to microbial degradation (Benner & Amon, 2014). The proportion of biodegradable DOC within total DOC pools in aquatic environments varies widely, ranging from as low as 1% in humic substances to over 50% in labile or anthropogenically derived DOC (Meyer, 1994). The global average for biodegradable DOC (BDOC) is approximately 14% of the total DOC in lakes, whilst refractory organic carbon (RDOC) constitutes about 86% (Søndergaard & Middelboe, 1995). Despite anthropogenic urban runoff and wastewater effluent often carrying relatively low BDOC, they may greatly alter the natural water bodies into which they flow (Lv et al., 2024). For instance, municipal and industrial discharges contribute a large proportion of the DOC (and COD) increase in Dianchi Lake, with sewage effluent being a major source, and much of the input comprising refractory or difficult-to-degrade organic C (Guo et al., 2017). Both allochthonous DOC derived from catchment soils and from treated effluent display limited biodegradability, contributing to long-term accumulation in lacustrine environments (Nguyen & Hur, 2011). The biodegradability of OC in aquatic systems is influenced not only by the source and composition of the C pool, but also by environmental context and geographic factors such as latitude. High-latitude forests typically contain elevated levels of humic substances and lignin, combined with lower microbial activity due to cooler temperatures, which results in the water column containing OC with lower biodegradability. Conversely, coastal waters in low-latitude regions tend to exhibit higher microbial activity driven by warmer ambient temperatures, thereby enhancing the degradation of organic C (Lv et al., 2024).

Spectrophotometric indices have been widely adopted to assess the quality of DOC and its relative lability or recalcitrance. In particular, the specific ultraviolet absorbance at 254 nm ($SUVA_{254}$) has been shown to correlate strongly with the aromatic C content of DOC, thereby serving as a reliable proxy for the refractory and less bioavailable fractions (Weishaar et al., 2003; Spencer et al., 2009). In addition, absorbance ratios such as $\alpha_{254}:\alpha_{365}$ provide information on average molecular size, with higher ratios indicating the presence of relatively smaller, more labile organic molecules (Assaad et al., 2015). These indices enable a rapid, cost-effective characterisation of DOC pools in aquatic systems. They are employed to infer the quality of C and to link spectrophotometric properties between labile and stable organic C.

2.6. Isotopes of C applied to the investigation of organic carbon biogeochemistry

Natural abundance stable (^{12}C, ^{13}C) and/or radiocarbon (^{14}C) isotopes have been applied for investigating organic carbon (OC) sources and C cycling in the oceans (Bauer et al., 2002), estuaries (Peterson et al., 1994), rivers (Raymond and Bauer, 2001; Kaiser et al., 2004), and lakes (Bade et al. 2007; Karlsson et al., 2007; McCallister and del Giorgio, 2008).

Natural-abundance radiocarbon (^{14}C) has been applied to investigate OC dynamics in aquatic environments, offering a valuable complement to traditional C budget assessments and studies on C reactivity through photochemical and microbial processes (McNichol & Aluwihare, 2007). Radiocarbon's half-life of 5730 years generally leads to dating typically being used to trace C cycling over centennial to millennial timescales (Godwin, 1962). However, the artificial introduction of ^{14}C into the global C cycle during the 1950s atmospheric nuclear weapons testing has enabled the extension of radiocarbon applications to decadal timescales (Minor & Oyler, 2021). The atmospheric ^{14}C has been redistributed into terrestrial and aquatic C reservoirs such as vegetation, soils, and oceanic DIC, depending on their respective exchange dynamics with the atmosphere. In aquatic C studies, radiocarbon content is commonly expressed as $\Delta^{14}C$, a standardised metric that accounts for isotopic fractionation and is normalised to a reference value set as zero for the year 1950 (Stuiver & Polach, 1977). An increase in positive $\Delta^{14}C$ values indicates that recent C exchange with the atmosphere, whilst negative or zero values reflect older or pre-bomb C sources, with more negative (or ^{14}C-depleted) values meaning older C pools. (McNichol and Aluwihare 2007). In addition to constraining DOC sources, isotopic data has also been used to study DOC reactivity, indicating that apparently refractory DOC (in terms of radiocarbon age and thermal lability) is consumed on seasonal timescales, perhaps due to priming effects (Minor & Oyler, 2021).

Stable carbon isotopes ($\delta^{13}C$) provide an important tool for tracing sources and transformation processes of organic matter in aquatic ecosystems. Unlike radiocarbon (^{14}C), which constrains carbon age and residence time, $\delta^{13}C$ primarily reflects fractionation during C fixation and subsequent microbial or abiotic processing. This makes stable isotope measurements especially valuable for evaluating pathways of primary production, organic matter degradation, and C cycling within lakes and rivers. Distinct $\delta^{13}C$ signatures of autochthonous phytoplankton, terrestrial inputs, and anthropogenic sources allow partitioning of POC and DOC into their respective origins. Moreover, isotopic fractionation during processes such as respiration, methanogenesis, and photo-oxidation further modifies $\delta^{13}C$ values, thereby providing insights into transformation mechanisms and metabolic fluxes. As reviewed by Meyers

(2003), compound-specific isotope analysis has advanced this field by enabling the study of individual biomarker molecules, linking isotopic patterns directly to biochemical pathways and environmental conditions. In the context of this study, $\delta^{13}C$ of POC can thus be used not only to distinguish allochthonous versus autochthonous carbon sources but also to assess seasonal variability in carbon cycling and its relation to nutrient dynamics.

2.7. Phosphorus biogeochemistry in river-lake networks

Allochthonous phosphorus (P) inputs, including both organic P and inorganic P species, are key triggers for eutrophication in river-lake networks and a range of associated adverse impacts, such as algal blooms. In the absence or minimal presence of anthropogenic sources of P, natural sources dominate the inputs to aquatic ecosystems. These natural sources primarily include the weathering of soil parent materials, atmospheric deposition, input from shoreside vegetation and soil erosion, and release of P from aquatic organisms during metabolism or following death and cell lysis (Withers & Jarvie, 2008). Anthropogenic inputs of P to river-lake networks are primarily derived from wastewater, either within municipal or private infrastructure, or from runoff from impervious and pervious surfaces in agricultural or urban areas in which P is present within these surfaces. Transfers of P from anthropogenic sources to receiving waters in catchments can either be continuous or intermittent in nature. In contrast to the continuous input of P from final wastewater treatment work effluent, diffuse urban and agricultural sources of P are largely mobilised during intermittent rainfall-runoff events. The pattern of runoff generation is dependent on stochastic patterns of rainfall and represents a semi-continuous supply of mobilised P throughout the year, because ‘impervious’ surfaces have no, or very limited, infiltration capacity even in rural areas (Withers et al., 2009). For example, it was reported in Scotland that storm runoff from farmyards contained very large TP concentrations, with the majority in soluble reactive phosphorus (SRP) form (Edwards et al., 2008). In forestry, cultivated land and pasture, as rainwater passes over or through the soil at various rates, it facilitates the mobilisation and transport of both inorganic and organic P via surface and subsurface hydrological pathways, ultimately delivering them to receiving water bodies (Withers & Jarvie, 2008).

As initially introduced in Chapter 1, phosphorus typically enters aquatic ecosystems in the form of complex mixtures of physical and chemical form, but with P largely in the pentavalent form. Phosphorus is not a conservative element within aquatic ecosystems, and the initial physical and chemical speciation of P can be either chemically or enzymatically altered within these ecosystems. Many of these processes yield the orthophosphate ion, the only form of P readily assimilable by organisms. Once introduced into lakes, reservoirs or estuaries, phosphorus is often assimilated by biota and incorporated within biomass, or may be sorbed to particulate material and deposited within bottom sediments. Over recent decades, extensive research led many ecologists to conclude that P is the key factor limiting primary production in lakes and rivers (Edmondson, 1970; Peterson et al., 1985), whilst marine environments were understood to be more strongly limited by the availability of N (Nixon, 1980; Ryther & Dunstan, 1971). Although both rivers and lakes may demonstrate P limitation, primary production within lakes is often more responsive to phosphorus input, since rivers generally do not develop prolonged anoxic conditions necessary for substantial phosphate release from sediments, other than in cases where they are highly nutrient-enriched or with a sufficiently long water retention time (Correll, 1998). P uptake, turnover and regeneration times in streams can be on a shorter scale (seconds/minutes/hours) than those in lakes (Mulholland et al., 1997). P retention within rivers not only influences the magnitude and timing of P delivery to downstream aquatic systems, but can also modify the transported form of P, thereby affecting its bioavailability and ecological impact (Withers & Jarvie, 2008). P retention within riverine systems arises from a combination of biogeochemical and physical processes that act to temporarily remove or transform P during its downstream transport, thereby creating opportunities for both biotic uptake and abiotic assimilation (e.g. sediment adsorption or precipitation; Withers & Jarvie, 2008). These retention processes support ecosystem functioning by sustaining productivity in nutrient-poor headwaters and buffering anthropogenic P inputs during sensitive periods such as summer low flows (Triska et al., 1989; Svendsen et al., 1995).

2.8. The role of organic phosphorus in river-lake P biogeochemistry

Much past monitoring and research work has focussed on the importance of reactive P within freshwaters, in which reactive P has often been used as a surrogate for immediately bioavailable P. Bioavailable P represents those forms of P with the potential to be transported across a cell membrane and enter the intracellular environment to meet metabolic demand for P. Predominantly, although not exclusively, this is the orthophosphate ion. There is now increasing recognition of the potential importance of non-soluble reactive forms of P within freshwater ecosystems. Operationally, soluble non-reactive or soluble unreactive P (SUP) represents all forms of P that are <0.45 µm in size and do not react with the acidic molybdate reagent commonly used in colourimetric determination of SRP. Soluble unreactive P is sometimes conflated solely with organic P compounds. However, in the absence of direct quantification of individual organic P compounds, SUP is a surrogate measure of organic P concentration and can be prone to error. However, it is the case that a substantial proportion of SUP will likely be comprised of organic P compounds, containing C and P atoms alongside a range of other elements in the same molecule.

It is now increasingly recognised that research is required that focuses on the importance and dynamics of OP in aquatic environments, including evaluation of the fate and impacts of specific OP compounds or categories of OP compounds. For example, where the availability of orthophosphate is too low to meet metabolic demand for P, alternative sources of P may be accessed in order to yield bioavailable orthophosphate. Particulate forms of P require initial solubilisation in order to produce forms of P that are able to enter the intracellular environment. However, even after solubilisation, most organic P compounds are too large for direct diffusion across cytoplasmic cell membranes (Liang and Blake, 2006). Therefore, organic P must be hydrolysed through enzyme-mediated reactions involving phosphohydrolases that are either attached to the outside of a cell membrane or are secreted by organisms into the extracellular environment (Liang and Blake, 2006). These hydrolysis reactions cleave P-O bonds and release orthophosphate as a by-product that can subsequently be transported into a cell via diffusion or via ATP-driven pumps or transport proteins. Therefore, the role of OP within river-lake networks may be important not only as a component of P fluxes through these freshwater ecosystems, but also in terms of understanding how metabolic demands for nutrient resources within river-lake networks can be met.

Phosphorus is an essential component of nucleic acids and many intermediary metabolites, such as sugar phosphates, phospholipids, nucleic acids, and inositol phosphates Among these, the major bioavailable organic phosphorus (BOP) is monoester P and diester P (Copetti et al., 2019; Ni et al., 2019). Ni et al. (2019) concluded that stable DOM structure is responsible for decreasing the degradation and release of diester P. On the contrary, increasing algal biomass has been reported as promoting the degradation of diester P, suggesting that increases in algal production may be a potential contributor to enhanced releases of OP and increased eutrophication risk in downstream ecosystems.

2.9. Nitrogen cycles in rivers and lakes

The intensification of eutrophication risks in surface waters that has been observed in recent years is associated not only with increased loads of phosphorus (P), but also of N entering aquatic ecosystems. In this context, human activity, driven primarily by increasing global demand for food production, has approximately doubled the input of reactive N into the Earth’s ecosystems (Gruber & Galloway, 2008). However, much of this N is ultimately lost, either to the atmosphere as gaseous N or to aquatic ecosystems via surface or subsurface pathways, via a range of export processes that are controlled by many environmental factors (Janicka et al., 2022). Similarly to P, a wide range of sources of reactive N may influence nutrient availability within receiving waters, including wastewater, diffuse urban and agricultural pollution, and atmospheric deposition. Despite this, understanding of N transfer through freshwaters remains perhaps the most poorly constrained among the macronutrients, and there remains an urgent need to better understand the fate of N during transfer through these freshwater interfaces (Maranger et al. 2018).

Dissolved N in aquatic ecosystems exists in various forms, primarily as NO_3^-, but also as nitrite (NO_2^-), ammonium (NH_4^+), and organic nitrogen (ON). Organic nitrogen typically arises from the decomposition of organic matter and is converted to ammonium through mineralisation. Ammonium may then undergo nitrification, a microbial oxidation process that sequentially transforms it into nitrite and then NO_3^-.

Among these forms, NO_3^- is the most prevalent in freshwater due to its high solubility and mobility, being commonly derived from both nitrification and the application of nitrogen-based fertilisers (Causse et al., 2015). Once in aquatic environments, NO_3^- can be assimilated by primary producers, reduced to gaseous nitrogen via denitrification, or converted back into ammonium through dissimilatory reduction to ammonium under anoxic conditions (Robertson & Groffman, 2007).

2.10. Coupled biogeochemical cycles of C and N under anthropogenic influence

The acceleration of the reactive N cycle by anthropogenic activity is coupled with parallel alterations to the cycles of many other elements, most notably those of phosphorus, sulphur and C (Falkowski et al., 2000). The acceleration of the global C cycle is in part linked to perturbations of the global N cycle. For example, the atmosphere plays an efficient role in dispersing N oxides and ammonia generated from energy and food production, which are subsequently deposited in bioavailable forms that stimulate plant growth and enhance terrestrial as well as marine C uptake from the atmosphere (Gruber & Galloway, 2008). The coupled cycles of C and N are a direct consequence of the presence of metabolic processes supporting life, leading to fundamental coupling of the elemental cycles of C, N, and other elements at the molecular level, driven by the biological necessity of organisms to acquire these elements for tissue formation. This coupling operates through specific elemental stoichiometries, whose magnitude and variability influence both the rate and degree of integration among biogeochemical cycles (Sterner & Elser, 2003). For example, the C/N ratio of the autotrophic phytoplankton remains relatively consistent, whilst the more variable and generally higher C/N ratios are observed in terrestrial plants (Gruber & Galloway, 2008).

2.11. Impacts of seasons and trophic states on nutrients cycling in river-lake networks

Season is a significant factor influencing lake processes such as nutrient cycling, nutrient limitation, trophic control, productivity, precipitation and water temperature (Brown et al., 2004; Deng et al., 2019; Griffith & Golder, 2020; McCann et al., 1998). In dimictic lakes, stratification in summer and winter typically reduces water-column mixing, N fixation, and sediment phosphorus release, whereas spring and autumn turnover promote vertical mixing, sediment–water exchange, and microbial activity (Selig & Schlungbaum, 2003). These seasonal dynamics generate distinct nutrient patterns, with higher TN in spring and winter, but elevated TP in summer when sediment P release is enhanced (Xu et al., 2017; Wang et al., 2019). Such processes illustrate the importance of internal loading, which often sustains eutrophication and slows water-quality recovery despite reductions in external nutrient inputs (Janssen et al., 2019; Tong et al., 2019).

Seasonal variation is also reflected in the composition and transformation of DOC and POC. Sources of lacustrine POC generally include autochthonous POC, terrestrial POC, resuspended sediment POC, and bacterial POC (Zigah et al., 2012, 2017). These sources exhibit distinct seasonal patterns, particularly under regimes of winter mixing and summer stratification, with autochthonous POC dominating during mixing and contributing more strongly to the epilimnion than to the hypolimnion (Chen et al., 2018). Inlets may contain higher concentrations of DOC during snowmelt than their lakes, as a result of increasing runoff discharge in the catchment and dilution in lakes (Cory et al., 2007), whereas summer DOC (e.g. nonhumic quinone-like and amino acid-like fluorophores) can be degraded by UV photolysis, adsorption to sediments, and heterotrophic uptake (Miller & McKnight, 2010). Different fractions of DOC display seasonal contrasts, with relatively low concentrations of BDOC during summer and extremely low labile DOC (LDOC) during spring and summer, whereas semi-labile DOC (SDOC) and BDOC were considerably enriched during summer and fall (Bai et al., 2023; Zhou et al., 2021). However, mixing of terrestrial inputs with low lability may buffer DOC variability, resulting in mild seasonal differences between the dry and wet seasons (Mao & Li, 2019). Phytoplankton blooms further modulate C cycling, generating DOC during bloom and post-bloom periods (Begum et al., 2023; Bai et al., 2023). These studies highlight that external hydrological inputs and internal biogeochemical processes jointly drive the temporal variability of C pools in lakes.

The ecological consequences of these seasonal cycles differ across lakes of contrasting trophic status. In summer, increasing denitrification typically results in low NO_3^- concentration, whereas P within the sediment positively corresponds with TP concentration. Seasonal stratification variation influences the interactions among sediments, water and organisms, driving cycling processes of N and P. However, lake water has intensive turnover during spring and autumn, which is fundamental to impeding stratification. In eutrophic systems such as Lake Taihu and Lake Mendota, strong internal P release under summer stratification sustains phytoplankton blooms, whilst high grazing pressure and nutrient enrichment jointly regulate phytoplankton communities (Vanni & Temte, 1990; Wang et al., 2019). By contrast, in oligotrophic lakes, where external nutrient supply is low and internal recycling is weaker, phytoplankton productivity is often nutrient-limited and less responsive to seasonal stratification. Mesotrophic lakes occupy an intermediate state, with moderate seasonal variation in nutrient limitation and primary production (Finger et al., 2013; Rogers et al., 2020; Schulhof et al., 2019). Nutrient concentration and stoichiometry could control the nutrient limitation of primary producers, thereby affecting the bottom-up effect (Elser et al., 2000).

Meteorological factors such as precipitation further modulate seasonal nutrient dynamics by altering hydrological inputs and retention time. It has been demonstrated that increased runoff in the Maumee River basin enhances P delivery to Lake Erie during wet periods, intensifying productivity (Stow et al., 2015). Similarly, dissolved organic matter (e.g. DOC and DON) shows marked seasonal and spatial variation between inlets and outlets, reflecting hydrological controls on nutrient delivery and transformation (Kang et al., 2016). Overall, seasonal and trophic status interact to shape the timing, magnitude, and pathways of C, N, and P cycling in lakes, with eutrophic systems generally exhibiting stronger internal feedbacks than oligotrophic systems. These interactions are critical for understanding nutrient dynamics within river–lake networks and constitute the basis for the research questions explored in this thesis.

Recent research in Lake Malawi provides a notable example of how internal phosphorus dynamics can influence C fluxes in large tropical lakes. Based on observations of pCO_2 exchange, chlorophyll concentration, and carbon-to-phosphorus (C:P) ratios in upwelled waters, Ngochera and Bootsma (2020) concluded that Lake Malawi behaves as a net autotrophic system, in contrast to other large lakes such as Lake Superior. This autotrophic tendency appears to stem from the lake’s meromictic structure and anoxic deep waters, which facilitate P mobilisation whilst limiting OC remineralisation at depth. The upwelling of P-enriched deep water into P-depleted surface layers stimulates phytoplankton growth, thereby enhancing atmospheric CO_2

uptake. Such findings highlight the critical role of internal nutrient cycling and vertical mixing in modulating the metabolic balance of deep tropical lakes.

It is widely recognised that changes in inflow, outflow, water level and resulting water retention time also directly affect the cycling of nutrient elements within lakes. Soares et al. (2012) demonstrated that variability in biomass in Funil Reservoir is strongly correlated with water retention time. Precipitation directly impacts stream discharge, in turn, it determines the water retention time of the lakes, especially for short retention time lake systems (Jones & Elliott, 2007). For example, Grasmere is a lake located in the English Lake District with an approximate 30-day retention time. Reynolds & Lund (1988) describe how the populations of phytoplankton in Grasmere could be significantly altered during periods of heavy rainfall, with subsequent consequences for nutrient cycling within the lake. Further, Talling (1993) hypothesised that the different chlorophyll-a concentrations between Blelham Tarn and Esthwaite Water, two lakes with similar mean depth, light penetration and nutrient availability, in winter could be explained by differences in water retention time between these two systems.

The aim of this chapter has been to synthesise knowledge regarding key factors that control the cycling of C, N and P across river-lake networks, including those related to the sources, mobilisation, transport and fate of these elements. Further, the chapter has introduced the importance of seasonal variation within natural lakes, of the trophic status of natural lakes, and of water residence time within natural lakes for determining the influence of natural lakes on C, N and P cycles. However, despite the conceptual development of the river-lake network framework by Jones (2010), key empirical tests of this framework remain to be undertaken. In this context, Chapter 3 that follows describes a programme of empirical field and laboratory research designed to address the following core research questions within this thesis:

1. How do natural lakes within river-lake networks alter the concentration and speciation of the coupled macronutrient elements C, N and P during transport through these freshwater ecosystems?
2. How does the impact of natural lakes on C, N and P cycles within river-lake networks vary through the ecologically critical spring-summer season?
3. To what extent does the impact of natural lakes on C, N and P cycles within river-lake networks depend on lake trophic status and/or average annual water residence time?

Chapter 3: Influence of Seasonal Variation and Trophic State on Nutrient Dynamics in River–Lake Networks

3.1. Methodology

3.1.1. Selection of river-lake networks for field programme of research

Catchments selected for the research reported in this thesis included two contrasting lakes and four associated rivers located at both the inlets and outlets of these lakes. The resulting two river-lake networks were located in catchments within the northwestern and southeastern English Lake District (ELD), Cumbria, UK, hereafter termed the Ennerdale-network and the Esthwaite-network (Fig. 7, Table 1). These networks comprised sampling sites located across main inflow and outflow rivers as well as within two natural lakes, with each river–lake network containing a single natural lake discontinuity in the network. The research reported in this thesis employed a synoptic sampling strategy to capture near-instantaneous snapshots of biogeochemical conditions within each river–lake network. This sampling strategy allowed the research to address the main objective of the thesis, which was to investigate how natural lakes influence the biogeochemistry of river-lake networks across upstream-to-downstream river reaches, focussed on contemporaneous changes in a network context.

The Ennerdale Water is characterised by steep topographical relief, particularly along its southern perimeter, which imposes significant logistical constraints on fieldwork. Consequently, accessible areas for sampling are restricted to the north-western and northern shores (Fig. 7). The northern reaches of the catchment are partially utilised for forestry. The catchment is predominantly occupied by acid grassland, followed by coniferous woodland and heather comprising the secondary and tertiary land cover types, respectively (Fig. 6). This composition suggests a landscape dominated by semi-natural vegetation and relatively low nutrient loading from the surrounding terrain.

In contrast, the Esthwaite Water occupies a more subdued landscape with gentle altitudinal gradients, which facilitated more extensive anthropogenic development, with dense human settlements concentrated primarily in the north (the primary inflow passing through) and the south-east. The catchment is dominated by improved grassland, indicating a higher degree of agricultural intensification compared to the Ennerdale Water. This is followed by broadleaved woodland and coniferous woodland, reflecting a more managed and nutrient-enriched terrestrial environment.

The two study sites are situated in close proximity within the Cumbria (UK), and thus experience a comparable temperate maritime climate.

Table 1. Lake and associated catchment characteristics for the two river–lake networks used in the research reported in this thesis (adapted from Maberly et al., 2016).

Lake	Ennerdale Water	Esthwaite Water
Lake trophic states	Oligotrophic	Mesotrophic
Mean total phosphorus (mg m^{-3})	5.6	35.8
Mean chlorophyll-a (mg m^{-3})	0.9	19.1
Maximum phytoplankton chlorophyll-a (mg m^{-3})	1.2	32.7
Lake surface area (km^2)	3.0	1.0
Mean Depth (m)	17.8	6.9
Volume (m^3 x 10^6)	53.2	6.7
Approx. mean retention time (d)	200	100
Main inflow river	River Liza	Black Beck
Main outflow river	River Ehen	Cunsey Beck
Catchment area (ha)	4346.25	1700.75

The two lakes (Ennerdale Water and Esthwaite Water) were selected to span a range of average water residence times, trophic states, and broader lake and catchment characteristics (Table 1). Identifying two contrasting river-lake networks was important in order to address the research questions at the heart of this thesis, particularly how lake trophic status influences the changes introduced by natural lakes to C, N and P biogeochemistry in river-lake networks. Both catchments are affected, but to varying extents, by anthropogenic activity including atmospheric deposition of nutrients, agricultural production, and resident/visitor human population (Fig. 6). In particular, the catchment of Esthwaite Water is associated with a much greater proportion of improved grassland than the catchment of Ennerdale Water, reflecting increased intensity of agricultural production within the Esthwaite Water catchment. Whilst still low in absolute terms, the greater area of urban and suburban land within the catchment of Esthwaite Water compared to Ennerdale Water reflects the larger resident and visitor population within the catchment of Esthwaite Water. Increased agricultural intensity and elevated pressure from higher resident and visitor populations contribute to greater nutrient enrichment of Esthwaite Water compared to Ennerdale Water, as reflected in the trophic status, total P and chlorophyll-a data reported in Table 1. Indeed, Esthwaite Water is widely recognised as one of the most nutrient-enriched lakes within the ELD, providing a strong contrast with the oligotrophic status of Ennerdale Water.

