Towards Climate-Robust Aquatic Ecosystem Restoration:

Lessons learned from controlled experiments and modeling

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