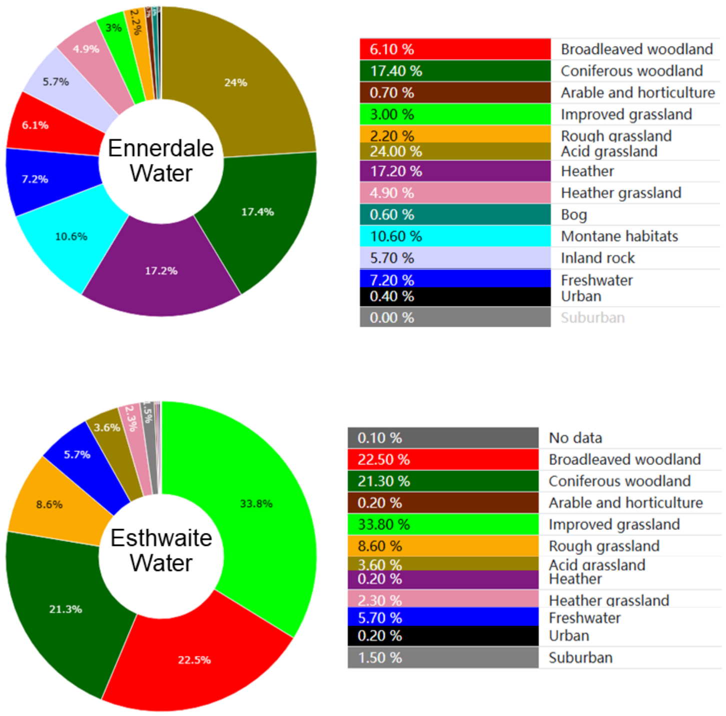

Fig. 6. Land use data within the catchments of Ennerdale Water and the Esthwaite Water. Contains public sector information licensed under the Open Government Licence v3.0

Individual sampling sites were selected along river reaches according to their position relative to the natural lakes within the river-lake networks (Fig. 7). Within the Esthwaite network, one sampling site was located on the main inflow river to the lake (Black Beck), which drains >50% of the lake's total catchment area (Maberly et al., 2011). This site was positioned approximately 693 metres upstream of the discharge of the river into the lake, and upstream of Hawkshead wastewater treatment works that discharges final treated effluent into Black Beck downstream of the sampling site used in this thesis and before the beck discharges into Esthwaite Water. Therefore, the Black Beck sampling site used in the research reported here characterises river biogeochemical conditions as determined by the upstream catchment, before any significant impact of effluent from the wastewater treatment work. The configuration ensures that the baseline hydrochemical signature of the catchment is captured, which is comparable with the counterpart, facilitating a more nuanced understanding of how land use governs the nutrients into the lacustrine system. In addition to a sampling site on the shore of Esthwaite Water itself, three further sampling sites were located on the outflow river (Cunsey Beck) at approximately 35, 1370, and 2850 metres downstream of the outflow from Esthwaite Water, respectively. Within the Ennerdale network, one sampling site was located on the main inflow river to the lake (River Liza), approximately 681 metres upstream of the point at which the river discharges into the lake. In addition to a sampling site on the shoreline of Ennerdale Water itself, three further sampling sites were located on the outflow river (River Ehen) at approximately 47, 1320, and 3760 metres downstream from the outflow of Ennerdale Water. Lake surface water samples from both Ennerdale Water and Esthwaite Water were collected at locations near to the lakeshore and away from the influence of major inflows or the outflow. Within both the Ennerdale and Esthwaite networks, multiple sampling sites were located on the outflow rivers from each lake. This enabled an assessment to be made of the extent to which changes in C, N or P biogeochemistry, driven by the natural lake, persisted within the outflow river, as opposed to being over-printed by processes within the river or by nutrient inputs from the surrounding catchment that occurred downstream of the lake.

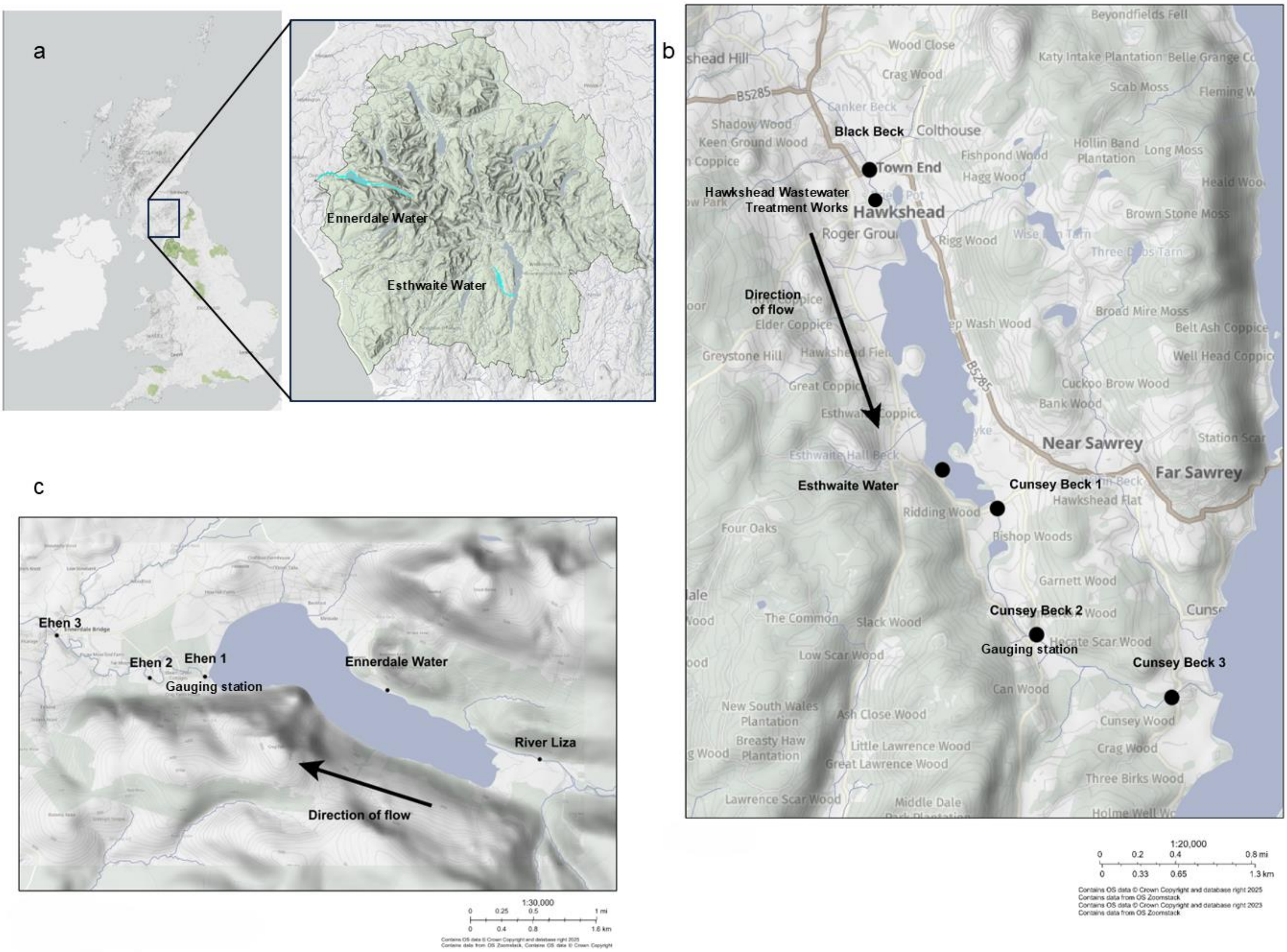

Fig. 7. The two river–lake networks and individual sampling sites used in the research reported in this thesis. (a) Overview of the English Lake District, UK. Sampled river–lake networks are highlighted in blue. (b) Esthwaite Water network with sampling locations identified along the main inflow river (Black Beck), on the shoreline of Esthwaite Water, and along the outflow river (Cunsey Beck). The river flow station is near the Cunsey Beck 2 sampling site; (c) Ennerdale Water network with sampling locations identified along the main inflow river (River Liza), on the shoreline of Ennerdale Water itself, and on the outflow river (River Ehen). The river flow station is near the Ehen 1 sampling site. This resource is made available under the Open Government Licence v3 (OGL). Contains OS data Crown Copyright and database right 2025. Contains data from OS Zoomstack. Contains OS data Crown Copyright and

database right 2023. Contains data from OS Zoomstack. Contains data supplied by UK Centre for Ecology & Hydrology. Contains Ordnance Survey Data.

Fig. 8. Images providing overview of channel and riparian conditions at sampling sites used in the research reported in this thesis: (a) River Liza, (b) Ennerdale Water, (c) Ehen 1, (d) Ehen 2, (e) Ehen 3, (f) Black Beck, (g) Esthwaite Water, (h) Cunsey Beck 1, (i) Cunsey Beck 2, (j) Cunsey Beck 3.

3.1.2. Field programme of water sample collection

Water samples for a wide range of water quality analyses designed to address the research questions within this thesis were collected from the individual locations in the river–lake networks described in Section 3.1.1 on an approximately monthly basis from March 2025 to August 2025 (25th March, 10th April, 29th April, 5th June, 3rd July and 31st July, respectively). This sampling period was deliberately designed to capture variation in the impacts of natural lakes on C, N and P biogeochemistry within river networks as driven by seasonal changes in key controlling factors within lakes, including phytoplankton community composition, rates of primary production, and extent of stratification. In particular, sampling across the spring to late summer period in the Ennerdale and Esthwaite networks was designed to capture spring and summer increases in diatom and other planktonic algal production, alongside substantial increases in water temperature and day length. These factors were expected to drive significant changes in C, N and P cycling within the lakes, with potentially important consequences for the biogeochemistry of downstream rivers fed by outflow from these lakes.

On each sampling date, water samples were collected from every river and lake location within both the Ennerdale and Esthwaite networks on the same day, in order to minimises any changes across the networks that may have been caused by fluctuating weather conditions if sampling windows had been extended. River samples were collected from road bridges or footbridges using a HDPE sample bottle connected to a rope, enabling water to be collected from well-mixed areas of the flow without disturbing the river bed sediments. The HDPE sample bottle was rinsed with water from each site three times to avoid any cross-contamination between sites, before being filled again for sample collection. Water temperature, electrical conductivity (EC) and pH were measured on unfiltered samples immediately after collection in the field using handheld probes and meters (WTW 3420 and WTW 340i; Xylem, Inc., Washington, DC, USA). Water samples for analysis of DOC, nitrate [NO_3^-], nitrite [NO_2^-], ammonia [NH_3], and SRP concentrations were then immediately filtered in the field using 0.45 µm surfactant free cellulose acetate (SFCA) syringe filters. The SFCA filters were deliberately selected in order to minimise blank concentrations of DOC that can be released from other filter materials (Karanfil et al., 2003). Prior to each sampling event, SFCA syringe filters were cleaned by passing >50 mL of >18.2

M Ohm milliQ water through each filter to waste. Cleaned filters were then stored in sealed bags before use. Unfiltered water samples were collected for total organic C (TOC), particulate organic C (POC), TN and TP analyses. For the method detection limit (MDL), please see Supplementary Information (SI, Table S2 - S7 and S10 - S13) All the samples collected in the field were immediately stored and transported in the dark within cool boxes with ice packs to minimise sample degradation, before being transferred to storage in the dark at 4 °C within the laboratory before analysis. For stable isotope analysis of particulate organic matter, unfiltered water samples were collected directly into pre-combusted 1 L glass bottles and stored prior to laboratory processing. To ensure data quality, field blanks were taken during each sampling visit for C, N, and P analyses. Samples designated for DOC analysis were stored in pre-combusted amber glass vials, in order to minimise potential contamination from background DOC and to prevent photodegradation during storage and transport. By contrast, samples intended for N and P analyses were transferred into acid-washed high-density polyethene (HDPE) centrifuge tubes, which are inert and suitable for nutrient determinations.

3.1.3. Nutrient concentration and speciation, DOC quality, and particulate organic C and N isotope measurements

The concentrations of NO_2^-, NO_3^-, NH_3, TN, TDN, TP, total dissolved phosphorus (TDP) and SRP in water samples were analysed colourimetrically on an AQ2 Discrete Analyser (SEAL Analytical; Mequon, WI, USA). Analysis of NO_2^- was based on the US Environmental Protection Agency (USEPA) method 353.2, the reaction of NO_2^- with sulfanilamide. NO_3^- was analysed by the same method after reduction to NO_2^- using a copperised cadmium coil. Concentrations were calculated as the difference between NO_2^- measurements with and without cadmium reduction. TDN was measured by acidic persulphate digest to NO_3^- followed by cadmium reduction and reaction with sulfanilamide as described earlier. NH_3^+ was determined following USEPA Method 350.1, in which ammonia reacts with hypochlorite and salicylate at alkaline pH. Concentrations of TN, TDN, TP and TDP were analysed by the USGS (US Geological Survey) protocols, with BGC_SOP008 for TN and TDN, and BGC_SOP012 for TP and TDP. In both cases, all forms of inorganic and organic N were oxidised to nitrate and all forms of inorganic and organic phosphorus were hydrolysed to orthophosphate by digestion. TN and TP analyses were performed on unfiltered samples, whereas TDN and TDP analyses were conducted on samples filtered through 0.45 µm syringe membranes. Finally, analysis of SRP was equivalent to USEPA Method 365.1, in which phosphate ions react with an acidic molybdate reagent to form an antimony-phosphomolybdate complex, which is chemically reduced by ascorbic acid.

Dissolved organic carbon (filtered samples) and TOC (unfiltered samples) concentration measurements were performed on a Sievers InnovOx ES Laboratory TOC Analyser by oxidising organic compounds to CO_2 at high temperatures in a sealed reactor. Spectrophotometric characterisation of DOC was undertaken by measuring the absorbance of samples across the UV-Visible light range, using a Jenway recording spectrophotometer (model 7315). Absorbance measurements were made at a 1 nm resolution between 200 and 800 nm using a 10 mm quartz cell. All sample spectra were referenced to a blank spectrum of milli-Q water. To minimise temperature effects on spectrophotometric measurements, all samples were allowed to reach laboratory temperature prior to measurement. All absorbance data in this thesis are expressed as absorption coefficients, a(λ), in units of m^{-1}. $SUVA_{254}$ values were determined by dividing the UV absorbance measured at $\lambda = 254$ nm by the DOC concentration and are reported in the units of litre per milligram C per meter (Weishaar et al., 2003).

Unfiltered samples for stable C and N isotope analysis of particulate organic matter were filtered in the laboratory through 25 mm diameter, Whatman GF/F glass fibre filters. These filters had previously been combusted at 450°C for 6 hours to remove any background contamination. Following sample filtration, filter papers were soaked overnight in 10% volume:volume HCl solution, in order to remove any inorganic C from the particulate material retained on the filter papers. Following the HCl treatment, filter papers were washed with >200 mL of milliQ water to remove any residual HCl, then dried to constant weight at 60°C. Dried filters were wrapped into tin capsules, which were combusted in an Elementar Vario MICROcube elemental analyser at 950°C, and isotopes were measured on an Isoprime100 Isotope Ratio Mass Spectrometer. Calibration of C and N isotope ratios in samples used international standards USGS41a and IAEA600, alongside a variety of in-house standards that are traceable to international standards. In this thesis, N isotope data ($\delta^{15}N$) are expressed in per mil notation (‰) relative to the international standard of 'Air-N_2', whilst C isotope data

(δ^{13}C) are expressed in per mil notation (‰) relative to the international standard 'Vienna PeeDee Belemnite (VPDB)'.

To contextualise nutrient and isotope data, flow conditions and general physicochemical parameters were assessed for each sampling date. Hydrographs derived from gauging station records (Fig. 9) illustrate that the early part of the sampling campaign (first three visits) was characterised by relatively low and stable baseflow conditions, whereas the later part of the period included higher flow events, most notably on 5th June, when sampling coincided with elevated river discharge following substantial rainfall.

Spatial patterns of temperature, pH and electrical conductivity (EC) were examined across inflow, lake, and outflow sites in both study networks. These parameters provide important context for nutrient and C cycling. For example, consistent downstream increases in temperature may indicate that lakes acted as thermal buffers, exporting warmer water to connected rivers. Similarly, systematic shifts in pH or EC from upstream to downstream may reflect lake-mediated changes in water chemistry, with potential implications for nutrient solubility, microbial activity and biogeochemical processing. Where observed, such differences were further evaluated to determine whether they persisted in the outflow rivers compared to inflowing streams, thereby highlighting the extent to which lakes influenced physicochemical regimes within the river–lake networks.

3.2. Results

3.2.1. Changes in DOC pools driven by lake discontinuities within river networks

In all samples collected from lakes and rivers for the research reported here, the TOC pool was dominated by DOC, with DOC accounting for between 78 % and 100 % of the TOC concentration and reaching a maximum of 1.52 and 3.12 mg C/L in the Ennerdale-network and Esthwaite-network, respectively. The average concentration of DOC within Black Beck, the main inflow river to Esthwaite Water, was 1.95 mg C/L across all samples collected as part of the research reported here, substantially higher than the average DOC concentration of 0.56 mg C/L within the River Liza, the main inflow river to Ennerdale Water. The concentration of DOC within two river-lake networks showed a general tendency to increase from spring to summer, with maximum concentrations in the lakes of each network observed in samples collected on the final sampling event (31st July 2025), increasing by 61% and 110% compared to the first samples collected from Ennerdale Water and Esthwaite Water (25th March) respectively (Fig. 9).

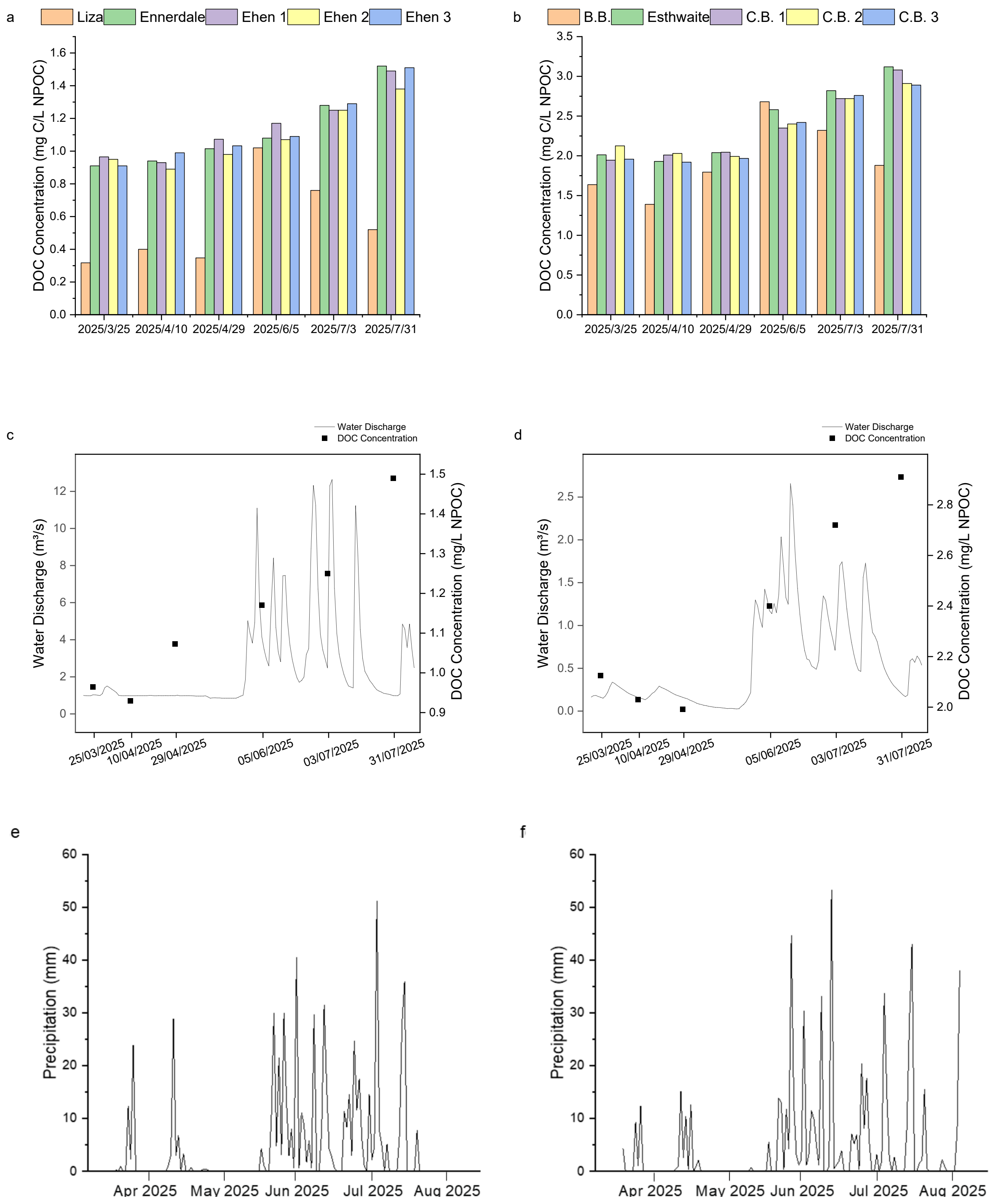

Fig. 9. Average DOC concentrations in the Ennerdale Water-network (a) and the Esthwaite Water-network (b) from spring (March and April) to summer (June and July)

2025; water discharge (Q) hydrograph for the River Ehen and Cunsey Beck sample sites at the outflow of Ennerdale Water into the River Ehen and Esthwaite Water into Cunsey Beck for sampling periods versus DOC (c and d). NPOC values are reported here as equivalent to DOC, since the non-purgeable organic C measured by TOC analysis corresponds to the DOC fraction after removal of inorganic C. B.B. represents the sampling site Black Beck, and C.B.1-3 represents the sampling sites Cunsey Beck 1-3. Daily total rainfall (mm) time series for the Ennerdale Water network (e) and for the Esthwaite Water network (f) from 22nd March to 3rd August. Due to the absence of a rainfall station in close proximity to the Esthwaite Water itself, precipitation records from the Tower Wood Rainfall Station, located about 5 km away, were employed as a proxy. Contains public sector information licensed under the Open Government Licence v3.0.

Table 2. Water residence time (Maberly et al., 2016) and changes in DOC absolute concentrations as well as percentage changes in lakes compared to main inflow rivers (DOC changes = $[(DOC_{lake}-DOC_{inflow})/DOC_{inflow}] \times 100\%$).

Lakes	Ennerdale Water		Esthwaite Water	
Average annual water residence time (d)	200		100	
Sampling date	Percentage changes in DOC from inflow to lake (%)	Absolute changes in DOC from inflow to lake (mg C/L)	Percentage changes in DOC from inflow to lake (%)	Absolute changes in DOC from inflow to lake (mg C/L)
25th March	187%	0.60	23%	0.375
10th April	135%	0.54	39%	0.54
29th April	192%	0.67	14%	0.245
5th June	5.8%	0.06	-3.7%	0.1
3rd July	68%	0.52	22%	0.5
31st July	192%	1.00	66%	1.24
Average values	130%	0.56	26%	0.47

Concentrations of DOC within lakes often differed very substantially compared to main inflow river sites immediately upstream. On average, the magnitude of these changes was greater for Ennerdale Water compared to Esthwaite Water, when expressed as both a proportion of the DOC concentration and the absolute concentration changes within the main inflow river. In the vast majority of sampling events reported here, the natural lakes acted as sources of DOC to downstream rivers, with concentration increases on individual sampling events ranging from 6% to 192% of the concentration within the main inflow rivers (Table 2). However, on 5th June 2025, this pattern was reversed and Esthwaite Water acted as a sink of DOC that caused a 3.7% decrease in concentration within the lake compared to Black Beck (Table 2). Whilst concentrations in Ennerdale Water continued to be higher than in the River Liza on 5th June, the magnitude of this increase was much reduced compared to other sampling dates, reaching only 5.8% or 0.06 mg C/L (Fig. 9).

Within outflow rivers immediately downstream of the natural lakes (Ehen 1 and Cunsey Beck 1), DOC concentrations remained at the same levels as within the lakes (Ennerdale Water - Ehen 1: $p = 0.344$, $\alpha=0.05$; Esthwaite Water - Cunsey Beck 1: $p = 0.228$, $\alpha=0.05$). Moving further downstream within the outflow rivers, concentrations of DOC remained relatively stable, with <10% change compared to the respective lakes. Therefore, DOC concentrations over approximately 3760 m for the Ennerdale-network and 2850 m for the Esthwaite network continued to differ significantly compared to those within the main inflow rivers upstream of the natural lakes.

Both river-lake networks displayed similar seasonal patterns in which the concentrations of DOC and TOC increased and peaked in early June in the two upstream river sites, after which concentrations decreased. In contrast, DOC and TOC concentrations in the lakes and downstream river sites continued to increase throughout July (Fig. 9). A strong seasonal relationship between DOC concentration and river discharge (Q) was also observed at sites from both the Ennerdale-network and the Esthwaite-network, with elevated DOC concentrations in both the River Ehen and Cunsey Beck observed during the late spring and summer period with increasing Q after an early spring period of relatively low DOC concentrations at a time of low and stable Q (Fig. 9c and Fig. 9d). For example, DOC concentrations were approximately 0.93 - 1.07 mg C/L (River Ehen) and 1.99 - 2.12 mg C/L (Cunsey Beck) at low Q in spring, and increased later in the summer at higher Q to 1.17 -1.49 mg C/L (River Ehen) and 2.40 - 2.91 mg C/L (Cunsey Beck).

$SUVA_{254}$ ranged from 0.09 – 5.96 L mg C^{-1} m^{-1} (mean = 4.03 L mg C^{-1} m^{-1}; n = 60) and varied with location, discharge and sampling date across the individual data points (Fig. 10a and Fig. 10b). The Esthwaite Water-network typically exhibited higher $SUVA_{254}$ values (average across all sites and sample dates = 4.34 L mg C^{-1} m^{-1}) compared to the Ennerdale Water-network (average across all sites and sample dates = 3.71 L mg C^{-1} m^{-1}. $SUVA_{254}$ values in the main inflow rivers within the two river-lake networks showed similar seasonal patterns, with decreases in values in March and April followed by increases in June and July, reaching maximum values of 5.04 L mg C^{-1} m^{-1} in Black Beck and 5.96 L mg C^{-1} m^{-1} in the River Liza. $SUVA_{254}$ values didn't exhibit a consistent trend related to Q either in the River Ehen or in Cunsey Beck. Although $SUVA_{254}$ decreased substantially in both outflow rivers during March and April, values then remained relatively constant in Cunsey Beck whilst $SUVA_{254}$ increased in June and July within the River Ehen (Fig. 10c and 10d).

Consistent with the patterns reported for DOC concentrations, $SUVA_{254}$ varied substantially between the main inflow rivers and the natural lakes in both the Ennerdale Water-network and the Esthwaite Water-network. In the Ennerdale Water-network, $SUVA_{254}$ values were lower in the inflow River Liza than in Ennerdale Water and in the outflow river between March and April, whilst the opposite pattern was observed during June and July, where $SUVA_{254}$ values decreased substantially from the inflow to the lake as well as the outflow (Fig. 10a). The pattern of $SUVA_{254}$ within the Esthwaite Water-network was different, with $SUVA_{254}$ values in the inflow river being continuously lower than in the lake and the outflow river (Fig. 10b). Absolute and proportional differences between the inflow river and the lake regarding the $SUVA_{254}$ values were greater within the Ennerdale Water-network than the Esthwaite Water-network (Table 3). Similar to DOC, the lake effect continued to have an impact on both downstream rivers until at least the sampling sites located at River Ehen 3 and Cunsey Beck 3.

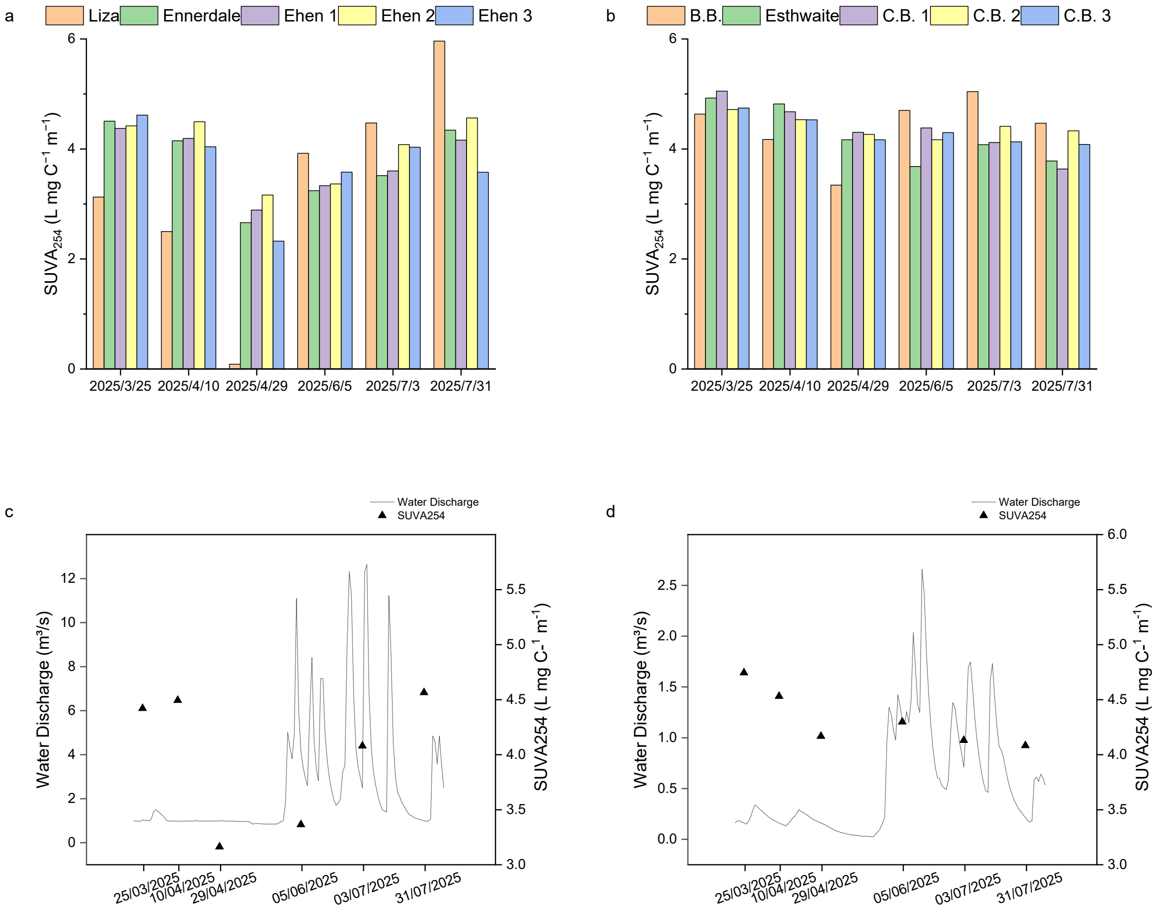

Fig. 10. Average $SUVA_{254}$ in Ennerdale Water-network (a) and Esthwaite Water-network (b) from spring (March and April) to summer (June and July); Water discharge (Q) hydrograph for the River Ehen and Cunsey Beck sample sites at the outflow of Ennerdale Water into the River Ehen and Esthwaite Water into Cunsey Beck for sampling periods versus DOC (c & d). Contains public sector information licensed under the Open Government Licence v3.0.

Table 3. Changes in $SUVA_{254}$ absolute values as well as percentage changes in lakes compared to main inflow rivers (SUVA254 changes = [(SUVA254lake−SUVA254inflow)/SUVA254 inflow] × 100%).

	Ennerdale Water		Esthwaite Water	
Sampling date	Percentage changes in $SUVA_{254}$ from inflow to lake (%)	Absolute changes in $SUVA_{254}$ from inflow to lake (L mg C^{-1} m^{-1})	Percentage changes in $SUVA_{254}$ from inflow to lake (%)	Absolute changes in $SUVA_{254}$ from inflow to lake (L mg C^{-1} m^{-1})
25th March	44%	1.38	6.3%	0.29
10th April	66%	1.66	15%	0.64
29th April	2981%	2.57	25%	0.82
5th June	-17%	0.68	-22%	1.02
3rd July	-21%	0.96	-19%	0.96
31st July	-27%	1.62	-15%	0.67
Average values	8.8%*	0.39	-1.6%	0.15

N.B.: * indicates the average value was calculated after excluding the 2981% value.

Average values of the α250 to α365 ratio were generally higher within the Ennerdale Water-network (average across all samples = 6.11) compared to the Esthwaite Water-network (average across all samples = 5.06). The α250:α365 ratio didn’t show a strong, consistent seasonal pattern in either river-lake network. Within the Ennerdale Water-network, the mean α250:α365 ratio was 6.15 (minimum-maximum range = 3.62–10.0) during spring, before decreasing somewhat during the summer to a mean value of 6.05 (minimum-maximum range = 3.78–13.67). In the Esthwaite Water-network, the mean α250:α365 ratio was 5.02 (minimum-maximum range = 4.27–6.07) during spring, before increasing to a mean value of 5.11 (minimum-maximum range = 4.14-5.83) in summer. There was also no clear relationship between α250:α365 and discharge within either the Ennerdale Water or Esthwaite Water networks (Figs 11c and 11d).

During five of the six sampling events, the α250 to α365 ratio was higher in the River Liza compared to Ennerdale Water and in the River Ehen downstream of Ennerdale Water (Fig. 11a, Table 4). In contrast, across all six sampling events within the Esthwaite Water-network, the α250 to α365 ratio increased between the main inflow of Black Beck and the lake, by an average of 0.68 across these events (Table 4). The higher α250 to α365 ratio created by Esthwaite Water also generally persisted within Cunsey Beck over the entire reach between sampling sites Cunsey Beck 1 and Cunsey Beck 3.

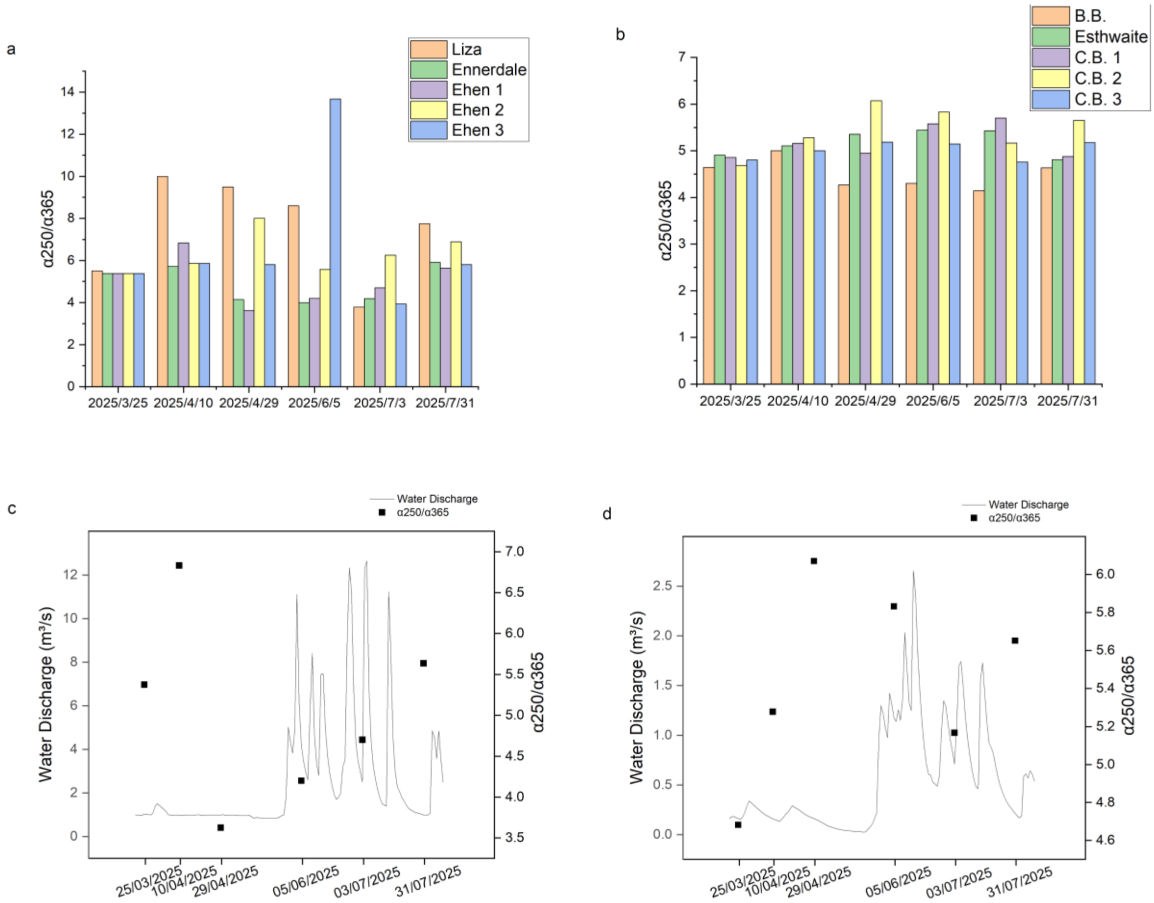

Fig. 11. Average α250/α365 in Ennerdale Water-network (a) and Esthwaite Water-network (b) from spring (March and April) to summer (June and July); Water discharge (Q) hydrograph for the River Ehen and Cunsey Beck sample sites at the mouth of the River Ehen and Cunsey Beck for sampling periods versus α250/α365 (c and d). Contains public sector information licensed under the Open Government Licence v3.0.

Table 4. Changes in α250:α365 absolute concentrations as well as percentage changes in lakes compared to main inflow rivers (α250:α365 changes = [(α250:α365$_{lake}$−α250:α365$_{inflow}$)/α250:α365$_{inflow}$] × 100%).

	Ennerdale Water		Esthwaite Water	
Sampling date	Percentage changes in α250:α365 from inflow to lake (%)	Absolute changes in α250:α365 from inflow to lake	Percentage changes in α250:α365 from inflow to lake (%)	Absolute changes in α250:α365 from inflow to lake
25th March	-2.3%	0.12	5.6%	0.26
10th April	-43%	4.29	2.1%	0.10
29th April	-56%	5.36	25%	1.09
5th June	-53%	4.60	27%	1.14
3rd July	11%	0.40	31%	1.29
31st July	-24%	1.84	3.8%	0.18
Average values	-28%	2.63	16%	0.688

Further to the characterisation of DOC concentration and quality reported above, elemental and stable isotope analyses were used to establish if signatures of natural lake biogeochemistry were transferred to particulate organic matter within river-lake networks. Across both the Ennerdale Water- and Esthwaite Water-networks, clear and consistent changes in $\delta^{13}C$ within particulate organic matter were observed between the major inflow rivers and natural lakes. Specifically, and other than one exception on 5th June in the Esthwaite Water-network, particulate organic matter became substantially more depleted in $\delta^{13}C$ (more negative values of $\delta^{13}C$) within the lakes compared to the main inflow rivers (Fig. 12a and 12c). This effect was more pronounced within the Esthwaite Water-network (average change in $\delta^{13}C$ between Black Beck and Esthwaite Water = 3.19‰) compared to the Ennerdale Water-network (average change in δ^{13}C between River Liza and Ennerdale Water = 1.44‰). Particulate organic matter with low δ^{13}C continued to affect outflow rivers throughout the sampled reaches downstream of both Ennerdale Water and Esthwaite Water, although this pattern was more consistently observed within Cunsey Beck compared to the River Ehen. Somewhat more elevated δ^{15}N was observed within the Esthwaite Water-network (average = 3.68‰, maximum to minimum range = -1.61‰ - 6.49‰) compared to the Ennerdale Water-network (average = -1.06, maximum to minimum range = -5.41‰ - 5.89‰). In contrast to patterns for δ^{13}C, no clear or consistent changes in δ^{15}N of particulate organic matter were observed between main inflow rivers and the natural lakes (Fig. 12c and 12d).

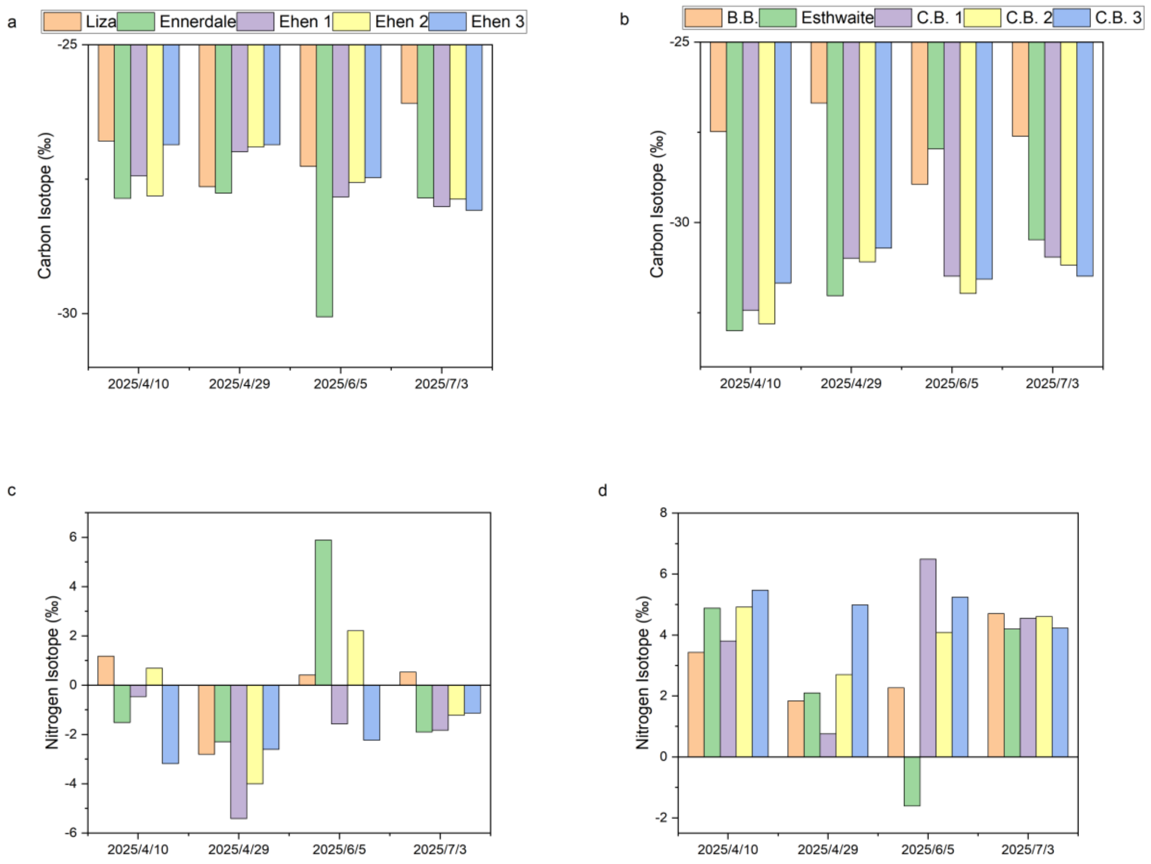

Fig. 12. Carbon isotope (δ^{13}C) data for (a) Ennerdale Water network and (b) Esthwaite Water network; N isotope (δ^{15}N) data for (c) Ennerdale Water network and (d) Esthwaite Water network. Carbon isotope data are expressed as per mil (‰) against VPDE, N isotope data as per mil (‰) again N_2 in air. One standard deviation = c.1 ‰ for δ^{15}N and c.0.3 ‰ for δ^{13}C.

3.2.2. Changes in N pools driven by lake discontinuities within river networks

In rivers immediately upstream of lake discontinuities, TN and TDN pools were dominated by NO_3^- throughout the spring and summer, with NO_3^- responsible for between 77% (River Liza) and 61% (Black Beck) of the TN concentrations and 82% (River Liza) and 62% （Black Beck） of the TDN concentrations across all samples from the main inflow rivers. The concentration of NO_3^- reached a maximum of 0.320 and 0.439 mg N/L in the River Liza and in Black Beck, respectively. The concentrations of NO_3^- in the River Liza tended to decline across the spring to summer period covered by the sampling reported here, from a maximum of 0.320 mg N/L on 25th March to a minimum of 0.179 mg N/L on 3rd July. In contrast, no consistent change in NO_3^- concentration was observed within Black Beck.

Concentrations of NO_3^- within lakes often differed very substantially compared to main river sites immediately upstream (Fig. 13a and 13b), although these changes were much more pronounced within the Esthwaite Water-network compared to the Ennerdale Water-network (Table 5). Within the Ennerdale Water-network, concentrations of NO_3^- within the lake were always within -16% or 0.043 mg N/L of those within the River Liza. However, across the sampling events between 25th March and 5th June 2025, concentrations of NO_3^- within Esthwaite Water were consistently above those within Black Beck, reaching a maximum difference of 92% or 0.289 mg N/L on 25th March. These increases in NO_3^- concentration were exported downstream into Cunsey Beck, with elevated concentrations compared to Black Beck observed along the entire sampling reach to site Cunsey Beck 3. During the final two sampling events on 3rd and 31st July, Esthwaite Water switched to become a substantial sink for NO_3^-. Concentrations within the lake decreased compared to the inflow river by a maximum of 78% or 0.344 mg N/L across these two events. These lower NO_3^- concentrations were subsequently exported from Esthwaite Water into Cunsey Beck, with concentrations in the outflow river never recovering to more than 53% of those within Black Beck across the 2850m of the outflow river covered by sample sites Cunsey Beck 1 to 3.

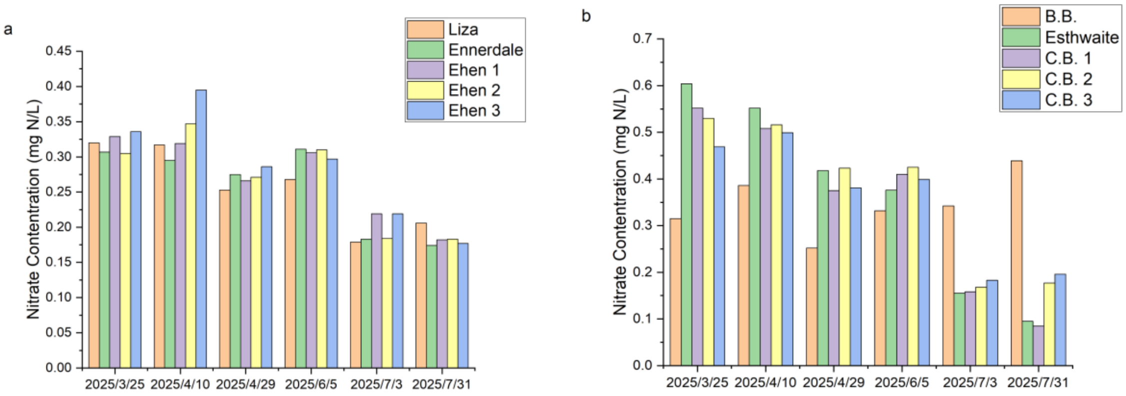

Fig. 13. NO_3^- concentrations within (a) Ennerdale Water-network and (b) Esthwaite Water-network from spring (March and April) to summer (June and July).

Table 5. Changes in NO_3^- absolute concentrations as well as percentage changes in lakes compared to main inflow rivers (NO_3^- changes = $[(NO_3^-{}_{\text{lake}} - NO_3^-{}_{\text{inflow}})/NO_3^-{}_{\text{inflow}}]$ × 100%).

	Ennerdale Water		Esthwaite Water	
Sampling date	Percentage changes in NO_3^- concentrations from inflow to lake (%)	Absolute changes in NO_3^- concentrations from inflow to lake (mg N/L)	Percentage changes in NO_3^- concentrations from inflow to lake (%)	Absolute changes in NO_3^- concentrations from inflow to lake (mg N/L)
25th March	-4.1%	0.013	92%	0.289
10th April	-6.9%	0.022	43%	0.166
29th April	8.7%	0.022	66%	0.166
5th June	16%	0.043	13%	0.044
3rd July	2.2%	0.004	-55%	0.187
31st July	-16%	0.032	-78%	0.344
Average values	0.07%	0.0003	13%	0.022

Concentrations of NH_4^+ in the vast majority of samples analysed in the research reported here were below the limit of detection and are not discussed further in this thesis. Concentrations of NO_2^- within the Ennerdale Water-network (Fig. 14a) were low in all samples and showed no clear patterns within the river-lake network. However, clearer patterns were observed within the Esthwaite Water-network (Fig. 14b). Concentrations of NO_2^- in the main inflow river Black Beck were generally low (minimum to maximum range = 0.0009 to 0.0029 mg N/L, mean value = 0.0018 mg N/L). However, concentrations increased substantially within Esthwaite Water on each of the six sampling dates, ranging between 0.0039 and 0.0105 mg N/L (mean concentration = 0.0069 mg N/L). Maximum concentrations were observed within Esthwaite Water in March 2025, with a consistent pattern of decreasing NO_2^- concentrations in the lake across the spring-summer period. Within the outflow river Cunsey Beck, NO_2^- concentrations did not remain constant but instead decreased consistently across sites Cunsey Beck 1 to Cunsey Beck 3, returning to or even falling below concentrations observed within Black Beck.

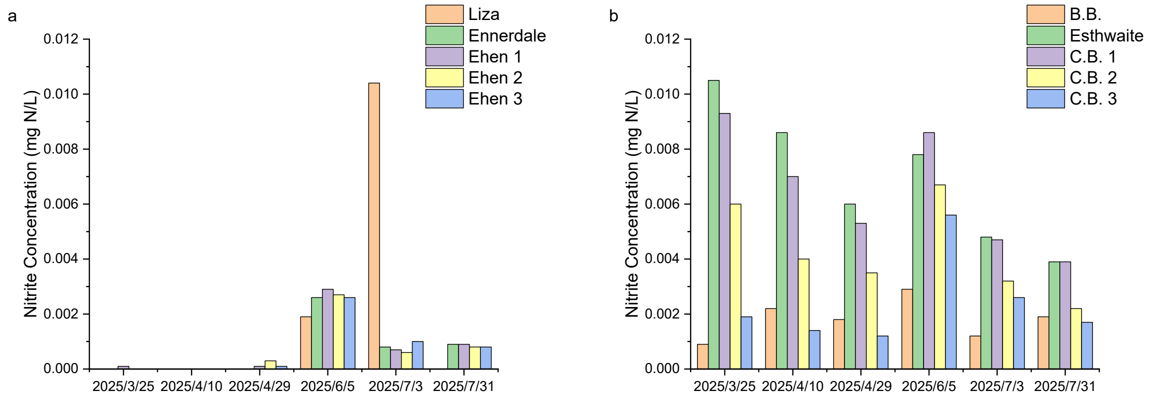

Fig. 14. NO_2^- concentrations within (a) Ennerdale Water-network and (b) Esthwaite Water-network from spring (March and April) to summer (June and July).

Dissolved organic nitrogen (DON) concentrations were calculated by subtracting NO_3^- concentrations from total dissolved nitrogen (TDN) concentrations. Concentrations of DON within the Ennerdale Water-network were generally low (Fig. 15a). Whilst concentrations of DON did appear to increase within the lake compared to the main inflow River Liza, the concentrations of DON from the lake shore site were not always observed at the first sampling site on the River Ehen (River Ehen 1), making interpretation of the downstream impacts of DON from Ennerdale Water difficult. Within the Esthwaite Water-network, the lake appeared to shift from a sink of DON during spring and early summer to a substantial source of DON to the downstream river in samples collected on 3rd and 31st July. During these final two sampling events, concentrations of DON in Esthwaite Water reached 188% of those in Black Beck. These elevated concentrations of DON persisted throughout all three sampling sites within Cunsey Beck, not returning to the concentrations observed in Black Beck on either sampling date. No clear or consistent patterns within either the Esthwaite Water-network or the Ennerdale Water-network were observed in terms of TPN concentrations.

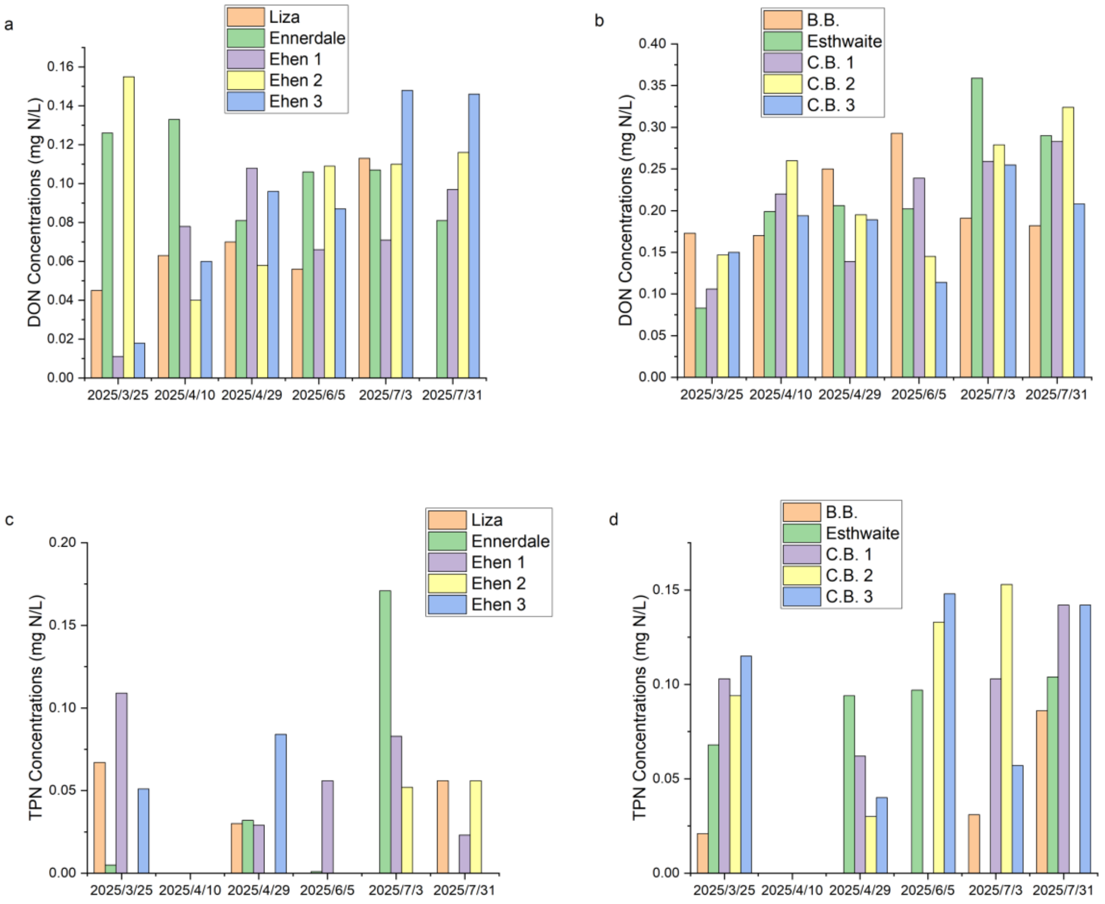

Fig. 15. DON and TPN concentrations within (a and c) Ennerdale Water-network and (b and d) Esthwaite Water-network from spring (March and April) to summer (June and July).

3.2.3. Changes in phosphorus pools driven by lake discontinuities within river networks

Concentrations of SRP within the two river-lake networks analysed for the research reported here were generally low (Fig. 16). Concentrations within the Ennerdale Water-network were often below detection and no clear patterns were observed through this river-lake network (Fig. 16a). In contrast, Esthwaite Water generally acted as a SRP sink compared to Black Beck, with decreases in concentration ranging between 0.001 mg P/L and 14% or 0.013 mg P/L and 93% (Fig. 16b). These lower concentrations of SRP were exported from Esthwaite Water into Cunsey Beck, and remained below concentrations within Black Beck throughout the reach to site Cunsey Beck 3.

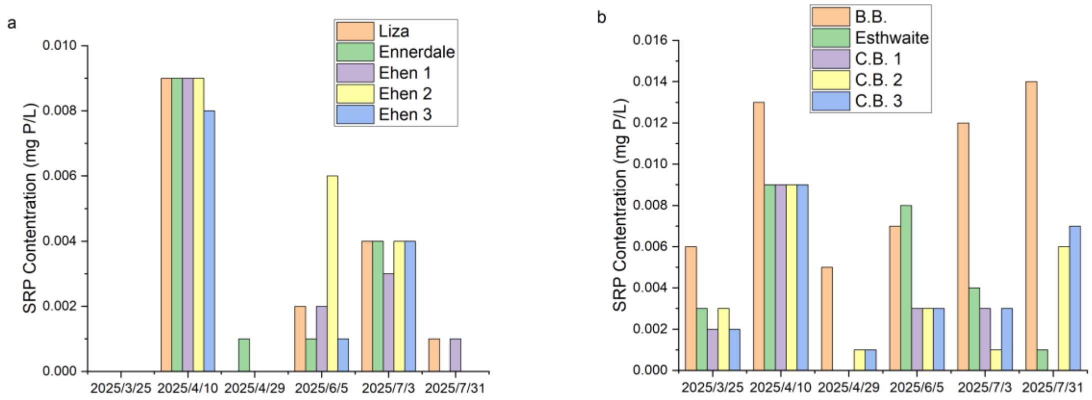

Fig. 16. SRP concentrations within (a) Ennerdale Water network and (b) Esthwaite Water network from spring (March and April) to summer (June and July).

Dissolved organic phosphorus (DOP) was calculated as the difference between total dissolved phosphorus (TDP) and SRP ([DOP] = [TDP] - [SRP]). Across the two river-lake networks, DOP concentrations maintained relatively stable levels both upstream of the lakes and within the lakes themselves (Fig. 17a and 17b). Total particulate phosphorus (TPP) was derived by subtracting TDP concentrations from TP, referring to the phosphorus fraction associated with particles larger than 0.45 μm that are captured on the filter. The majority of TPP concentrations were below the detection limit in the Ennerdale Water network (Fig. 17c). Despite the availability of most data in the Esthwaite Water network, no discernible patterns could be identified through either river-lake network (Fig. 17d).

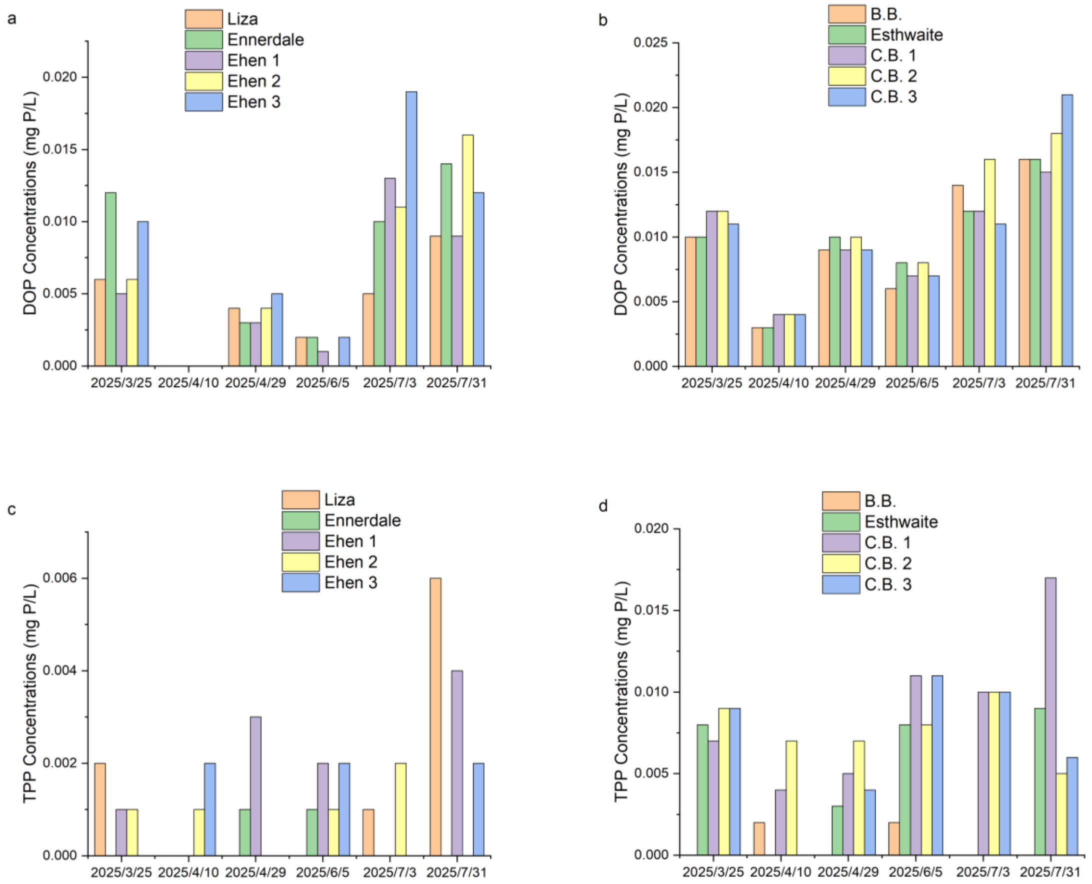

Fig. 17. DOP and TPP concentrations within (a and c) Ennerdale Water network and (b and d) Esthwaite Water network from spring (March and April) to summer (June and July).

Chapter 4: Discussion

The results reported in this thesis provide new insights into the changes introduced by natural lakes, within a river-lake network context, to the concentration, quality and speciation of C, N and P. The research has also considered the impacts of lake trophic status and of time through the critical spring-summer seasons on the role of lakes in the nutrient biogeochemistry of river-lake networks. The results reported here have potentially important implications for understanding both the nutrient conditions within river-lake networks, but also for the role of the freshwater interface in controlling the fluxes of nutrient elements moving between terrestrial and marine ecosystems.

It is recognised that only the major inflow river for each of the two natural lakes could be sampled within the research reported here: the River Liza for Ennerdale Water and Black Beck for Esthwaite Water. This sampling design inevitably introduces limitations, as it does not capture the full heterogeneity of all possible inflows to the lakes. However, two main factors suggest that the selected inflow river sites are likely to reflect the main upstream biogeochemical processes driving river-lake network interactions. Firstly, the main inflow rivers that were sampled are the major contributors to lake inflows, and thus provide representative upstream conditions. For example, Black Beck alone drains c.55% of the total catchment area of Esthwaite Water (Maberly et al., 2011). Secondly, minor inflows to each lake are believed likely to drain sub-catchments with broadly similar C, N and P sources and inputs compared to the major inflow rivers that were sampled, due to similar land use patterns and climate conditions within what remain relatively small total catchment areas for both the Ennerdale Water and Esthwaite Water networks.

As a preliminary point, the observation of temperature and pH indicates a consistent trend where values at the inflows were predominantly lower than those within the lakes and their outflows (Table S1). However, EC values were usually higher in the inflow rivers. Data from three successive downstream sampling highlight the pronounced regulatory influence of the lake, which effectively precludes the recovery to the inflow conditions. These findings establish a foundation context for the subsequent analysis of the primary parameters.

4.1 Biogeochemical processes driving changes in C concentrations and the quality of organic C in lake discontinuities

The DOC concentrations within Esthwaite Water and Ennerdale Water were relatively low compared to the mean concentrations in other fresh waters in the UK and to the European average DOC concentration of lakes (Lloyd et al., 2019; Toming et al., 2020). In this broader context, the results reported in this thesis demonstrate that significant changes in the concentration and speciation of C occur within lake discontinuities, which are subsequently exported to downstream river networks (Figs. 9-11). The natural lakes examined in the research reported here exerted a critical influence on the DOC concentration and DOC quality within both the wider Esthwaite Water and Ennerdale Water river-lake networks. Notably, across all three downstream sampling sites within the outflow rivers fed by both lakes, DOC concentrations remained relatively consistent with in-lake concentrations and never recovered to the same concentrations as observed within the inflow rivers immediately upstream of each lake. In contrast, within a river continuum without natural lake disruptions, abiotic and biotic parameters and processes can display predictable longitudinal continuity, with upstream conditions exerting significant control on those downstream given this linear perspective (Jones, 2010). However, rather than simply transmitting upstream signals, each lake established a new DOC concentration baseline that was exported and persisted for a significant distance within the downstream river network. The patterns revealed in Fig. 9 highlight the important role of lakes in biogeochemical processes influencing the DOC cycle. Both lakes considered in the research reported here acted as sources of increased DOC concentration across the spring-summer period, and these increased concentrations were subsequently exported via outflows to the downstream river network. These lake effects persisted within the downstream river network over substantial distances, being detectable for at least 3.8 km within the River Ehen downstream of Ennerdale Water and at least 2.8 km for Cunsey Beck downstream of Esthwaite Water.

Despite substantial differences in both lake and wider catchment characteristics between the Esthwaite Water and Ennerdale Water networks, a similar direction of DOC change was imposed on the river networks by both natural lakes, resulting in greater DOC concentrations within the river network downstream compared to upstream of the lakes. However, these changes were more pronounced in the

Ennerdale Water network, with a larger proportional change in DOC concentrations between the lake and the inflow river immediately upstream of the lake, alongside more stable DOC concentrations within the downstream river, compared to the patterns observed within the Esthwaite Water network. Several processes could account for these observations, including water residence time, optical conditions within the lakes, and external inputs of C (Cardille et al., 2007). Ennerdale Water is an oligotrophic lake but with a water retention time twice as long, a volume nearly eight times greater, and a depth more than twice that of Esthwaite Water (Table 1). Therefore, a longer hydraulic residence time within Ennerdale Water potentially provides greater opportunity for photochemical and microbial transformations of particulate organic matter to DOC, whilst lower light penetration across the entire water column of Ennerdale Water focusses both photochemical reactions and autochthonous DOC production within the near-surface water column, which is subsequently exported to the River Ehen (Hanson et al., 2011; Reche et al., 2000). However, these interpretations are not entirely consistent with research suggesting that microbial and abiotic processes, such as photo-oxidation, drive the decomposition of DOC, resulting in substantial CO_2 emissions to the atmosphere which possibly decreases DOC concentrations within lakes (Raymond et al., 2013). However, the depth of Ennerdale Water could prevent radiation from reaching deep areas of the water column, with this being an important determinant of the extent of DOC dynamics. In contrast, despite Esthwaite Water being a mesotrophic lake with more intensive biotic processes influencing the C cycle, the relatively small water volume and shorter hydraulic residence time compared to Ennerdale Water likely supports more efficient export of DOC from the upstream to the downstream river network, with smaller proportional changes in DOC concentration, which aligns with the observations of Toming et al. (2020).

Further, differences in the catchment characteristics and resulting inflow DOC concentrations may explain the varying magnitude of relative lake effects between Ennerdale Water and Esthwaite Water. The Ennerdale Water-network is located in the far northwest ELD, within a relatively remote catchment that is less strongly influenced by human activity and associated external inputs to the freshwater network (Worrall et al., 2017). In contrast, the catchment of Esthwaite Water encompasses higher-density settlements, more intensive agricultural and forestry industries. These contrasting catchment characteristics result in clear differences in the concentrations of DOC within the inflow rivers to both lakes (Fig. 9), consistent with a range of other research (Carpenter, 2008; Chen et al., 2008; Mainstone & Parr, 2002; Worrall et al., 2018), including research showing that the presence of forests consistently promotes DOC export, with this effect being particularly pronounced when plantations are established on drained peat soils to facilitate conifer growth (Williamson et al., 2021). Specifically, concentrations of DOC within the Black Beck inflow to Esthwaite Water were significantly higher than those within the River Liza inflow to Ennerdale Water. Therefore, in proportional terms, processes within Esthwaite Water produced a smaller change in DOC concentration compared to those within Ennerdale Water.

There was also a clear seasonal pattern in DOC concentrations within both Ennerdale Water and Esthwaite Water, in which concentrations increased between March and July in both lakes (Fig. 9). This seasonal change likely reflects the combined effect of increased primary production and DOC release from the resulting biomass within the lakes themselves during the summer months, alongside increased degradation of POC and production of DOC by heterotrophic communities and by photo-oxidation under warmer water conditions and high incident radiation as the summer progressed (Godin et al., 2017; Minor & Olyer, 2021). Importantly, the seasonal changes in DOC concentration observed within the lakes were also imposed on the downstream river network in both catchments, leading to a disconnected temporal pattern of DOC concentration in river reaches upstream versus downstream of the natural lakes in these river-lake networks. However, although similar patterns of seasonality in DOC concentrations were observed within Ennerdale Water and Esthwaite Water, the absolute concentrations reached within these seasonal patterns varied. Within the oligotrophic Ennerdale Water, with lower levels of primary production and of heterotrophic activity, DOC concentrations only reached a maximum <1.6 mg C/L, substantially below the maximum in the mesotrophic, more productive system of Esthwaite Water where maximum concentrations reached >3.0 mg C/L in July 2025.

In addition to autochthonous generation of DOC within lakes via release from autotrophic biomass or particulate organic C, allochthonous inputs also contribute to DOC pools. Allochthonous DOC may enter river-lake networks via multiple pathways, including groundwater and catchment runoff as driven by rainfall, with rainfall recognised as being positively related to, and in many cases the best predictor of, DOC yields (Williamson et al., 2021). Rainfall events contribute to DOC inputs both through direct deposition into the water bodies and by intensifying catchment processes including surface runoff and leaching, which mobilise terrestrial organic C and elevate DOC concentrations in the inflows (Bai et al., 2023). For example, rainfall moving through vegetation canopies and along vegetation stems is able to mobilise DOC derived from vegetation and atmospheric aerosols (Qualls & Haines, 1992). In the research reported in this thesis, the impact of rainfall and catchment sources of DOC are clearly evident. The sampling event on 5th June 2025 coincided with a period of heavy rainfall in both the Esthwaite Water and Ennerdale Water catchments, during which pronounced increases in DOC concentrations were observed in both inflow rivers compared to all other sampling events (Fig. 9), consistent with patterns that have been observed in other reaches of the Rivers Wylye and Ebble in the UK (Lloyd et al., 2019). However, this sharp increase in DOC concentrations within both Black Beck and the River Liza was not reflected within either the lakes or their outflow rivers, indicating that natural lakes within river-lake networks have the potential to buffer short-term increases in DOC concentrations within inflow rivers as driven by rainfall-runoff processes within upstream catchments. This may partly reflect a dilution effect, as water discharge from inflow rivers is mixed with a much larger lake water volume, limiting any increase in DOC concentration within outflow river. However, beyond dilution, active consumption of high DOC concentrations by heterotrophic processes and photo-degradation within the lakes may also have limited any transmission of elevated DOC concentrations to downstream rivers. Further research would be needed to examine how pulsed inputs of nutrients, such as DOC, are processed within lake systems before release to outflow rivers.

Beyond the event-driven increases in DOC concentration within both Black Beck and the River Liza on 5th June 2025, there was no clear and consistent change in DOC concentration within these inflow rivers when examined across the entire sampling period March – July 2025. This contrasts strongly with the consistent increases in DOC concentration observed across March – July within the outflow rivers of both catchments, as driven by the natural lake in both river-lake networks. Concentrations of DOC in both the River Liza and Black Beck did appear somewhat higher in the July samples compared to those in March and April. This likely reflects the fact that the inflow rivers mainly deliver terrestrially-derived DOC from the catchment to downstream ecosystems (Spencer et al., 2008), and that rainfall, runoff, and therefore delivery of catchment-derived DOC to the inflow rivers, was higher in the wetter summer period compared to the drier spring period (Fig. 9c, 9d, 9e and 9f). These observations suggest that not only do natural lakes within river-lake networks alter seasonal patterns of DOC concentration within river networks, but that lakes may also increasingly disconnect downstream river reaches from the influence of wider catchment runoff and catchment-derived sources of DOC.

Alongside the analysis of DOC concentrations, the research reported in this thesis also considered how natural lakes within river-lake networks influence the quality of DOM and thereby of DOC. The quality of DOM was characterised using two metrics derived from spectrophotometric analysis of water samples, $SUVA_{254}$ and α250:α365. $SUVA_{254}$ has been related to the percent aromaticity of DOM (Weishaar et al., 2003). For the majority of the sampling period, $SUVA_{254}$ was higher in samples collected from the inflow to Esthwaite Water than the inflow to Ennerdale Water (Fig. 10), indicating that the catchment of Esthwaite Water provided not only greater inputs of DOC to Black Beck but also that this DOC was associated with more aromatic compounds likely derived from terrestrial sources of DOM within the catchment (Aufdenkampe et al., 2001; Hernes et al., 2007). Across the spring months of March, April, May and June, $SUVA_{254}$ tended to increase between the main inflow rivers and both Ennerdale Water and Esthwaite Water. Whilst production of autochthonous DOC by phytoplankton in the lakes would be expected to yield less aromatic DOC within a lower $SUVA_{254}$ value (Weishaar et al., 2003), this was not observed in the research reported here when comparing inflow river to lake samples in terms of $SUVA_{254}$. It is possible that DOC within both lakes during these spring and early summer months was associated with residual DOM that had remained within the lakes over the winter period, and that this residual DOM was comprised of more aromatic compounds with relatively high $SUVA_{254}$ (Spencer et al., 2009). Later in the summer, within samples collected in July, the direction of change in $SUVA_{254}$ between inflow river and lake samples switched, with decreases observed in both Esthwaite Water and Ennerdale Water compared to their respective inflow rivers (Fig. 10). $SUVA_{254}$ within the lake samples themselves were somewhat lower in July than during the earlier sampling events, potentially suggesting a greater influence of new, phytoplankton-derived DOC within the lakes as primary production increased in the summer months (Weishaar et al., 2003). However, $SUVA_{254}$ within both inflow rivers also increased to the highest values observed in this research during the July sampling events, consistent with increased inputs of more aromatic DOM from terrestrial environments during the wetter period of July compared to the drier spring period (Fig. 10). Further research would be needed to examine in more detail how $SUVA_{254}$ within the inflow rivers and lakes of these networks related to allochthonous versus autochthonous sources of DOC. As described above for DOC concentration, the changes in $SUVA_{254}$ introduced by both Esthwaite Water and Ennerdale Water were exported to the outflow rivers and continued to influence both Cunsey Beck and the River Ehen across all three sample sites in the research reported here.

Previous interpretations of the ratio α250 to α365 have suggested that this metric should mirror the trends in $SUVA_{254}$, with lower values of α250:α365 interpreted as representing DOM with higher aromaticity and larger molecular size (Peuravuori & Pihlaja, 1997). However, this relationship was not observed clearly in the river-lake networks examined for the research reported here (Fig. 11). Within the Esthwaite Water network, α250:α365 on each sampling date appeared to increase slightly within the lake compared to Black Beck, a pattern that appeared to grow in magnitude throughout the spring-summer period apart from the final sampling event at the end of July 2025. In contrast, α250:α365 decreased within Ennerdale Water compared to the River Liza on all but one of the six sampling dates. The lack of a consistent inverse relationship between α250:α365 and $SUVA_{254}$ suggests that these metrics could be controlled by different processes that influence the pools of DOM in these freshwaters. Inconsistencies in the patterns of change across multiple spectrophometric-derived descriptions of DOM quality have been reported in previous research (e.g. Minor et al., 2006), although further research would be required to understand which processes and controlling factors give rise to contrasting patterns in α250:α365 and $SUVA_{254}$ across the Ennerdale Water and Esthwaite Water networks.

The isotopic analysis of particulate organic matter reported in this thesis reveals that signatures of natural lake processing of particulate nutrient fractions may also be exported into the downstream river network (Fig. 12). Specifically, in both river-lake networks, $\delta^{13}C$ values of particulate organic matter within inflow rivers were generally higher (less negative, and therefore less depleted in ^{13}C) than those measured in samples collected from the lakes and from the outflow rivers. This pattern was particularly pronounced for the Esthwaite Water network, in which $\delta^{13}C$ within Cunsey Beck remained much more depleted in ^{13}C (more negative $\delta^{13}C$) compared to conditions within the Black Beck inflow across the entire 2.8 km reach of the downstream river that was sampled in the research reported here. These observations likely reflect phytoplankton production of organic matter within Esthwaite Water, and export of this particulate organic matter into the downstream river network. In the absence of DIC limitation given plentiful CO_2 and/or HCO_3^-, phytoplankton are known to produce organic matter by preferentially utilising ^{12}C over ^{13}C during photosynthesis, thereby yielding $\delta^{13}C$ in biomass that is isotopically 'light' compared to the source dissolved inorganic C (e.g. O'Leary, 1988; Wolfe et al., 2001). The data reported in this thesis indicate that this signature of isotopically depleted particulate organic matter is present throughout the reaches of the downstream rivers that were sampled, suggesting that lake-derived particulate organic matter continues to influence river networks for a significant distance downstream of lakes. The geochemical and biological impacts of this lake-derived particulate organic matter should be the focus for future research, for example to determine if limiting nutrients may be liberated from the particulate organic matter to support primary production within the downstream river network. In comparison to the Esthwaite Water-network, the impact of Ennerdale Water on $\delta^{13}C$ within particulate organic matter was much less pronounced, likely reflecting the much more oligotrophic nature and reduced rates of phytoplankton primary production within Ennerdale Water compared to Esthwiate Water.

Somewhat more enriched values of $\delta^{15}N$ were observed in particulate organic matter from samples collected from the Esthwaite Water network (Fig. 12, mean = 3.68 ‰) compared to the Ennerdale Water network (mean = -1.06 ‰). This likely reflects the greater influence of sources of N including livestock manure, slurry and human wastewater in the catchment of Esthwiate Water compared to Ennerdale Water. These sources of N are known to have elevated $\delta^{15}N$ compared to the atmospheric sources that are likely to dominate N inputs to the Ennerdale catchment (Kendall, 1998), and elevated $\delta^{15}N$ in sources of N are likely to be transferred to organic matter during uptake and synthesis of new biomass within the catchments. In addition to a source signature, elevated $\delta^{15}N$ within particulate material in the Esthwaite catchment may also reflect greater opportunities for denitrification in the soils and sediments due to the prevalence of anoxic environments and high organic carbon availability. Slow transport of groundwater through the soil matrix and sediment-water interface within these substrates leaves a residual pool of N for biotic uptake that is enriched in ^{15}N (e.g. Tao et al., 2018). However, unlike δ^{13}C, δ^{15}N within particulate matter did not exhibit consistent patterns of change within the river-lake networks studied as part of the research reported here (Fig. 12). There was no clear seasonal pattern in δ^{15}N across either network, nor any consistent change when comparing sites upstream and downstream of the lakes in each network.

4.2. Changes in N and P pools driven by lake discontinuities within river-lake networks

Nitrate was the dominant form of inorganic N in the inflow rivers and lakes sampled as part of the research reported here, consistent with research reported from other fresh waters in the UK (Lloyd et al. 2019; Yates et al., 2019; Fig. 13). Average concentrations of NO_3^- within the Black Beck inflow to Esthwaite Water (average = 0.344 mg N/L) were somewhat higher than within the River Liza inflow to Ennerdale Water (average = 0.257 mg N/L), consistent with greater anthropogenic impacts and associated inputs of N to the catchment of Esthwaite Water compared to Ennerdale Water, inputs which reach freshwater ecosystems via multiple surface and sub-surface pathways (Di & Cameron, 2002; Huebsch et al., 2014; Lloyd et al., 2019). The two lakes examined in the research reported here alternated between sinks and sources of NO_3^- to downstream rivers, depending on the sampling date. However, perhaps most notably, the impacts of Esthwaite Water and of Ennerdale Water on NO_3^- within their respective river-lake networks differed significantly. For the Ennerdale Water-network, generally only small relative and absolute changes in NO_3^- concentration were observed within the lake compared to the main inflow river, averaging 0.07% or 0.0003 mg N/L over the six sampling dates. Whilst NO_3^- concentrations within the network as a whole tended to decrease through the spring-summer period, there were no clear or consistent changes in the impact of Ennerdale Water on NO_3^- concentrations from the River Liza before export into the River Ehen.

However, very different patterns of change in NO_3^- concentration were imposed by Esthwaite Water on its downstream river network compared to Ennerdale Water. Across March, April, May and June sampling events, Esthwaite Water provided a subsidy of NO_3^- to Cunsey Beck, within increases in NO_3^- concentration in the lake compared to the Black Beck inflow that averaged 40% or 0.126 mg N/L. These subsidies continued to maintain significantly higher concentrations of NO_3^- throughout the 2.8 km reach of Cunsey Beck that was sampled for the research reported here, compared to the inflow of Black Beck. Increased NO_3^- concentration within Esthwaite Water likely reflects a legacy of higher NO_3^- inputs to the lake from Black Beck over the winter months, before sampling for the research reported here began, combined with autochthonous generation of NO_3^- within the lake via ammonification and nitrification. However, by July 2025, NO_3^- concentrations had decreased significantly in Esthwaite Water, reaching <0.2 mg N/L and substantially below the concentrations within Black Beck. During the final two sampling events in July 2025 that are reported in this thesis, the lake acted as a significant sink of NO_3^-, decreasing concentrations by up to 78% or 0.344 mg N/L compared to the Black Beck inflow. Importantly, on both these sampling dates, NO_3^- concentrations within Cunsey Beck did not recover to those recorded within the inflow of Black Beck at any point along the 2.8 km reach that was sampled. These observations of Esthwaite Water acting as a significant sink for NO_3^- in the summer months are consistent with recent research reported by Grefe et al. (2024) that described an annual average reduction in NO_3^- concentration for Esthwaite water of 44% compared to concentrations within Black Beck. Based on stable isotope analysis of N and oxygen in NO_3^-, Grefe et al suggest that a combination of assimilation and of nitrification controls NO_3^- dynamics within Esthwaite Water, and are likely to explain the summer decreases in NO_3^- concentration reported here. In comparison, Cheng & Basu (2017) report an estimate of average NO_3^- removal by lakes of 59% ± 28% based on a global dataset, whilst annual average removal of NO_3^- by reservoirs has been reported to range between 4 and 58% (David et al., 2006). Whilst Grefe et al. (2024) reported that average NO_3^- drawdown across five lakes in the ELD, including Esthwaite Water, appeared to increase with increasing average annual water residence time, the greater residence time associated with Ennerdale Water compared to Esthwaite Water did not appear significant in controlling NO_3^- concentrations in the research reported in this thesis. Instead, the more eutrophic conditions within Esthwaite Water, and the associated greater biological demand for N during the summer months when phytoplankton production in the lake is maximal, appear to have been responsible for the substantial drawdown of NO_3^- concentrations reported here. This may have been compounded by decomposition and assimilation of organic matter within Esthwaite Water, particularly in the hypolimnion under summer stratification, thereby promoting anaerobic conditions conducive to denitrification and further reductions in NO_3^- concentrations within the lake (Bennion & Smith, 2000; Fairchild & Velinsky, 2006). Regardless of the exact mechanism responsible for NO_3^- drawdown within Esthwaite Water during the summer months, this pattern has important consequences for NO_3^- availability in the downstream river network.

In addition to NO_3^-, DON dynamics contrasted between the two river-lake networks in the research reported here (Fig. 15a and 15b). In the Ennerdale Water-network, the lake consistently acted as a source of elevated DON concentrations compared to the River Liza. However, concentrations were highly variable with the River Ehen downstream of Ennerdale Water, suggesting that in-river processes and/or inputs of DON from allochthonous sources downstream of the lake were important controls on DON concentrations within the river and seemed to over-print any control exerted by Ennerdale Water. In contrast, Esthwaite Water shifted from an apparent sink of DON in March, April, May and June, to act as a net source of DON in July, providing a subsidy of DON to Cunsey Beck downstream. This pattern was not entirely consistent with the changes observed in DOC concentration within Esthwaite Water (Fig. 9), particularly in March, April, May and June, suggesting differences in the pathways of organic matter processing and highlighting the selective mineralisation and transformation of nitrogenous versus carbonaceous compounds within this lake, at least in the spring and early summer months.

In contrast to DOC concentrations within the main inflow rivers of Black Beck and the River Liza, during the rainfall-runoff event on 5th June 2025 the concentrations of DON did not appear to change significantly, although some increase was observed in Black

Beck but not in the River Liza. These observations are in contrast to some other research, such as results from clay-dominated catchments of the River Sem, UK, where consistent peaks in both NO_3^- and DON were shown with storm events (Lloyd et al., 2019). This discrepancy could stem from the abundant DON sources within the intensively farmed dairy catchment of the River Sem, with livestock sources of DON activated by rainfall-runoff events, a process that was not significant in either the Esthwaite Water or, particularly, the Ennerdale Water networks.

Concentrations of SRP were generally extremely low or below the limit of detection for the Ennerdale Water network (Fig. 16), consistent with the oligotrophic nature of this catchment, limited anthropogenic inputs of P to the catchment, and rapid assimilation of any available SRP by biota within the catchment. In contrast, within the more nutrient-enriched Esthwaite Water network, higher concentrations of SRP were observed. Further, the lake acted relatively consistently as a sink for SRP delivered from Black Beck, with concentrations delivered downstream to Cunsey Beck decreasing substantially and often towards the detection limit. This pattern was maintained throughout the sampling events across March to July, with no evidence of a seasonal switch between the lake acting as a source and a sink to the downstream river network, as was described above for NO_3^-.

Other parameters including DOP and TPP showed no discernible patterns in the data that are above the limits of detection.

Chapter 5: Conclusion

This thesis has investigated the biogeochemical dynamics of carbon, nitrogen and phosphorus across two contrasting river–lake networks, with a focus on how lakes regulate nutrient concentration, fluxes and speciation under varying hydrological and seasonal conditions. Overall, the findings highlight the central role of lakes in modulating downstream nutrient transport and transformation, demonstrating that lakes act as key regulators of downstream biogeochemistry. In the oligotrophic Ennerdale Water network, dissolved nutrient concentrations were consistently low, whilst in the mesotrophic Esthwaite Water system, higher concentrations and stronger seasonal dynamics were observed, especially in respect of N and P biogeochemistry. Stable isotope analyses further revealed distinct patterns in the sources and processing of particulate organic matter, highlighting the role of lakes in altering the quality and isotopic signatures of particulate as well as dissolved material that is exported downstream. These findings confirm that lakes are not passive conduits but exert active controls on nutrient fluxes at the network scale.

5.1. Recommendations for future research

The implications of these findings are significant for understanding and managing river–lake networks. The contrasting behaviours of oligotrophic and mesotrophic systems emphasise that the lake trophic state should be considered in water management strategies. Future research should build on these results by examining the biological availability of lake-derived organic matter in receiving rivers on a longer timescale, and by extending isotope, concentration and speciation analyses to a wider range of catchments that provide more complete gradients of lake average water residence time and trophic status. This understanding will improve our capacity to predict and manage the functioning of river–lake networks under future environmental change.

References

Adams, J. L., Tipping, E., Bryant, C. L., Helliwell, R. C., Toberman, H., & Quinton, J. (2015). Aged riverine particulate organic carbon in four UK catchments. *Science of the Total Environment*, *536,* 648–654. https://doi.org/10.1016/j.scitotenv.2015.06.141

Alex Elliott, J. (2012). Predicting the impact of changing nutrient load and temperature on the phytoplankton of England's largest lake, Windermere. *Freshwater Biology, 57*(2), 400–413.

Arp, C. D., & Baker, M. A. (2007). Discontinuities in stream nutrient uptake below lakes in mountain drainage networks. *Limnology and Oceanography*, *52*(5), 1978–1990. https://doi.org/10.4319/lo.2007.52.5.1978

Asmala, E., Haraguchi, L., Markager, S., Massicotte, P., Riemann, B., Staehr, P. A., & Carstensen, J. (2018). Eutrophication Leads to Accumulation of Recalcitrant Autochthonous Organic Matter in Coastal Environment. *Global Biogeochemical Cycles, 32*(11), 1673–1687. https://doi.org/10.1029/2017GB005848

Assaad, A., Pontvianne, S., Corriou, J., & Pons, M. (2015). Spectrophotometric characterization of dissolved organic matter in a rural watershed: the Madon River (N-E France). *Environmental Monitoring and Assessment, 187*(4). https://doi.org/10.1007/s10661-015-4422-9

Aufdenkampe, A. K., Hedges, J. I., Richey, J. E., Krusche, A. V., & Llerena, C. A. (2001). Sorptive fractionation of dissolved organic nitrogen and amino acids onto fine sediments within the Amazon Basin. *Limnology and Oceanography, 46*(8), 1921–1935. https://doi.org/10.4319/lo.2001.46.8.1921

Averyjr, G., Willey, J., & Kieber, R. (2006). Carbon isotopic characterization of dissolved organic carbon in rainwater: Terrestrial and marine influences. *Atmospheric Environment, 40(*39), 7539–7545. https://doi.org/10.1016/j.atmosenv.2006.07.014

Ayling, S. M., Thompson, J., Gray, A., & McEwen, L. J. (2021). Impact of reduced rainfall on above ground dry matter production of semi-natural grassland in South Gloucestershire, UK: a rainfall manipulation study. *Frontiers in Environmental Science*, *9.* https://doi.org/10.3389/fenvs.2021.686668

Azam, F., & Hodson, R. E. (1977). Dissolved ATP in the sea and its utilisation by marine bacteria. *Nature*, *267*(5613), 696–698. https://doi.org/10.1038/267696a0

Bade, D. L., Carpenter, S. R., Cole, J. J., Pace, M. L., Kritzberg, E., Van De Bogert, M. C., Cory, R. M., & McKnight, D. M. (2007). Sources and fates of dissolved organic carbon in lakes as determined by whole-lake carbon isotope additions. *Biogeochemistry, 84*(2), 115–129. https://doi.org/10.1007/s10533-006-9013-y

Bai, L., Liu, X., Wu, Y., Cheng, H., Wang, C., Jiang, H., & Wang, A. (2023). Distinct seasonal variations of dissolved organic matter across two large freshwater lakes in

China: Lability profiles and predictive modeling. *Journal of Environmental Management, 339,* 117880. https://doi.org/10.1016/j.jenvman.2023.117880

Baldwin, D. S. (2013). Organic phosphorus in the aquatic environment. *Environmental Chemistry, 10*(6), 439. https://doi.org/10.1071/en13151

Balmer, M. B., & Downing, J. A. (2011). Carbon dioxide concentrations in eutrophic lakes: undersaturation implies atmospheric uptake. *Inland Waters, 1*(2), 125–132. https://doi.org/10.5268/IW-1.2.366

Barker, P. A., Pates, J. M., Payne, R. J., & Healey, R. M. (2005). Changing nutrient levels in Grasmere, English Lake District, during recent centuries. *Freshwater Biology, 50*(12), 1971–1981. https://doi.org/10.1111/j.1365-2427.2005.01439.x

Bastviken, D., Cole, J., Pace, M., & Tranvik, L. (2004). Methane emissions from lakes: Dependence of lake characteristics, two regional assessments, and a global estimate. *Global Biogeochemical Cycles, 18*(4). https://doi.org/10.1029/2004GB002238

Batjes, N. (1996). Total carbon and nitrogen in the soils of the world. *European Journal of Soil Science, 47*(2), 151–163. https://doi.org/10.1111/j.1365-2389.1996.tb01386.x

Bauer, J. E., Druffel, E. R., Wolgast, D. M., & Griffin, S. (2002). Temporal and regional variability in sources and cycling of DOC and POC in the northwest Atlantic continental shelf and slope. *Deep Sea Research Part II: Topical Studies in Oceanography, 49*(20), 4387–4419. https://doi.org/10.1016/S0967-0645(02)00123-6

Begum, M. S., Park, J., Yang, L., Shin, K. H., & Hur, J. (2023). Optical and molecular indices of dissolved organic matter for estimating biodegradability and resulting carbon dioxide production in inland waters: A review. *Water Research, 228,* 119362. https://doi.org/10.1016/j.watres.2022.119362

Belisle, B. S., Steffen, M. M., Pound, H. L., Watson, S. B., DeBruyn, J. M., Bourbonniere, R. A., Boyer, G. L., & Wilhelm, S. W. (2016). Urea in Lake Erie: Organic nutrient sources as potentially important drivers of phytoplankton biomass. *Journal of Great Lakes Research*, *42*(3), 599–607. https://doi.org/10.1016/j.jglr.2016.03.002

Bellmore, J. R., & Baxter, C. V. (2014). Effects of geomorphic process domains on river ecosystems: a comparison of floodplain and confined valley segments. *River research and applications, 30*(5), 617-630. https://doi.org/10.1002/rra.2672

Benitez-Nelson, C. R., Kolowith, L. C., Pellechia, P., & Thunell, R. (2004). Phosphonates and particulate organic phosphorus cycling in an anoxic marine basin. *Limnology and Oceanography, 49*(5), 1593–1604. https://doi.org/10.4319/lo.2004.49.5.1593

Benner, R., & Amon, R. M. (2014). The Size-Reactivity Continuum of Major Bioelements in the Ocean. *Annual Review of Marine Science, 7*(1), 185–205. https://doi.org/10.1146/annurev-marine-010213-135126

Bennion, H., & Smith, M. A. (2000). Variability in the water chemistry of shallow ponds in southeast England, with special reference to the seasonality of nutrients and implications for modelling trophic status. *Hydrobiologia, 436*(1), 145–158.

Bernhard, A. (2010). The nitrogen cycle: processes, players, and human impact. *Nature Education Knowledge, 3*(10), 25.

Bertilsson, S., & Jones, J. B. (2003). Supply of dissolved organic matter to aquatic ecosystems. In *Aquatic Ecosystems* (pp. 3–24). https://doi.org/10.1016/b978-012256371-3/50002-0

Beusen, A. H. W., Bouwman, A. F., Van Beek, L. P. H., Mogollón, J. M., & Middelburg, J. J. (2016). Global riverine N and P transport to ocean increased during the 20th century despite increased retention along the aquatic continuum. *Biogeosciences, 13*(8), 2441–2451. https://doi.org/10.5194/bg-13-2441-2016

Blanchet, C. C., Arzel, C., Davranche, A., Kahilainen, K. K., Secondi, J., Taipale, S., Lindberg, H., Loehr, J., Manninen-Johansen, S., Sundell, J., Maanan, M., & Nummi, P. (2022). Ecology and extent of freshwater browning - What we know and what should be studied next in the context of global change. *Science of The Total Environment, 812,* 152420. https://doi.org/10.1016/j.scitotenv.2021.152420

Bose, S. K., Francis, R. C., Govender, M., Bush, T., & Spark, A. (2008). Lignin content versus syringyl to guaiacyl ratio amongst poplars. *Bioresource Technology, 100*(4), 1628–1633. https://doi.org/10.1016/j.biortech.2008.08.046

Bouwman, A. F., Bierkens, M. F. P., Griffioen, J., Hefting, M. M., Middelburg, J. J., Middelkoop, H., & Slomp, C. P. (2013). Nutrient dynamics, transfer and retention along the aquatic continuum from land to ocean: towards integration of ecological and biogeochemical models. *Biogeosciences, 10*(1), 1–22. https://doi.org/10.5194/bg-10-1-2013

Bravo, A. G., Wildi, W., & Poté, J. (2010). Kinetics of plant material mass loss and DNA release in freshwater column. *Ecotoxicology and Environmental Safety, 73*(7), 1548–1552. https://doi.org/10.1016/j.ecoenv.2010.05.019

Brearley, C. A., & Hanke, D. E. (1996). Inositol phosphates in the duckweed Spirodela polyrhiza L. *Biochemical Journal, 314*(1), 215–225. https://doi.org/10.1042/bj3140215

Brett, M. T., Bunn, S. E., Chandra, S., E. Galloway, A. W., Guo, F., Kainz, M. J., Kankaala, P., P. Lau, D. C., Moulton, T. P., Power, M. E., Rasmussen, J. B., Taipale, S. J., Thorp, J. H., & Wehr, J. D. (2017). How important are terrestrial organic carbon inputs for secondary production in freshwater ecosystems? *Freshwater Biology, 62*(5), 833–853. https://doi.org/10.1111/fwb.12909

Brown, J. H., Gillooly, J. F., Allen, A. P., Savage, V. M., & West, G. B. (2004). Toward a metabolic theory of ecology. *Ecology, 85*(7), 1771–1789. https://doi.org/10.1890/03-9000

Bruns, A., NüBel, U., Cypionka, H., & Overmann, J. (2003). Effect of signal compounds and incubation conditions on the culturability of freshwater bacterioplankton. *Applied and Environmental Microbiology, 69*(4), 1980–1989. https://doi.org/10.1128/aem.69.4.1980-1989.2003

Burgazzi, G., Laini, A., Racchetti, E., & Viaroli, P. (2017). Mesohabitat mosaic in lowland braided rivers: Short-term variability of macroinvertebrate metacommunities. *Journal of Limnology*, *76*(s1). https://doi.org/10.4081/jlimnol.2017.1650

Burgin, A. J., & Hamilton, S. K. (2007). Have we overemphasized the role of denitrification in aquatic ecosystems? A review of nitrate removal pathways. *Frontiers in Ecology and the Environment, 5*(2), 89–96. https://doi.org/10.1890/1540-9295(2007)5[89:HWOTRO]2.0.CO;2

Burzyńska, I. (2019). Monitoring of selected fertilizer nutrients in surface waters and soils of agricultural land in the river valley in Central Poland. *Journal of water and land development*, (43). https://DOI.org/10.2478/jwld-2019-0061

Cai, W. (2010). Estuarine and Coastal Ocean carbon paradox: CO2 sinks or sites of terrestrial carbon incineration? *Annual Review of Marine Science, 3*(1), 123–145. https://doi.org/10.1146/annurev-marine-120709–142723

Cai, W., Hu, X., Huang, W., Murrell, M. C., Lehrter, J. C., Lohrenz, S. E., Chou, W., Zhai, W., Hollibaugh, J. T., Wang, Y., Zhao, P., Guo, X., Gundersen, K., Dai, M., & Gong, G. (2011). Acidification of subsurface coastal waters enhanced by eutrophication. *Nature Geoscience, 4*(11), 766–770. https://doi.org/10.1038/ngeo1297

Carpenter, S. R., Cole, J. J., Kitchell, J. F., & Pace, M. L. (1998). Impact of dissolved organic carbon, phosphorus, and grazing on phytoplankton biomass and production in experimental lakes. *Limnology and Oceanography, 43*(1), 73–80. https://doi.org/10.4319/lo.1998.43.1.0073

Canfield, D. E., Glazer, A. N., & Falkowski, P. G. (2010). The Evolution and Future of Earth's Nitrogen Cycle. *Science.* https://doi.org/1186120

Carpenter, S. R. (2008). Phosphorus control is critical to mitigating eutrophication. *Proceedings of the National Academy of Sciences, 105*(32), 11039–11040. https://doi.org/10.1073/pnas.0806112105

Cardille, J. A., Carpenter, S. R., Coe, M. T., Foley, J. A., Hanson, P. C., Turner, M. G., & Vano, J. A. (2007). Carbon and water cycling in lake-rich landscapes: Landscape connections, lake hydrology, and biogeochemistry. *Journal of Geophysical Research: Biogeosciences, 112*(G2). https://doi.org/10.1029/2006JG000200

Causse, J., BaurèS, E., Mery, Y., Jung, A., & Thomas, O. (2015). Variability of N Export in water: a review. *Critical Reviews in Environmental Science and Technology, 45*(20), 2245–2281. https://doi.org/10.1080/10643389.2015.1010432

Chen, M., Chen, J., & Sun, F. (2008). Agricultural phosphorus flow and its environmental impacts in China. *Science of The Total Environment, 405*(1-3), 140–152. https://doi.org/10.1016/j.scitotenv.2008.06.031

Chen, J., Yang, H., Zeng, Y., Guo, J., Song, Y., & Ding, W. (2018). Combined use of radiocarbon and stable carbon isotope to constrain the sources and cycling of particulate organic carbon in a large freshwater lake, China. *Science of The Total Environment, 625,* 27–38. https://doi.org/10.1016/j.scitotenv.2017.12.275

Cheng, F. Y., & Basu, N. B. (2017). Biogeochemical hotspots: Role of small water bodies in landscape nutrient processing. *Water Resources Research, 53*(6), 5038–5056. https://doi.org/10.1002/2016wr020102

Copetti, D., Tartari, G., Valsecchi, L., Salerno, F., Viviano, G., Mastroianni, D., Yin, H., & Viganò, L. (2018). Phosphorus content in a deep river sediment core as a tracer of long-term (1962–2011) anthropogenic impacts: A lesson from the Milan metropolitan area. *Science of the Total Environment, 646,* 37–48. https://doi.org/10.1016/j.scitotenv.2018.07.256

Cordell, D., Drangert, J., & White, S. (2009). The story of phosphorus: Global food security and food for thought. *Global Environmental Change, 19*(2), 292–305. https://doi.org/10.1016/j.gloenvcha.2008.10.009

Correll, D. L. (1998). The Role of Phosphorus in the Eutrophication of Receiving Waters: A Review. *Journal of Environmental Quality, 27*(2), 261–266. https://doi.org/10.2134/jeq1998.00472425002700020004x

Cory, R. M., McKnight, D. M., Chin, P., Miller, P., & Jaros, C. L. (2007). Chemical characteristics of fulvic acids from Arctic surface waters: Microbial contributions and photochemical transformations. *Journal of Geophysical Research: Biogeosciences, 112*(G4). https://doi.org/10.1029/2006JG000343

Cooley, S. R., Coles, V. J., Subramaniam, A., & Yager, P. L. (2007). Seasonal variations in the Amazon plume-related atmospheric carbon sink. *Global Biogeochemical Cycles, 21*(3). https://doi.org/10.1029/2006GB002831

Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., Duarte, C. M., Kortelainen, P., Downing, J. A., Middelburg, J. J., & Melack, J. (2007). Plumbing the Global Carbon Cycle: Integrating Inland Waters into the Terrestrial Carbon Budget. *Ecosystems, 10*(1), 172–185. https://doi.org/10.1007/s10021-006-9013-8

Craig, D. (2002). A new view of the river continuum concept. *Bull. North. Amer. Benthol. Soc, 19,* 380–381.

Crumpton, W. G., Isenhart, T. M., & Mitchell, P. D. (1992). Nitrate and organic N analyses with second-derivative spectroscopy. *Limnology and Oceanography, 37*(4), 907–913. https://doi.org/10.4319/lo.1992.37.4.0907

David, M. B., Wall, L. G., Royer, T. V., & Tank, J. L. (2006). Denitrification and the nitrogen budget of a reservoir in an agricultural landscape. *Ecological Applications*, *16*(6), 2177-2190. https://doi.org/10.1890/1051-0761(2006)016

De Kluijver, A., Schoon, P. L., Downing, J. A., Schouten, S., & Middelburg, J. J. (2014). Stable carbon isotope biogeochemistry of lakes along a trophic gradient. *Biogeosciences, 11*(22), 6265–6276. https://doi.org/10.5194/bg-11-6265-2014

Deng, J., Salmaso, N., Jeppesen, E., Qin, B., & Zhang, Y. (2019). The relative importance of weather and nutrients determining phytoplankton assemblages differs between seasons in large Lake Taihu, China. *Aquatic Sciences, 81,* 1–14.

Di, H. J., & Cameron, K. C. (2002). Nitrate leaching in temperate agroecosystems: sources, factors and mitigating strategies. *Nutrient cycling in agroecosystems, 64*(3), 237–256.

Dittmar, T., Lara, R. J., & Kattner, G. (2001). River or mangrove? Tracing major organic matter sources in tropical Brazilian coastal waters. *Marine Chemistry, 73*(3–4), 253–271. https://doi.org/10.1016/s0304-4203(00)00110-9

Dodds, W. K., & Smith, V. H. (2016). Nitrogen, phosphorus, and eutrophication in streams. *Taylor & Francis*. https://www.tandfonline.com/doi/abs/10.5268/IW-6.2.909

Doney, S. C. (2010). The growing human footprint on coastal and Open-Ocean biogeochemistry. *Science, 328*(5985), 1512–1516. https://doi.org/10.1126/science.1185198

Doretto, A., Piano, E., & Larson, C. E. (2020). The River Continuum Concept: lessons from the past and perspectives for the future. Canadian *Journal of Fisheries and Aquatic Sciences, 77*(11), 1853–1864. https://doi.org/10.1139/cjfas-2020-0039

Duda, A. M. (1993). Addressing nonpoint sources of water pollution must become an international priority. *Water Science & Technology, 28*(3–5), 1–11. https://doi.org/10.2166/wst.1993.0398

Elser, J. J., Fagan, W. F., Denno, R. F., Dobberfuhl, D. R., Folarin, A., Huberty, A., Interlandi, S., Kilham, S. S., McCauley, E., Schulz, K. L., Siemann, E. H., & Sterner, R. W. (2000). Nutritional constraints in terrestrial and freshwater food webs. *Nature, 408*(6812), 578–580. https://doi.org/10.1038/35046058

Edmondson, W. T. (1970). Phosphorus, Nitrogen, and Algae in Lake Washington after Diversion of Sewage. *Science, 169*(3946), 690–691. https://doi.org/10.1126/science.169.3946.690

Edwards, A. C., Kay, D., McDonald, A. T., Francis, C., Watkins, J., Wilkinson, J., & Wyer, M. (2008). Farmyards, an overlooked source for highly contaminated runoff.

Journal of Environmental Management, 87(4), 551–559. https://doi.org/10.1016/j.jenvman.2006.06.027

Elser, J., & Bennett, E. (2011). A broken biogeochemical cycle. *Nature, 478*(7367), 29–31. https://doi.org/10.1038/478029a

Evans, C. D., Futter, M. N., Moldan, F., Valinia, S., Frogbrook, Z., & Kothawala, D. N. (2017). Variability in organic carbon reactivity across lake residence time and trophic gradients. *Nature Geoscience, 10*(11), 832–835. https://doi.org/10.1038/ngeo3051

FAO. (2018). The role of cities in the transformation of food systems: sharing lessons from Milan pact cities. https://www.milanurbanfoodpolicypact.org/wp-content/uploads/2022/01/The-Role-Of-Cities-In-The-Transformation-Of-Food-Systems-Sharing-Lessons-From-Milan-Pact-Cities.pdf

Fairchild, G. W., & Velinsky, D. J. (2006). Effects of small ponds on stream water chemistry. *Lake and Reservoir Management, 22*(4), 321–330. https://doi.org/10.1080/07438140609354366

Falkowski, P., Scholes, R. J., Boyle, E., Canadell, J., Canfield, D., Elser, J., Gruber, N., Hibbard, K., Högberg, P., Linder, S., Mackenzie, F. T., Moore, B., III, Pedersen, T., Rosenthal, Y., Seitzinger, S., Smetacek, V., & Steffen, W. (2000). The Global Carbon Cycle: a test of our knowledge of Earth as a system. *Science, 290*(5490), 291–296. https://doi.org/10.1126/science.290.5490.291

Fallon, R. D., & Brock, T. D. (1979). Decomposition of Blue-Green algal (Cyanobacterial) blooms in Lake Mendota, Wisconsin. *Applied and Environmental Microbiology, 37*(5), 820–830. https://doi.org/10.1128/aem.37.5.820-830.1979

Fee, E. J., Hecky, R. E., M. Kasian, S. E., & Cruikshank, D. R. (1996). Effects of lake size, water clarity, and climatic variability on mixing depths in Canadian Shield lakes. *Limnology and Oceanography, 41*(5), 912–920. https://doi.org/10.4319/lo.1996.41.5.0912

Feng, W., Yang, F., Zhang, C., Liu, J., Song, F., Chen, H., Zhu, Y., Liu, S., & Giesy, J. P. (2020). Composition characterization and biotransformation of dissolved, particulate and algae organic phosphorus in eutrophic lakes. *Environmental Pollution, 265,* 114838. https://doi.org/10.1016/j.envpol.2020.114838

Fielding, J. J., Croudace, I. W., Kemp, A. E., Pearce, R. B., Cotterill, C. J., Langdon, P., & Avery, R. (2020). Tracing lake pollution, eutrophication and partial recovery from the sediments of Windermere, UK, using geochemistry and sediment microfabrics. *Science of the Total Environment, 722,* 137745. https://doi.org/10.1016/j.scitotenv.2020.137745

Finger, D., Wüest, A., & Bossard, P. (2013). Effects of oligotrophication on primary production in peri-alpine lakes. *Water Resources Research, 49*(8), 4700–4710. https://doi.org/10.1002/wrcr.20355

Fink, G., Alcamo, J., Flörke, M., & Reder, K. (2018). Phosphorus Loadings to the World's Largest Lakes: Sources and Trends. *Global Biogeochemical Cycles, 32*(4), 617–634. https://doi.org/10.1002/2017GB005858

Foster, G. D., Roberts, E. C., Gruessner, B., & Velinsky, D. J. (2000). Hydrogeochemistry and transport of organic contaminants in an urban watershed of Chesapeake Bay (USA). *Applied Geochemistry, 15*(7), 901–915. https://doi.org/10.1016/S0883-2927(99)00107-9

Field, C. B., Behrenfeld, M. J., Randerson, J. T., & Falkowski, P. (1998). Primary production of the biosphere: integrating terrestrial and oceanic components. *Science*, *281*(5374), 237–240. https://doi.org/10.1126/science.281.5374.237

Fixen, P. E., & West, F. B. (2002). Nitrogen Fertilizers: Meeting contemporary challenges. *AMBIO, 31*(2), 169–176. https://doi.org/10.1579/0044-7447-31.2.169

Garzon-Garcia, A., Burton, J., Franklin, H. M., Moody, P. W., De Hayr, R. W., & Burford, M. A. (2018). Indicators of phytoplankton response to particulate nutrient bioavailability in fresh and marine waters of the Great Barrier Reef. *Science of the Total Environment, 636,* 1416–1427. https://doi.org/10.1016/j.scitotenv.2018.04.334

Godin, P., Macdonald, R. W., Kuzyk, Z. Z. A., Goñi, M. A., & Stern, G. A. (2017). Organic matter compositions of rivers draining into Hudson Bay: Present-day trends and potential as recorders of future climate change. *Journal of Geophysical Research Biogeosciences, 122*(7), 1848–1869. https://doi.org/10.1002/2016jg003569

Godwin, H. (1962). Half-life of radiocarbon. *Nature, 195*(4845), 984. https://doi.org/10.1038/195984a0

Grefe, I., Mackay, E. B., Wynn, P. M., Barker, P. A., Grant, H. K., Pereira, M. G., Maberly, S. C., & Surridge, B. W. J. (2024). The impact of lake discontinuities on nitrogen biogeochemistry in river networks. *Inland Waters,* 1–16. https://doi.org/10.1080/20442041.2024.2379149

Griffith, A. W., & Gobler, C. J. (2020). Harmful algal blooms: A climate change costressor in marine and freshwater ecosystems. *Harmful Algae, 91,* 101590.

Gruber, N., & Galloway, J. N. (2008). An Earth-system perspective of the global nitrogen cycle. *Nature, 451*(7176), 293–296. https://doi.org/10.1038/nature06592

Guo, W., Yang, F., Li, Y., & Wang, S. (2017). New insights into the source of decadal increase in chemical oxygen demand associated with dissolved organic carbon in Dianchi Lake. *Science of the Total Environment,* 603–604, 699–708. https://doi.org/10.1016/j.scitotenv.2017.02.024

Hanson, P. C., Bade, D. L., Carpenter, S. R., & Kratz, T. K. (2003). Lake metabolism: Relationships with dissolved organic carbon and phosphorus. *Limnology and Oceanography, 48*(3), 1112–1119. https://doi.org/10.4319/lo.2003.48.3.1112

Hanson, P. C., Pollard, A. I., Bade, D. L., Predick, K., Carpenter, S. R., & Foley, J. A. (2004). A model of carbon evasion and sedimentation in temperate lakes. *Global Change Biology, 10*(8), 1285–1298. https://doi.org/10.1111/j.1529-8817.2003.00805.x

Hanson, P. C., Hamilton, D. P., Stanley, E. H., Preston, N., Langman, O. C., & Kara, E. L. (2011). Fate of Allochthonous Dissolved Organic Carbon in Lakes: A Quantitative Approach. *PLOS ONE, 6*(7), e21884. https://doi.org/10.1371/journal.pone.0021884

Hanson, P. C., Pace, M. L., Carpenter, S. R., Cole, J. J., & Stanley, E. H. (2014). Integrating Landscape Carbon cycling: Research needs for resolving organic carbon budgets of lakes. *Ecosystems, 18*(3), 363–375. https://doi.org/10.1007/s10021-014-9826-9

Haygarth, P., Condron, L., Heathwaite, A., Turner, B., & Harris, G. (2005). The phosphorus transfer continuum: Linking source to impact with an interdisciplinary and multi-scaled approach. *Science of The Total Environment, 344*(1–3), 5–14. https://doi.org/10.1016/j.scitotenv.2005.02.001

He, C., Zhang, L., DeMarchi, C., & Croley II, T. E. (2014). Estimating point and nonpoint source nutrient loads in the Saginaw Bay watersheds. *Journal of Great Lakes Research, 40,* 11–17. https://doi.org/10.1016/j.jglr.2014.01.013

He, D., Wang, K., Pang, Y., He, C., Li, P., Li, Y., Xiao, S., Shi, Q., & Sun, Y. (2020). Hydrological management constraints on the chemistry of dissolved organic matter in the Three Gorges Reservoir. *Water Research, 187,* 116413. https://doi.org/10.1016/j.watres.2020.116413

Hernes, P. J., Robinson, A. C., & Aufdenkampe, A. K. (2007). Fractionation of lignin during leaching and sorption and implications for organic matter “freshness.” *Geophysical Research Letters, 34*(17). https://doi.org/10.1029/2007gl031017

Houser, J. N., Bade, D. L., Cole, J. J., & Pace, M. L. (2003). The dual influences of dissolved organic carbon on hypolimnetic metabolism: Organic substrate and photosynthetic reduction. *Biogeochemistry, 64*(2), 247–269.

Howarth, R. W., & Marino, R. (2006). Nitrogen as the limiting nutrient for eutrophication in coastal marine ecosystems: Evolving views over three decades. *Limnology and Oceanography, 51*(1, part 2), 364–376. https://doi.org/10.4319/lo.2006.51.1_part_2.0364

Huebsch, M., Fenton, O., Horan, B., Hennessy, D., Richards, K. G., Jordan, P., Goldscheider, N., Butscher, C., & Blum, P. (2014). Mobilisation or dilution? Nitrate response of karst springs to high rainfall events. Hydrology and Earth System *Sciences, 18*(11), 4423–4435. https://doi.org/10.5194/hess-18-4423-2014

Janicka, E., Kanclerz, J., Wiatrowska, K., & Budka, A. (2022). Variability of nitrogen and phosphorus content and their forms in waters of a River-Lake system. *Frontiers in Environmental Science*, *10*. https://doi.org/10.3389/fenvs.2022.874754

Janssen, A. B., Van Wijk, D., Van Gerven, L. P., Bakker, E. S., Brederveld, R. J., DeAngelis, D. L., Janse, J. H., & Mooij, W. M. (2019). Success of lake restoration depends on spatial aspects of nutrient loading and hydrology. *Science of The Total Environment, 679,* 248–259. https://doi.org/10.1016/j.scitotenv.2019.04.443

Jarvie, H. P., Neal, C., Leach, D. V., Ryland, G. P., House, W. A., & Robson, A. J. (1997). Major ion concentrations and the inorganic carbon chemistry of the Humber rivers. *Science of The Total Environment, 194,* 285–302. https://doi.org/10.1016/S0048-9697(96)05371-5

Jarvie, H. P., Smith, D. R., Norton, L. R., Edwards, F. K., Bowes, M. J., King, S. M., Scarlett, P., Davies, S., Dils, R. M., & Bachiller-Jareno, N. (2018). Phosphorus and nitrogen limitation and impairment of headwater streams relative to rivers in Great Britain: A national perspective on eutrophication. *The Science of the Total Environment*, *621*, 849–862. https://doi.org/10.1016/j.scitotenv.2017.11.128

Jiang, T., Skyllberg, U., Björn, E., Green, N. W., Tang, J., Wang, D., Gao, J., & Li, C. (2017). Characteristics of dissolved organic matter (DOM) and relationship with dissolved mercury in Xiaoqing River-Laizhou Bay estuary, Bohai Sea, China. *Environmental Pollution, 223,* 19–30. https://doi.org/10.1016/j.envpol.2016.12.006

Jonas, R. B., & Tuttle, J. H. (1990). Bacterioplankton and organic carbon dynamics in the lower Mesohaline Chesapeake Bay. *Applied and Environmental Microbiology, 56*(3), 747–757. https://doi.org/10.1128/aem.56.3.747-757.1990

Jones, A. S., Horsburgh, J. S., Mesner, N. O., Ryel, R. J., & Stevens, D. K. (2012). Influence of sampling frequency on estimation of annual total phosphorus and total suspended solids loads. *Journal of the American Water Resources Association, 48*(6), 1258–1275. https://doi.org/10.1111/j.1752-1688.2012.00684.x

Jones, N. E. (2010). Incorporating lakes within the river discontinuum: longitudinal changes in ecological characteristics in stream–lake networks. *Canadian Journal of Fisheries and Aquatic Sciences*, *67*(8), 1350–1362. https://doi.org/10.1139/f10-069

Jones, I. D., & Elliott, J. A. (2007). Modelling the effects of changing retention time on abundance and composition of phytoplankton species in a small lake. *Freshwater Biology, 52*(6), 988–997. https://doi.org/10.1111/j.1365-2427.2007.01746.x

Jones, S. E., Solomon, C. T., & Weidel, B. C. (2012). Subsidy or subtraction: How do terrestrial inputs influence consumer production in lakes? *Freshwater Reviews, 5*(1), 37. https://doi.org/10.1608/frj-5.1.475

Joset-Espardellier, F., Astier, C., Evans, E. H., & Carr, N. G. (1978). Cyanobacteria grown under photoautotrophic, photoheterotrophic, and heterotrophic regimes: Sugar metabolism and carbon dioxide fixation. *FEMS Microbiology Letters, 4*(5), 261–264. https://doi.org/10.1111/j.1574-6968.1978.tb02875.x

Kaiser, E., Arscott, D. B., Tockner, K., & Sulzberger, B. (2004). Sources and distribution of organic carbon and nitrogen in the Tagliamento River, Italy. *Aquatic Sciences, 66*(1), 103–116.

Kang, P. G., Mitchell, M. J., McHale, P. J., Driscoll, C. T., Inamdar, S., & Park, J. H. (2016). Importance of within-lake processes in affecting the dynamics of dissolved organic carbon and dissolved organic and inorganic nitrogen in an Adirondack forested lake/watershed. *Biogeosciences, 13*(9), 2787–2801.

Karanfil, T., Erdogan, I., & Schlautman, M. A. (2003). SELECTING FILTER MEMBRANES for measuring DOC and UV_{254}. *Journal AWWA, 95*(3), 86–100. https://www.jstor.org/stable/41311011

Karlsson, J., Jansson, M., & Jonsson, A. (2007). Respiration of allochthonous organic carbon in unproductive forest lakes determined by the Keeling plot method. *Limnology and Oceanography, 52*(2), 603–608.

Kendall, C. (1998). Tracing Nitrogen Sources and Cycling in Catchments. *Isotope Tracers in Catchment Hydrology,* 519–576. https://doi.org/10.1016/B978-0-444-81546-0.50023-9

Kling, G. W., Kipphut, G. W., Miller, M. M., & O'Brien, W. J. (2000). Integration of lakes and streams in a landscape perspective: the importance of material processing on spatial patterns and temporal coherence. *Freshwater Biology*, *43*(3), 477–497. https://doi.org/10.1046/j.1365-2427.2000.00515.x

Knudson, B. M. (1954). The Ecology of the Diatom Genus Tabellaria in the English Lake District. *Journal of Ecology, 42*(2), 345–358. https://doi.org/10.2307/2256866

Koch, B. J. (2005). *Invertebrate-mediated nitrogen cycling in three connected aquatic ecosystems* (Doctoral dissertation). University of Wyoming. ProQuest Dissertations Publishing.

Kosten, S., M. Huszar, V. L., Bécares, E., Costa, L. S., Hansson, A., Jeppesen, E., Kruk, C., Lacerot, G., Mazzeo, N., Meester, L. D., Moss, B., Lürling, M., Nõges, T., Romo, S., & Scheffer, M. (2012). Warmer climates boost cyanobacterial dominance in shallow lakes. *Global Change Biology, 18*(1), 118–126. https://doi.org/10.1111/j.1365-2486.2011.02488.x

Kragh, T., & Sand-Jensen, K. (2018). Carbon limitation of lake productivity. *Proceedings of the Royal Society B Biological Sciences, 285*(1891), 20181415. https://doi.org/10.1098/rspb.2018.1415

Kritzberg, E. S., Langenheder, S., & Lindström, E. S. (2006). Influence of dissolved organic matter source on lake bacterioplankton structure and function – implications for seasonal dynamics of community composition. *FEMS Microbiology Ecology, 56*(3), 406–417. https://doi.org/10.1111/j.1574-6941.2006.00084.x

Kronvang, B., Grant, R., Larsen, S. E., Svendsen, L. M., & Kristensen, P. (1995). Nonpoint-source nutrient losses to the aquatic environment in Denmark: Impact of agriculture. *Marine and Freshwater Research, 46*(1), 167–177.

Lankoski, J., & Ollikainen, M. (2013). Innovations in nonpoint source pollution policy—European perspectives. Choices, 28(3), 1–5.

Lawlor, A. J., Rigg, E., May, L., Woof, C., James, J. B., & Tipping, E. (1998). Dissolved nutrient concentrations and loads in some upland streams of the English Lake District. *Hydrobiologia, 377*(1-3), 85–93.

Li, J., Sun, W., Cao, Y., Wu, J., Duan, L., Zhang, M., Luo, X., Deng, Q., Peng, Z., Mou, X., Li, W., & Wang, P. (2025). Increased temperature enhances microbial-mediated lignin decomposition in river sediment. *Microbiome, 13*(1). https://doi.org/10.1186/s40168-025-02076-z

Li, Z., & Zhou, L. (2010). Cadmium transport mediated by soil colloid and dissolved organic matter: A field study. *Journal of Environmental Sciences, 22*(1), 106–115. https://doi.org/10.1016/s1001-0742(09)60081-4

Liang, Y., & Blake, R. (2006). Oxygen isotope signature of Pi regeneration from organic compounds by phosphomonoesterases and photooxidation. *Geochimica et Cosmochimica Acta, 70*(15), 3957–3969. https://doi.org/10.1016/j.gca.2006.04.036

Limpert, K. E., Carnell, P. E., Trevathan-Tackett, S. M., & Macreadie, P. I. (2020). Reducing emissions from degraded floodplain wetlands. *Frontiers in Environmental Science*, *8*, 8. https://doi.org/10.3389/fenvs.2020.00008

Liu, Z., Yan, H., & Zeng, S. (2021). Increasing autochthonous production in inland waters as a contributor to the missing carbon sink. *Frontiers in Earth Science*, *9*, 620513. https://doi.org/10.3389/feart.2021.620513

Lloyd, C., Johnes, P., Freer, J., Carswell, A., Jones, J., Stirling, M., Hodgkinson, R., Richmond, C., & Collins, A. (2019). Determining the sources of nutrient flux to water in headwater catchments: Examining the speciation balance to inform the targeting of mitigation measures. *Science of The Total Environment, 648,* 1179–1200. https://doi.org/10.1016/j.scitotenv.2018.08.190

Loreau, M., Mouquet, N., & Holt, R. D. (2003). Meta‐ecosystems: a theoretical framework for a spatial ecosystem ecology. *Ecology Letters, 6*(8), 673–679.

Luu, T. N. M., Nga, T., Do, Matiatos, I., Panizzo, V. N., & Trinh, A. D. (2020). Stable isotopes as an effective tool for N nutrient source identification in a heavily urbanized and agriculturally intensive tropical lowland basin. *Biogeochemistry, 149*(1), 17–35. https://doi.org/10.1007/s10533-020-00663-w

Lv, Z., Ran, X., Liu, J., Feng, Y., Zhong, X., & Jiao, N. (2024). Effectiveness of chemical oxygen demand as an indicator of organic pollution in aquatic environments. *Ocean-Land-Atmosphere Research*, *3*, 0050. https://doi.org/10.34133/olar.0050

Maberly, S. C., De Ville, M. M., Thackeray, S. J., Ciar, D., Clarke, M., Fletcher, J. M., James, J. B., Keenan, P., Mackay, E. B., Patel, M. (2016). *A survey of the status of the lakes of the English Lake District: the Lakes Tour 2015.* NERC/Centre for Ecology & Hydrology [Accessed 2025 August 30].

Maberly, S.C.; De Ville, M.M.; Feuchtmayr, H.; Jones, I.D.; Mackay, E.B.; May, L.; Thackeray, S.J.; & Winfield, I.J. (2011) *The limnology of Esthwaite Water: historical change and its causes, current state and prospects for the future.* NERC/Centre for Ecology & Hydrology, 155pp. (CEH Project Number: C04038) (Unpublished)

Maberly, S. C., & Elliott, J. A. (2012). Insights from long‐term studies in the Windermere catchment: external stressors, internal interactions and the structure and function of lake ecosystems. *Freshwater Biology, 57*(2), 233–243.

Mainstone, C. P., & Parr, W. (2002). Phosphorus in rivers — Ecology and management. *Science of The Total Environment, 282-283,* 25–47. https://doi.org/10.1016/S0048-9697(01)00937-8

Marcé, R., Von Schiller, D., Aguilera, R., Martí, E., & Bernal, S. (2018). Contribution of hydrologic opportunity and biogeochemical reactivity to the variability of nutrient retention in river networks. *Global Biogeochemical Cycles, 32*(3), 376–388. https://doi.org/10.1002/2017gb005677

Martens, D. A., Reedy, T. E., & Lewis, D. T. (2004). Soil organic carbon content and composition of 130-year crop, pasture and forest land-use managements. *Global Change Biology, 10*(1), 65-78. https://doi.org/10.1046/j.1529-8817.2003.00722.x

Matiatos, I. (2015). Nitrate source identification in groundwater of multiple land-use areas by combining isotopes and multivariate statistical analysis: A case study of Asopos basin (Central Greece). *Science of the Total Environment, 541,* 802–814. https://doi.org/10.1016/j.scitotenv.2015.09.134

Mayer, L. M., Keil, R. G., Macko, S. A., Joye, S. B., Ruttenberg, K. C., & Aller, R. C. (1998). Importance of suspended participates in riverine delivery of bioavailable nitrogen to coastal zones. *Global Biogeochemical Cycles, 12*(4), 573–579. https://doi.org/10.1029/98gb02267

McCallister, S. L., & Del Giorgio, P. A. (2008). Direct measurement of the d13C signature of carbon respired by bacteria in lakes: Linkages to potential carbon sources, ecosystem baseline metabolism, and CO2 fluxes. *Limnology and Oceanography, 53*(4), 1204–1216. https://doi.org/10.4319/lo.2008.53.4.1204

McCallister, S. L., Ishikawa, N. F., & Kothawala, D. N. (2018). Biogeochemical tools for characterizing organic carbon in inland aquatic ecosystems. *Limnology and Oceanography Letters, 3*(6), 444–457. https://doi.org/10.1002/lol2.10097

McCann, K., Hastings, A., & Huxel, G. R. (1998). Weak trophic interactions and the balance of nature. *Nature*, *395*(6704), 794–798. https://doi.org/10.1038/27427

McNichol, A. P., & Aluwihare, L. I. (2007). The Power of Radiocarbon in Biogeochemical Studies of the Marine Carbon Cycle: Insights from Studies of Dissolved and Particulate Organic Carbon (DOC and POC). *Chemical Reviews, 107*(2), 443–466. https://doi.org/10.1021/cr050374g

Meyer, J. L. (1994). The microbial loop in flowing waters. *Microbial Ecology, 28*(2), 195–199. https://doi.org/10.1007/bf00166808

Meyers, P. A. (2003). Applications of organic geochemistry to paleolimnological reconstructions: A summary of examples from the Laurentian Great Lakes. *Organic Geochemistry, 34*(2), 261–289. https://doi.org/10.1016/S0146-6380(02)00168-7

Miller, A. G., Espie, G. S., & Canvin, D. T. (1990). Physiological aspects of CO2 and HCO3− transport by cyanobacteria: a review. *Canadian Journal of botany*, *68*(6), 1291-1302. https://doi.org/10.1139/b90-165

Mills, M. S., Thurman, E. M., Ertel, J., & Thorn, K. A. (1996). Organic geochemistry and sources of natural aquatic foams. In *ACS symposium series* (pp. 151–192). https://doi.org/10.1021/bk-1996-0651.ch011

Miller, M. P., & McKnight, D. M. (2010). Comparison of seasonal changes in fluorescent dissolved organic matter among aquatic lake and stream sites in the Green Lakes Valley. *Journal of Geophysical Research: Biogeosciences*, *115*(G1). https://doi.org/10.1029/2009JG000985

Minor, E. C., & Oyler, A. R. (2021). Dissolved organic matter in large lakes: a key but understudied component of the carbon cycle. *Biogeochemistry, 164*(1), 295–318. https://doi.org/10.1007/s10533-020-00733-z

Minor, E. C., Simjouw, J., & Mulholland, M. R. (2006). Seasonal variations in dissolved organic carbon concentrations and characteristics in a shallow coastal bay. *Marine Chemistry, 101*(3–4), 166–179. https://doi.org/10.1016/j.marchem.2006.02.005

Minshall, G. W., Cummins, K. W., Petersen, R. C., Cushing, C. E., Bruns, D. A., Sedell, J. R., & Vannote, R. L. (1985). Developments in stream ecosystem theory. *Canadian Journal of Fisheries and Aquatic Sciences, 42*(5), 1045–1055.

Motomizu, S., Wakimoto, T., & Tôei, K. (1983). Spectrophotometric determination of phosphate in river waters with molybdate and malachite green. *Analyst, 108*(1284), 361–367.

Moore, W., Beck, M., Riedel, T., Rutgers van der Loeff, M., Dellwig, O., Shaw, T., Schnetger, B., & Brumsack, H. (2011). Radium-based pore water fluxes of silica, alkalinity, manganese, DOC, and uranium: A decade of studies in the German Wadden Sea. *Geochimica et Cosmochimica Acta, 75*(21), 6535–6555. https://doi.org/10.1016/j.gca.2011.08.037

Moran, M. A., Kujawinski, E. B., Stubbins, A., Fatland, R., Aluwihare, L. I., Buchan, A., Crump, B. C., Dorrestein, P. C., Dyhrman, S. T., Hess, N. J., Howe, B., Longnecker, K., Medeiros, P. M., Niggemann, J., Obernosterer, I., Repeta, D. J., & Waldbauer, J. R. (2016). Deciphering ocean carbon in a changing world. *Proceedings of the National Academy of Sciences, 113*(12), 3143–3151. https://doi.org/10.1073/pnas.1514645113

Mulholland, P. J. (2003). Large-Scale patterns in dissolved organic carbon concentration, flux, and sources. In *Aquatic Ecosystems* (pp. 139–159). https://doi.org/10.1016/b978-012256371-3/50007-x

Mulholland, P. J., Marzolf, E. R., Webster, J. R., Hart, D. R., & Hendricks, S. P. (1997). Evidence that hyporheic zones increase heterotrophic metabolism and phosphorus uptake in forest streams. *Limnology and Oceanography, 42*(3), 443–451. https://doi.org/10.4319/lo.1997.42.3.0443

Myers-Pigg, A. N., Louchouarn, P., W. Amon, R. M., Prokushkin, A., Pierce, K., & Rubtsov, A. (2015). Labile pyrogenic dissolved organic carbon in major Siberian Arctic rivers: Implications for wildfire-stream metabolic linkages. *Geophysical Research Letters, 42*(2), 377-385. https://doi.org/10.1002/2014GL062762

Ngochera, M. J., & Bootsma, H. A. (2020). Spatial and temporal dynamics of pCO2 and CO2 flux in tropical Lake Malawi. *Limnology and Oceanography, 65*(7), 1594–1607. https://doi.org/10.1002/lno.11408

Nguyen, H. V., & Hur, J. (2011). Tracing the sources of refractory dissolved organic matter in a large artificial lake using multiple analytical tools. *Chemosphere, 85*(5), 782–789. https://doi.org/10.1016/j.chemosphere.2011.06.068

Ni, Z., Wang, S., Cai, J., Li, H., Jenkins, A., Maberly, S. C., & May, L. (2019). The potential role of sediment organic phosphorus in algal growth in a low nutrient lake. *Environmental pollution, 255*, 113235.

Nixon, S. W. (1981). Remineralization and nutrient cycling in coastal marine ecosystems. In *Estuaries and nutrients* (pp. 111–138). https://doi.org/10.1007/978-1-4612-5826-1_6

Odum, W. E., Fisher, J. S., & Pickral, J. C. (1979). Factors Controlling the Flux of Particulate Organic Carbon from Estuarine Wetlands. In *Ecological processes in coastal and marine systems* (pp. 69–80). https://doi.org/10.1007/978-1-4615-9146-7_5

O’Leary, M. H. (1988). Carbon isotopes in photosynthesis. *BioScience, 38*(5), 328–336. https://doi.org/10.2307/1310735

Oren Benaroya, R., Zamski, E., & Tel-Or, E. (2004). L-Myo-inositol 1-phosphate synthase in the aquatic fern Azolla filiculoides. *Plant Physiology and Biochemistry, 42*(2), 97–102. https://doi.org/10.1016/j.plaphy.2003.11.008

Ostapenia, A. P., Parparov, A., & Berman, T. (2009). Lability of organic carbon in lakes of different trophic status. *Freshwater Biology, 54*(6), 1312–1323. https://doi.org/10.1111/j.1365-2427.2009.02183.x

Paerl, H. W., Scott, J. T., McCarthy, M. J., Newell, S. E., Gardner, W. S., Havens, K. E., Hoffman, D. K., Wilhelm, S. W., & Wurtsbaugh, W. A. (2016). It takes two to tango: When and where dual nutrient (N & P) reductions are needed to protect lakes and downstream ecosystems. *Environmental Science & Technology*, *50*(20), 10805–10813. https://doi.org/10.1021/acs.est.6b02575

Partensky, F., Hess, W. R., & Vaulot, D. (1999). Prochlorococcus, a marine photosynthetic prokaryote of global significance. *Microbiology and Molecular Biology Reviews, 63*(1), 106–127. https://doi.org/10.1128/mmbr.63.1.106-127.1999

Pasek, M. A., Sampson, J. M., & Atlas, Z. (2014). Redox chemistry in the phosphorus biogeochemical cycle. *Proceedings of the National Academy of Sciences, 111*(43), 15468–15473. https://doi.org/10.1073/pnas.1408134111

Peterson, B., Fry, B., Hullar, M., Saupe, S., & Wright, R. (1994). The distribution and stable carbon isotopic composition of dissolved organic carbon in estuaries. *Estuaries, 17*(1), 111–121.

Peterson, B. J., Hobbie, J. E., Hershey, A. E., Lock, M. A., Ford, T. E., Vestal, J. R., McKinley, V. L., Hullar, M. a. J., Miller, M. C., Ventullo, R. M., & Volk, G. S. (1985). Transformation of a Tundra River from Heterotrophy to Autotrophy by Addition of *Phosphorus. Science, 229*(4720), 1383–1386. https://doi.org/10.1126/science.229.4720.1383

Peuravuori, J., & Pihlaja, K. (1997). Molecular size distribution and spectroscopic properties of aquatic humic substances. *Analytica Chimica Acta, 337*(2), 133–149. https://doi.org/10.1016/S0003-2670(96)00412-6

Polis, G. A. (1999). Why are parts of the world green? Multiple factors control productivity and the distribution of biomass. *Oikos*, 3–15.

Poole, G. C. (2002). Fluvial landscape ecology: addressing uniqueness within the river discontinuum. *Freshwater biology, 47*(4), 641–660.

Price, G. D., Badger, M. R., Woodger, F. J., & Long, B. M. (2008). Advances in understanding the cyanobacterial CO2-concentrating-mechanism (CCM): Functional components, Ci transporters, diversity, genetic regulation and prospects for engineering into plants. *Journal of Experimental Botany*, *59*(7), 1441–1461. https://doi.org/10.1093/jxb/erm112

Qin, B., Gao, G., Zhu, G., Zhang, Y., Song, Y., Tang, X., Xu, H., & Deng, J. (2012). Lake eutrophication and its ecosystem response. *Chinese Science Bulletin, 58*(9), 961–970. https://doi.org/10.1007/s11434-012-5560-x

Qualls, R. G., & Haines, B. L. (1992). Biodegradability of Dissolved Organic Matter in Forest Throughfall, Soil Solution, and Stream Water. *Soil Science Society of America Journal, 56*(2), 578-586. https://doi.org/10.2136/sssaj1992.03615995005600020038x

Read, E. K., Ivancic, M., Hanson, P., Cade-Menun, B. J., & McMahon, K. D. (2014). Phosphorus speciation in a eutrophic lake by 31P NMR spectroscopy. *Water Research, 62*, 229–240. https://doi.org/10.1016/j.watres.2014.06.005

Reche, I., Pace, M. L., & Cole, J. J. (2000). Modeled effects of dissolved organic carbon and solar spectra on photobleaching in lake ecosystems. *Ecosystems, 3*(5), 419–432. https://doi.org/10.1007/s100210000038

Reynolds, C. S., & Lund, J. W. G. (1988). The phytoplankton of an enriched, soft - water lake subject to intermittent hydraulic flushing (Grasmere, English Lake District). *Freshwater Biology, 19*(3), 379–404.

Rippka, R. (1972). Photoheterotrophy and chemoheterotrophy among unicellular blue-green algae. *Archives of Microbiology, 87*(1), 93–98. https://doi.org/10.1007/bf00424781

Robertson, G., & Groffman, P. (2007). NITROGEN TRANSFORMATIONS. In *Soil microbiology, ecology and biochemistry,* pp. 341–364. https://doi.org/10.1016/b978-0-08-047514-1.50017-2

Rogers, T. L., Munch, S. B., Stewart, S. D., Palkovacs, E. P., Giron-Nava, A., Matsuzaki, S., & Symons, C. C. (2020). Trophic control changes with season and nutrient loading in lakes. *Ecology Letters, 23*(8), 1287–1297. https://doi.org/10.1111/ele.13532

Rosmarin, A. (2004). The precarious geopolitics of phosphorous. *Down to earth, 30*(33), 27–34.

Ryther, J. H., & Dunstan, W. M. (1971). Nitrogen, phosphorus, and eutrophication in the coastal marine environment. *Science, 171*(3975), 1008–1013. https://doi.org/10.1126/science.171.3975.1008

SanClements, M. D., Oelsner, G. P., McKnight, D. M., Stoddard, J. L., & Nelson, S. J. (2012). New Insights into the Source of Decadal Increases of Dissolved Organic Matter in Acid-Sensitive Lakes of the Northeastern United States. *Environmental Science & Technology, 46*(6), 3212–3219. https://doi.org/10.1021/es204321x

Sammond, D. W., Yarbrough, J. M., Mansfield, E., Bomble, Y. J., Hobdey, S. E., Decker, S. R., Taylor, L. E., Resch, M. G., Bozell, J. J., Himmel, M. E., Vinzant, T. B., & Crowley, M. F. (2014). Predicting Enzyme Adsorption to Lignin Films by Calculating Enzyme Surface Hydrophobicity. *Journal of Biological Chemistry, 289*(30), 20960–20969. https://doi.org/10.1074/jbc.m114.573642

Schindler, D. W. (1974). Eutrophication and recovery in Experimental lakes: Implications for Lake Management. *Science, 184*(4139), 897–899. https://doi.org/10.1126/science.184.4139.897

Schindler, D. W., Carpenter, S. R., Chapra, S. C., Hecky, R. E., & Orihel, D. M. (2016). Reducing Phosphorus to Curb Lake Eutrophication is a Success.

Environmental Science & Technology, 50(17), 8923–8929. https://doi.org/10.1021/acs.est.6b02204

Schulhof, M. A., Shurin, J. B., & J. Declerck, S. A. (2019). Phytoplankton growth and stoichiometric responses to warming, nutrient addition and grazing depend on lake productivity and cell size. *Global Change Biology, 25*(8), 2751–2762. https://doi.org/10.1111/gcb.14660

Seekell, D. A., Lapierre, F., Ask, J., Bergström, K., Deininger, A., Rodríguez, P., & Karlsson, J. (2015). The influence of dissolved organic carbon on primary production in northern lakes. *Limnology and Oceanography, 60*(4), 1276–1285. https://doi.org/10.1002/lno.10096

Selig, U. (2003). Characterisation and quantification of phosphorus release from profundal bottom sediments in two dimictic lakes during summer stratification. *Journal of Limnology, 62*(2), 151–162. https://doi.org/10.4081/jlimnol.2003.151

Shinohara, R., Imai, A., Kawasaki, N., Komatsu, K., Kohzu, A., Miura, S., Sano, T., Satou, T., & Tomioka, N. (2012). Biogenic phosphorus compounds in sediment and suspended particles in a shallow eutrophic lake: a 31P-Nuclear Magnetic Resonance (31P NMR) study. *Environmental Science & Technology, 46*(19), 10572–10578. https://doi.org/10.1021/es301887z

Smith, V. H., & Schindler, D. W. (2009). Eutrophication science: where do we go from here? *Trends in Ecology & Evolution, 24*(4), 201–207. https://doi.org/10.1016/j.tree.2008.11.009

Soares, M. C. S., Marinho, M. M., Azevedo, S. M., Branco, C. W., & Huszar, V. L. (2012). Eutrophication and retention time affecting spatial heterogeneity in a tropical reservoir. *Limnologica, 42*(3), 197–203. https://doi.org/10.1016/j.limno.2011.11.002

Sobek, S., Tranvik, L. J., Prairie, Y. T., Kortelainen, P., & Cole, J. J. (2007). Patterns and regulation of dissolved organic carbon: An analysis of 7,500 widely distributed lakes. *Limnology and Oceanography, 52*(3), 1208–1219. https://doi.org/10.4319/lo.2007.52.3.1208

Søndergaard, M., & Middelboe, M. (1995). A cross-system analysis of labile dissolved organic carbon. *Marine Ecology Progress Series, 118,* 283–294. https://doi.org/10.3354/meps118283

Song, K., Wen, Z., Shang, Y., Yang, H., Lyu, L., Liu, G., Fang, C., Du, J., & Zhao, Y. (2018). Quantification of dissolved organic carbon (DOC) storage in lakes and reservoirs of mainland China. *Journal of Environmental Management, 217,* 391–402. https://doi.org/10.1016/j.jenvman.2018.03.121

Spears, B.M., (2014). *Scientific challenge UK Centre for Ecology and Hydrology, UK lake restoration* https://www.ceh.ac.uk/our-science/projects/uk-lake-restoration

Spencer, R. G. M., Aiken, G. R., Wickland, K. P., Striegl, R. G., & Hernes, P. J. (2008). Seasonal and spatial variability in dissolved organic matter quantity and composition from the Yukon River basin, Alaska. *Global Biogeochemical Cycles, 22*(4). https://doi.org/10.1029/2008gb003231

Stanford, J. W. J., & Ward, J. V. (1983). The serial discontinuity concept of lotic ecosystems. *Ann Arbor Science Publishers.*

Sterner, R. & Elser, J. (2003). *Ecological Stoichiometry: The Biology of Elements from Molecules to the Biosphere.* Princeton: Princeton University Press. https://doi.org/10.1515/9781400885695

Stow, C. A., Cha, Y., Johnson, L. T., Confesor, R., & Richards, R. P. (2015). Long-term and seasonal trend decomposition of Maumee River nutrient inputs to western Lake Erie. *Environmental Science & Technology, 49*(6), 3392–3400.

Striegl, R. G., Dornblaser, M. M., Aiken, G. R., Wickland, K. P., & Raymond, P. A. (2007). Carbon export and cycling by the Yukon, Tanana, and Porcupine rivers, Alaska, 2001–2005. *Water Resources Research, 43*(2). https://doi.org/10.1029/2006wr005201

Stuiver, M., & Polach, H. A. (1977). Discussion reporting of 14C data. *Radiocarbon, 19*(3), 355–363. https://doi.org/10.1017/s0033822200003672

Subramaniam, A., Yager, P. L., Carpenter, E. J., Mahaffey, C., Björkman, K., Cooley, S., Kustka, A. B., Montoya, J. P., Sañudo-Wilhelmy, S. A., Shipe, R., & Capone, D. G. (2008). Amazon River enhances diazotrophy and carbon sequestration in the tropical North Atlantic Ocean. *Proceedings of the National Academy of Sciences, 105*(30), 10460–10465. https://doi.org/10.1073/pnas.0710279105

Svendsen, L. M., Kronvang, B., Kristensen, P., & Græsbøl, P. (1995). Dynamics of phosphorus compounds in a lowland river system: Importance of retention and non‐point sources. *Hydrological Processes, 9*(2), 119–142. https://doi.org/10.1002/hyp.3360090202

Talling, J. F. (1993). Comparative seasonal changes, and inter-annual variability and stability, in a 26-year record of total phytoplankton biomass in four English lake basins. *Hydrobiologia*, *268*(2), 65-98. https://doi.org/10.1007/BF00006879

Talling, J. F. (1976). The Depletion of Carbon Dioxide from Lake Water by Phytoplankton. *Journal of Ecology*, *64*(1), 79–121. https://doi.org/10.2307/2258685

Tao, Y., Dan, D., Kun, L., Chengda, H., Haibing, C., Guo, F., Qiujin, X., Fuhong, S., & Fengchang, W. (2018). δ15N and nutrient stoichiometry of water, aquatic organisms and environmental implications in Taihu lake, China. *Environmental Pollution, 237,* 166–173. https://doi.org/10.1016/j.envpol.2018.02.048

Toming, K., Kotta, J., Uuemaa, E., Sobek, S., Kutser, T., & Tranvik, L. J. (2020). Predicting lake dissolved organic carbon at a global scale. *Scientific Reports, 10*(1), 1–8. https://doi.org/10.1038/s41598-020-65010-3

Tong, Y., Li, J., Qi, M., Zhang, X., Wang, M., Liu, X., ... & Lin, Y. (2019). Impacts of water residence time on nitrogen budget of lakes and reservoirs. *Science of the Total Environment, 646,* 75–83.

Tranvik, L. J., Downing, J. A., Cotner, J. B., Loiselle, S. A., Striegl, R. G., Ballatore, T. J., Dillon, P., Finlay, K., Fortino, K., Knoll, L. B., Kortelainen, P. L., Kutser, T., Larsen, S., Laurion, I., Leech, D. M., McCallister, S. L., McKnight, D. M., Melack, J. M., Overholt, E., . . . Weyhenmeyer, G. A. (2009). Lakes and reservoirs as regulators of carbon cycling and climate. *Limnology and Oceanography, 54*(6part2), 2298–2314. https://doi.org/10.4319/lo.2009.54.6_part_2.2298

Triska, F. J., Kennedy, V. C., Avanzino, R. J., Zellweger, G. W., & Bencala, K. E. (1989). Retention and transport of nutrients in a Third-Order stream: channel processes. *Ecology, 70*(6), 1877–1892. https://doi.org/10.2307/1938119

Urban, N. R., Auer, M. T., Green, S. A., Lu, X., Apul, D. S., Powell, K. D., & Bub, L. (2005). Carbon cycling in Lake Superior. *Journal of Geophysical Research: Oceans*, *110*(C6). https://doi.org/10.1029/2003JC002230

U.S. Environmental Protection Agency. (2008). *Nutrient criteria technical guidance manual: Wetlands* (EPA-822-B-08-001). U.S. Environmental Protection Agency. http://www2.epa.gov/nutrient-policy-data/nutrient-criteria-technical-guidancemanual-wetlands

Van Andel, J., & Aronson, J. (2012). Restoration ecology. *Restoration Ecology: The New Frontier,* 233-247. https://doi.org/10.1002/9781118223130

Van Mooy, B. A., Moutin, T., Duhamel, S., Rimmelin, P., & Van Wambeke, F. (2008). Phospholipid synthesis rates in the eastern subtropical South Pacific Ocean. *Biogeosciences, 5*(1), 133–139. https://doi.org/10.5194/bg-5-133-2008

Vanni, M. J., & Temte, J. (1990). Seasonal patterns of grazing and nutrient limitation of phytoplankton in a eutrophic lake. *Limnology and Oceanography*, *35*(3), 697–709. https://doi.org/10.4319/lo.1990.35.3.0697

Vannote, R. L., Minshall, G. W., Cummins, K. W., Sedell, J. R., & Cushing, C. E. (1980). The river continuum concept. *Canadian journal of fisheries and aquatic sciences, 37*(1), 130–137. https://doi.org/10.1139/f80-017

Vannote, R. L., & Minshall, G. W. (1982). Fluvial processes and local lithology controlling abundance, structure, and composition of mussel beds. *Proceedings of the National Academy of Sciences*, *79*(13), 4103–4107. https://doi.org/10.1073/pnas.79.13.4103

Verschoor, A. M., Van Dijk, M. A., Huisman, J., & Van Donk, E. (2012). Elevated CO_2 concentrations affect the elemental stoichiometry and species composition of an experimental phytoplankton community. *Freshwater Biology*, *58*(3), 597–611. https://doi.org/10.1111/j.1365-2427.2012.02833.x

Visser, P. M., Verspagen, J. M., Sandrini, G., Stal, L. J., Matthijs, H. C., Davis, T. W., Paerl, H. W., & Huisman, J. (2016). How rising CO2 and global warming may stimulate harmful cyanobacterial blooms. *Harmful Algae*, *54*, 145–159. https://doi.org/10.1016/j.hal.2015.12.006

Wang, M., Xu, X., Wu, Z., Zhang, X., Sun, P., Wen, Y., Wang, Z., Lu, X., Zhang, W., Wang, X., & Tong, Y. (2019). Seasonal Pattern of Nutrient Limitation in a Eutrophic Lake and Quantitative Analysis of the Impacts from Internal Nutrient Cycling. *Environmental Science & Technology*, *53*(23), 13675–13686. https://doi.org/10.1021/acs.est.9b04266

Wang, S., Gao, Y., Jia, J., Lu, Y., Sun, K., Ha, X., Li, Z., & Deng, W. (2022). Vertically stratified water source characteristics and associated driving mechanisms of particulate organic carbon in a large floodplain lake system. *Water Research*, *209*, 117963. https://doi.org/10.1016/j.watres.2021.117963

Ward, J. V., & Stanford, J. A. (1995). Ecological connectivity in alluvial river ecosystems and its disruption by flow regulation. *Regulated rivers: research & management, 11*(1), 105–119.

Ward, N. D., Bianchi, T. S., Medeiros, P. M., Seidel, M., Richey, J. E., Keil, R. G., & Sawakuchi, H. O. (2017). Where Carbon Goes When Water Flows: Carbon Cycling across the Aquatic Continuum. *Frontiers in Marine Science, 4,* 232439. https://doi.org/10.3389/fmars.2017.00007

Wassenaar, L. I. (1995). Evaluation of the origin and fate of nitrate in the Abbotsford Aquifer using the isotopes of15N and18O in NO3−. *Applied Geochemistry, 10*(4), 391–405. https://doi.org/10.1016/0883-2927(95)00013-a

Wehrli, B. (2013). Conduits of the carbon cycle. *Nature, 503*(7476), 346–347. https://doi.org/10.1038/503346a

Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R., & Mopper, K. (2003). Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environmental Science & Technology, 37*(20), 4702–4708. https://doi.org/10.1021/es030360x

Wetzel, R. G. (2001). *Limnology: lake and river ecosystems.* Gulf professional publishing.

White, A. K., & Metcalf, W. W. (2007). Microbial metabolism of reduced phosphorus compounds. *Annual Review of Microbiology, 61*(1), 379–400. https://doi.org/10.1146/annurev.micro.61.080706.093357

Wilkinson, G. M., Pace, M. L., & Cole, J. J. (2012). Terrestrial dominance of organic matter in north temperate lakes. *Global Biogeochemical Cycles, 27*(1), 43–51. https://doi.org/10.1029/2012gb004453

Williamson, J. L., Tye, A., Lapworth, D. J., Monteith, D., Sanders, R., Mayor, D. J., Barry, C., Bowes, M., Bowes, M., Burden, A., Callaghan, N., Farr, G., Felgate, S., Fitch, A., Gibb, S., Gilbert, P., Hargreaves, G., Keenan, P., Kitidis, V., . . . Evans, C. (2021). Landscape controls on riverine export of dissolved organic carbon from Great Britain. *Biogeochemistry, 164*(1), 163–184. https://doi.org/10.1007/s10533-021-00762-2

Withers, P. J. A., Jarvie, H. P., Hodgkinson, R. A., Palmer‐Felgate, E. J., Bates, A., Neal, M., Howells, R., Withers, C. M., & Wickham, H. D. (2009). Characterization of phosphorus sources in rural watersheds. *Journal of Environmental Quality, 38*(5), 1998–2011. https://doi.org/10.2134/jeq2008.0096

Wolfe, B. B., Edwards, T. W. D., Elgood, R. J., & Beuning, K. R. M. (2002). Carbon and oxygen isotope Analysis of lake sediment cellulose: methods and applications. In *Developments in paleoenvironmental research* (pp. 373–400). https://doi.org/10.1007/0-306-47670-3_14

Worrall, F., Howden, N. J., Burt, T. P., & Bartlett, R. (2018). Declines in the dissolved organic carbon (DOC) concentration and flux from the UK. *Journal of Hydrology, 556,* 775–789. https://doi.org/10.1016/j.jhydrol.2017.12.001

Worsfold, P. J., Monbet, P., Tappin, A. D., Fitzsimons, M. F., Stiles, D. A., & McKelvie, I. D. (2008). Characterisation and quantification of organic phosphorus and organic nitrogen components in aquatic systems: A Review. *Analytica Chimica Acta, 624*(1), 37-58. https://doi.org/10.1016/j.aca.2008.06.016

Wu, R., Guo, W., Li, Y., Deng, S., & Chang, J. (2023). Land use regulates the spectroscopic properties and sources of dissolved organic matter in the inflowing rivers of a large plateau lake in southwestern China: implication for organic pollution control. *Environmental Science and Pollution Research, 30*(41), 94623–94638. https://doi.org/10.1007/s11356-023-29037-z

Xia, F., Liu, Z., Zhao, M., He, H., He, Q., Lai, C., He, X., Ma, Z., Wu, Y., & Ma, S. (2023). High stability of autochthonous organic matter in inland aquatic ecosystems. *Journal of Hydrology, 627,* 130407. https://doi.org/10.1016/j.jhydrol.2023.130407

Xu, H., Paerl, H. W., Zhu, G., Qin, B., Hall, N. S., & Zhu, M. (2017). Long-term nutrient trends and harmful cyanobacterial bloom potential in hypertrophic Lake Taihu, China. *Hydrobiologia*, *787*(1), 229–242. https://doi.org/10.1007/s10750-016-2967-4

Yang, F., Xu, Z., Zhu, Y., He, C., Wu, G., Qiu, J. R., Fu, Q., & Liu, Q. (2013). Evaluation of agricultural nonpoint source pollution potential risk over China with a Transformed-Agricultural Nonpoint Pollution Potential Index method. *Environmental Technology*, *34*(21), 2951–2963. https://doi.org/10.1080/09593330.2013.796008

Yates, C. A., Johnes, P. J., Owen, A. T., Brailsford, F. L., Glanville, H. C., Evans, C. D., Marshall, M. R., Jones, D. L., Lloyd, C. E. M., Jickells, T., & Evershed, R. P. (2019). Variation in dissolved organic matter (DOM) stoichiometry in U.K. freshwaters: Assessing the influence of land cover and soil C:N ratio on DOM composition. *Limnology and Oceanography, 64*(6), 2328–2340. https://doi.org/10.1002/lno.11186

Yuan, Z., Jiang, S., Sheng, H., Liu, X., Hua, H., Liu, X., & Zhang, Y. (2018). Human perturbation of the global phosphorus Cycle: changes and consequences. *Environmental Science & Technology, 52*(5), 2438–2450. https://doi.org/10.1021/acs.est.7b03910

Zhang, Y., Li, F., Zhang, Q., Li, J., & Liu, Q. (2014). Tracing nitrate pollution sources and transformation in surface- and ground-waters using environmental isotopes. *Science of the Total Environment, 490,* 213–222. https://doi.org/10.1016/j.scitotenv.2014.05.004

Zhou, Y., Yao, X., Zhou, L., Zhao, Z., Wang, X., Jang, K., Tian, W., Zhang, Y., Podgorski, D. C., Spencer, R. G. M., Kothawala, D. N., Jeppesen, E., & Wu, F. (2021). How hydrology and anthropogenic activity influence the molecular composition and export of dissolved organic matter: Observations along a large river continuum. *Limnology and Oceanography*, *66*(5), 1730–1742. https://doi.org/10.1002/lno.11716

Zigah, P. K., Minor, E. C., & Werne, J. P. (2012). Radiocarbon and stable-isotope geochemistry of organic and inorganic carbon in Lake Superior. *Global Biogeochemical Cycles*, *26*(1). https://doi.org/10.1029/2011GB004132

Zigah, P. K., Minor, E. C., McNichol, A. P., Xu, L., & Werne, J. P. (2017). Constraining the sources and cycling of dissolved organic carbon in a large oligotrophic lake using radiocarbon analyses. *Geochimica et Cosmochimica Acta*, *208*, 102–118. https://doi.org/10.1016/j.gca.2017.03.021

Supplementary Information (SI)

Table S1 Data of temperature, electrical conductivity (EC) and pH

ID	Time	Temperature (℃)	EC (μm/cm)	pH
25/Mar/2025				
Liza	10.40 a.m.	8.3	43.5	6.453
Ennerdale	11.00 a.m.	8.1	38.6	6.610
Ehen 1	11.30 a.m.	8.5	38.1	6.618
Ehen 2	12.02 p.m.	8.7	38.5	6.667
Ehen 3	12.26 p.m.	9.4	39.5	6.721
Black Beck (B.B.)	2.03 p.m.	12.0	124.8	7.023
Esthwaite Water (E.W.)	2.34 p.m.	10.4	95.9	7.618
Cunsey Beck (C.B.) 1	2.53 p.m.	11.8	97.2	7.503
Cunsey Beck (C.B.) 2	3.12 p.m.	11.0	102.1	7.216
Cunsey Beck (C.B.) 3	3.41 p.m.	11.9	101.5	7.465
10/Apr/2025				
Liza	10.30 a.m.	8.9	41.5	6.231
Ennerdale	11.10 a.m.	11.2	37.5	6.308
Ehen 1	12.20 a.m.	10.2	37.1	6.385
Ehen 2	1.03 p.m.	10.8	36.8	6.365
Ehen 3	1.30 p.m.	11.7	37.4	6.312
Black Beck (B.B.)	3.45 p.m.	13.2	119.0	7.130
Esthwaite Water (E.W.)	4.20 p.m.	12.5	93.4	7.700
Cunsey Beck (C.B.) 1	5.00 p.m.	14.4	93.4	7.458
Cunsey Beck (C.B.) 2	5.30 p.m.	12.6	97.7	7.000
Cunsey Beck (C.B.) 3	6.07 p.m.	13.5	98.2	7.310
29/Apr/2025				
Liza	9.17 a.m.	10.9	40.8	6.148
Ennerdale	10.00 a.m.	11.8	36.7	6.303
Ehen 1	10.32 a.m.	11.9	36.8	6.476
Ehen 2	11.00 a.m.	11.9	36.8	6.476
Ehen 3	11.20 a.m.	12.2	36.8	6.481
Black Beck (B.B.)	13.10 p.m.	15.5	118.7	7.212
Esthwaite Water (E.W.)	13.30 p.m.	14.8	94.0	7.336
Cunsey Beck (C.B.) 1	13.50 p.m.	15.6	94.6	7.205
Cunsey Beck (C.B.) 2	14.00 p.m.	14.3	99.0	6.966
Cunsey Beck (C.B.) 3	14.30 p.m.	16.0	97.6	7.638
5/Jun/2025				
Liza	10.20 a.m.	10.3	36.9	5.907
Ennerdale	10.50 a.m.	13.5	38.7	6.137
Ehen 1	11.40 a.m.	13.1	36.6	6.311
Ehen 2	12.10 p.m.	13.3	37.1	6.308
Ehen 3	12.42 p.m.	13.3	38.2	6.396

ID	Time	Temperature (℃)	EC (μm/cm)	pH
Black Beck (B.B.)	2.30 p.m.	12.6	88.0	6.429
Esthwaite Water (E.W.)	3.12 p.m.	15.9	94.9	7.109
Cunsey Beck (C.B.) 1	3.30 p.m.	15.9	94.1	6.990
Cunsey Beck (C.B.) 2	4.00 p.m.	15.3	95.4	6.840
Cunsey Beck (C.B.) 3	4.30 p.m.	15.1	94.7	6.929
3/Jul/2025				
Liza	10.06 a.m.	12.7	34.9	5.966
Ennerdale	10.45 a.m.	16.8	36.4	6.356
Ehen 1	11.30 a.m.	16.4	35.2	6.431
Ehen 2	11.57 a.m.	16.4	35.5	6.413
Ehen 3	12.40 p.m.	16.1	36.5	6.305
Black Beck (B.B.)	2.35 p.m.	14.6	103.4	6.531
Esthwaite Water (E.W.)	3.10 p.m.	20.0	91.7	7.514
Cunsey Beck (C.B.) 1	3.30 p.m.	19.8	90.9	7.504
Cunsey Beck (C.B.) 2	4.00 p.m.	18.8	93.0	6.839
Cunsey Beck (C.B.) 3	4.30 p.m.	18.4	92.7	7.105
31/Jul/2025				
Liza	10.23 a.m.	14.2	35.9	6.114
Ennerdale	10.55 a.m.	17.8	34.3	6.715
Ehen 1	11.41 a.m.	17.7	35.1	6.778
Ehen 2	12.13 p.m.	17.6	35.4	6.629
Ehen 3	12.40 p.m.	17.6	36.2	6.606
Black Beck (B.B.)	2.35 p.m.	17.2	123.4	6.793
Esthwaite Water (E.W.)	3.17 p.m.	20.2	90.4	7.606
Cunsey Beck (C.B.) 1	3.43 p.m.	20.6	90.9	7.135
Cunsey Beck (C.B.) 2	4.03 p.m.	19.8	95.6	6.666
Cunsey Beck (C.B.) 3	4.34 p.m.	19.6	94.7	7.289

Table S2 Data of ammonia

	Ammonia (mg N/L) MDL = 0.005 mg N/L					
	25-Mar	10-Apr	29-Apr	5-Jun	3-Jul	31-Jul
Field Blank	0.0002	-0.0073	0.0141	-0.0129	-0.0049	-0.0021
Liza	0.0021	-0.0041	-0.0052	-0.0165	-0.0048	-0.0048
Ennerdale	0.0061	-0.0012	-0.0002	-0.0103	-0.0063	-0.0016
Ehen 1	0.0087	-0.0029	-0.0022	-0.0114	-0.0052	0.0011
Ehen 2	0.0052	-0.0027	-0.0032	-0.0091	-0.0044	-0.0025
Ehen 3	0.007	-0.0041	-0.0006	-0.0101	-0.0049	0.0007
Black Beck	0.0145	0.0004	0.0086	-0.0086	0.0072	0.0112
Esthwaite Water	0.0041	-0.003	0.0121	0.0026	0.0001	0.0059
Cunsey Beck 1	0.0062	-0.0013	0.0109	-0.0056	-0.0044	0.0131
Cunsey Beck 2	0.0046	-0.0026	0.0028	-0.0013	0.0111	0.0228
Cunsey Beck 3	0.0057	-0.0007	-0.0001	-0.0077	0.0033	0.0009

Table S3 Data of SRP

	SRP (mg P/L) MDL = 0.002 mg P/L					
	25-Mar	10-Apr	29-Apr	5-Jun	3-Jul	31-Jul
Field Blank	0.001	0.007	0.001	0.002	0.005	0.002
Liza	0	0.009	-0.001	0.002	0.004	0.001
Ennerdale	0	0.009	0.001	0.001	0.004	0
Ehen 1	0	0.009	-0.002	0.002	0.003	0.001
Ehen 2	0	0.009	-0.001	0.006	0.004	0
Ehen 3	0	0.008	-0.001	0.001	0.004	0
Black Beck	0.006	0.013	0.005	0.007	0.012	0.014
Esthwaite Water	0.003	0.009	0	0.008	0.004	0.001
Cunsey Beck 1	0.002	0.009	0	0.003	0.003	0
Cunsey Beck 2	0.003	0.009	0.001	0.003	0.001	0.006
Cunsey Beck 3	0.002	0.009	0.001	0.003	0.003	0.007

Table S4 Data of nitrate

Nitrate (mg N/L) MDL = 0.0006 mg N/L												
Field Blank	25-Mar	-0.004	10-Apr	0.012	29-Apr	0.019	5-Jun	0.001	3-Jul	-0.001	31-Jul	-0.002
Liza		0.32		0.317		0.253		0.268		0.179		0.206
Ennerdale		0.307		0.295		0.275		0.311		0.183		0.174
Ehen 1		0.329		0.319		0.266		0.306		0.219		0.182
Ehen 2		0.305		0.347		0.271		0.31		0.184		0.183
Ehen 3		0.336		0.395		0.286		0.297		0.219		0.177
Black Beck		0.315		0.386		0.252		0.332		0.342		0.439
Esthwaite Water		0.604		0.552		0.418		0.376		0.155		0.095
Cunsey Beck 1		0.552		0.508		0.375		0.41		0.158		0.085
Cunsey Beck 2		0.53		0.516		0.423		0.425		0.168		0.177
Cunsey Beck 3		0.469		0.499		0.381		0.399		0.183		0.196

Table S5 Data of nitrite

Nitrite (mg N/L) MDL = 0.0006 mg N/L												
Field Blank	25-Mar	-0.0006	10-Apr	-0.0011	29-Apr	-0.0008	5-Jun	0.0017	3-Jul	-0.0005	31-Jul	-0.0006
Liza		-0.0003		-0.0008		-0.0006		0.0019		0.0104		-0.0003
Ennerdale		0		-0.0002		0		0.0026		0.0008		0.0009
Ehen 1		0.0001		-0.0003		0.0001		0.0029		0.0007		0.0009
Ehen 2		-0.0003		-0.0001		0.0003		0.0027		0.0006		0.0008
Ehen 3		0		-0.0001		0.0001		0.0026		0.001		0.0008
Black Beck		0.0009		0.0022		0.0018		0.0029		0.0012		0.0019
Esthwaite Water		0.0105		0.0086		0.006		0.0078		0.0048		0.0039
Cunsey Beck 1		0.0093		0.007		0.0053		0.0086		0.0047		0.0039
Cunsey Beck 2		0.006		0.004		0.0035		0.0067		0.0032		0.0022
Cunsey Beck 3		0.0019		0.0014		0.0012		0.0056		0.0026		0.0017

Table S6 Data of TOC

TOC (NPOC(ppm)) MDL = 0.05 ppm												
Field Blank	25-Mar	0.01	10-Apr	0.06	29-Apr	0.1075	5-Jun	0.11	3-Jul	0.21	31-Jul	0.09
Liza		0.2675		0.31		0.4175		0.95		0.91		0.58
Ennerdale		0.8775		0.92		1.0525		1.21		1.52		1.51
Ehen 1		0.9075		0.87		1.05		1.27		1.49		1.51
Ehen 2		0.88		0.92		1.1025		1.32		1.47		1.55
Ehen 3		0.9775		0.93		1.115		1.4		1.49		1.55
Black Beck		1.52		1.34		1.88		2.69		2.44		1.87
Esthwaite Water		2.0025		1.96		2.3925		2.53		2.95		3.16
Cunsey Beck 1		1.9725		2.06		2.1375		2.42		3.03		3.22
Cunsey Beck 2		2.0325		2.01		2.0825		2.51		3.04		3.11
Cunsey Beck 3		2.0025		1.9		2.0525		2.49		2.96		2.78

Table S7 Data of DOC

DOC (NPOC(ppm)) MDL = 0.05 ppm												
Field Blank	25-Mar	0.0625	10-Apr	0.17	29-Apr	0.125	5-Jun	0.07	3-Jul	0.08	31-Jul	0.1
Liza		0.3175		0.4		0.3475		1.02		0.76		0.52
Ennerdale		0.91		0.94		1.015		1.08		1.28		1.52
Ehen 1		0.965		0.93		1.0725		1.17		1.25		1.49
Ehen 2		0.95		0.89		0.98		1.07		1.25		1.38
Ehen 3		0.91		0.99		1.0325		1.09		1.29		1.51
Black Beck		1.6375		1.39		1.795		2.68		2.32		1.88
Esthwaite Water		2.0125		1.93		2.04		2.58		2.82		3.12
Cunsey Beck 1		1.945		2.01		2.045		2.35		2.72		3.08
Cunsey Beck 2		2.125		2.03		1.9925		2.4		2.72		2.91
Cunsey Beck 3		1.9575		1.92		1.9675		2.42		2.76		2.89

Table S8 Data of particulate organic C and N isotope

	C and N isotope (‰)											
		15N	13C		15N	13C		15N	13C		15N	13C
Liza	10-Apr	1.18	-26.79	29-Apr	-2.8	-27.64	5-Jun	0.41	-27.260	3-Jul	0.53	-26.09
Ennerdale		-1.51	-27.86		-2.3	-27.76		5.89	-30.060		-1.9	-27.85
Ehen 1		-0.46	-27.44		-5.41	-26.99		-1.57	-27.830		-1.83	-28.01
Ehen 2		0.69	-27.81		-4	-26.9		2.21	-27.560		-1.22	-27.87
Ehen 3		-3.18	-26.86		-2.6	-26.86		-2.23	-27.47		-1.14	-28.08
Black Beck		3.43	-27.48		1.84	-26.69		2.27	-28.94		4.7	-27.61
Esthwaite Water		4.88	-33		2.1	-32.03		-1.61	-27.960		4.2	-30.48
Cunsey Beck 1		3.8	-32.43		0.76	-30.99		6.49	-31.490		4.55	-30.96
Cunsey Beck 2		4.92	-32.81		2.7	-31.09		4.09	-31.97		4.61	-31.18
Cunsey Beck 3		5.47	-31.68		4.99	-30.71		5.24	-31.57		4.23	-31.49

Table S9 Data of α250:α365 and $SUVA_{254}$

	λ=250	λ=365	α250:α365	λ=254	[DOC]/(mg/L)	$SUVA_{254}$
26/03						
Liza	0.011	0.002	5.500	0.010	0.32	3.125
Ennerdale	0.043	0.008	5.375	0.041	0.91	4.505495
Ehen 1	0.043	0.008	5.375	0.042	0.96	4.375
Ehen 2	0.043	0.008	5.375	0.042	0.95	4.421053
Ehen 3	0.043	0.008	5.375	0.042	0.91	4.615385
Black Beck	0.079	0.017	4.647	0.076	1.64	4.634146
Esthwaite	0.103	0.021	4.905	0.099	2.01	4.925373
Cunsey Beck 1	0.102	0.021	4.857	0.098	1.94	5.051546
Cunsey Beck 2	0.103	0.022	4.682	0.100	2.12	4.716981
Cunsey Beck 3	0.096	0.020	4.800	0.093	1.96	4.744898
Field Blank	0.000	0.000	N.A.	0.000	0.06	0
10/04						
Liza	0.010	0.001	10.000	0.010	0.4	2.5
Ennerdale	0.040	0.007	5.714	0.039	0.94	4.148936
Ehen 1	0.041	0.006	6.833	0.039	0.93	4.193548
Ehen 2	0.041	0.007	5.857	0.040	0.89	4.494382
Ehen 3	0.041	0.007	5.857	0.040	0.99	4.040404
Black Beck	0.060	0.012	5.000	0.058	1.39	4.172662
Esthwaite	0.097	0.019	5.105	0.093	1.93	4.818653
Cunsey Beck 1	0.098	0.019	5.158	0.094	2.01	4.676617
Cunsey Beck 2	0.095	0.018	5.278	0.092	2.03	4.53202
Cunsey Beck 3	0.090	0.018	5.000	0.087	1.92	4.53125
Field Blank	0.000	0.000	N.A.	0.000	0.17	0
29/04						
Liza	0.019	0.002	9.5	0.000	0.3475	0.086331
Ennerdale	0.029	0.007	4.142857	0.027	1.015	2.660099
Ehen 1	0.029	0.008	3.625	0.031	1.0725	2.890443
Ehen 2	0.032	0.004	8	0.031	0.98	3.163265
Ehen 3	0.029	0.005	5.8	0.024	1.0325	2.324455
Black Beck	0.064	0.015	4.266667	0.060	1.795	3.342618
Esthwaite	0.091	0.017	5.352941	0.085	2.04	4.166667
Cunsey Beck 1	0.089	0.018	4.944444	0.088	2.045	4.303178
Cunsey Beck 2	0.085	0.014	6.071429	0.085	1.9925	4.265997
Cunsey Beck 3	0.083	0.016	5.1875	0.082	1.9675	4.167726
Field Blank	0.007	0.002	3.5	0.008	0.125	6.4
05/06						

	λ=250	λ=365	α250:α365	λ=254	[DOC]/(mg/L)	SUVA$_{254}$
Liza	0.043	0.005	8.600	0.040	1.02	3.921569
Ennerdale	0.036	0.009	4.000	0.035	1.08	3.240741
Ehen 1	0.042	0.010	4.200	0.039	1.17	3.333333
Ehen 2	0.039	0.007	5.571	0.036	1.07	3.364486
Ehen 3	0.041	0.003	13.667	0.039	1.09	3.577982
Black Beck	0.129	0.030	4.300	0.126	2.68	4.701493
Esthwaite	0.098	0.018	5.444	0.095	2.58	3.682171
Cunsey Beck 1	0.106	0.019	5.579	0.103	2.35	4.382979
Cunsey Beck 2	0.105	0.018	5.833	0.100	2.4	4.166667
Cunsey Beck 3	0.108	0.021	5.143	0.104	2.42	4.297521
Field Blank	-0.0006	0.001	-0.600	0.004	0.07	5.714286
			03/07			
Liza	0.034	0.009	3.778	0.034	0.76	4.473684
Ennerdale	0.046	0.011	4.182	0.045	1.28	3.515625
Ehen 1	0.047	0.010	4.700	0.045	1.25	3.6
Ehen 2	0.050	0.008	6.250	0.051	1.25	4.08
Ehen 3	0.055	0.014	3.929	0.052	1.29	4.031008
Black Beck	0.116	0.028	4.143	0.117	2.32	5.043103
Esthwaite	0.114	0.021	5.429	0.115	2.82	4.078014
Cunsey Beck 1	0.114	0.020	5.700	0.112	2.72	4.117647
Cunsey Beck 2	0.124	0.024	5.167	0.120	2.72	4.411765
Cunsey Beck 3	0.119	0.025	4.760	0.114	2.76	4.130435
Field Blank	-0.0030	0.0010	-3.000	-0.0010	0.08	-1.25
			31/07			
Liza	0.031	0.004	7.750	0.031	0.52	5.961538
Ennerdale	0.065	0.011	5.909	0.066	1.52	4.342105
Ehen 1	0.062	0.011	5.636	0.062	1.49	4.161074
Ehen 2	0.062	0.009	6.889	0.063	1.38	4.565217
Ehen 3	0.058	0.010	5.800	0.054	1.51	3.576159
Black Beck	0.088	0.019	4.632	0.084	1.88	4.468085
Esthwaite	0.125	0.026	4.808	0.118	3.12	3.782051
Cunsey Beck 1	0.117	0.024	4.875	0.112	3.08	3.636364
Cunsey Beck 2	0.130	0.023	5.652	0.126	2.91	4.329897
Cunsey Beck 3	0.119	0.023	5.174	0.118	2.89	4.083045
Field Blank	0.002	0.0005	4.000	0.0014		

Table S10 Data of TP

	TP (mg P/L) MDL = 0.003 mg P/L											
Field Blank	25-Mar	0.007	10-Apr	0.005	29-Apr	0.002	5-Jun	0.003	3-Jul	0.009	31-Jul	0.01
Liza		0.008		0.008		0.003		0.004		0.01		0.016
Ennerdale		0.011		0.007		0.005		0.004		0.01		0.012
Ehen 1		0.006		0.007		0.004		0.005		0.013		0.014
Ehen 2		0.007		0.007		0.003		0.005		0.017		0.012
Ehen 3		0.008		0.008		0.004		0.005		0.014		0.014
Black Beck		0.015		0.018		0.013		0.015		0.021		0.03
Esthwaite Water		0.021		0.012		0.013		0.024		0.016		0.026
Cunsey Beck 1		0.021		0.017		0.014		0.021		0.025		0.032
Cunsey Beck 2		0.024		0.02		0.018		0.019		0.027		0.029
Cunsey Beck 3		0.022		0.013		0.014		0.021		0.024		0.034

Table S11 Data of TN

	TN (mg N/L) MDL = 0.003 mg N/L											
Field Blank	25-Mar	0.018	10-Apr	0.032	29-Apr	0.03	5-Jun	0.109	3-Jul	0	31-Jul	0.136
Liza		0.432		0.365		0.353		0.323		0.259		0.261
Ennerdale		0.438		0.401		0.388		0.418		0.461		0.254
Ehen 1		0.449		0.349		0.403		0.428		0.373		0.302
Ehen 2		0.387		0.381		0.319		0.411		0.346		0.355
Ehen 3		0.405		0.404		0.466		0.383		0.361		0.322
Black Beck		0.509		0.509		0.491		0.588		0.564		0.707
Esthwaite Water		0.755		0.701		0.718		0.675		0.429		0.489
Cunsey Beck 1		0.761		0.664		0.576		0.638		0.52		0.51
Cunsey Beck 2		0.771		0.712		0.648		0.703		0.6		0.473
Cunsey Beck 3		0.734		0.609		0.61		0.661		0.495		0.546

Table S12 Data of TDP

TDP (mg P/L) MDL = 0.003 mg P/L												
Field Blank	25-Mar	0.005	10-Apr	0.004	29-Apr	0.003	5-Jun	0.004	3-Jul	0.016	31-Jul	0.013
Liza		0.006		0.009		0.003		0.004		0.009		0.01
Ennerdale		0.012		0.009		0.004		0.003		0.014		0.014
Ehen 1		0.005		0.007		0.001		0.003		0.016		0.01
Ehen 2		0.006		0.006		0.003		0.004		0.015		0.016
Ehen 3		0.01		0.006		0.004		0.003		0.023		0.012
Black Beck		0.016		0.016		0.014		0.013		0.026		0.03
Esthwaite Water		0.013		0.012		0.01		0.016		0.016		0.017
Cunsey Beck 1		0.014		0.013		0.009		0.01		0.015		0.015
Cunsey Beck 2		0.015		0.013		0.011		0.011		0.017		0.024
Cunsey Beck 3		0.013		0.013		0.01		0.01		0.014		0.028

Table S13 Data of TDN

TDN (mg N/L) MDL = 0.003 mg N/L												
Field Blank	25-Mar	0.036	10-Apr	0.014	29-Apr	0.063	5-Jun	0.067	3-Jul	0.026	31-Jul	-0.004
Liza		0.365		0.38		0.323		0.324		0.292		0.205
Ennerdale		0.433		0.428		0.356		0.417		0.29		0.255
Ehen 1		0.34		0.397		0.374		0.372		0.29		0.279
Ehen 2		0.46		0.387		0.329		0.419		0.294		0.299
Ehen 3		0.354		0.455		0.382		0.384		0.367		0.323
Black Beck		0.488		0.556		0.502		0.625		0.533		0.621
Esthwaite Water		0.687		0.751		0.624		0.578		0.514		0.385
Cunsey Beck 1		0.658		0.728		0.514		0.649		0.417		0.368
Cunsey Beck 2		0.677		0.776		0.618		0.57		0.447		0.501
Cunsey Beck 3		0.619		0.693		0.57		0.513		0.438		0.404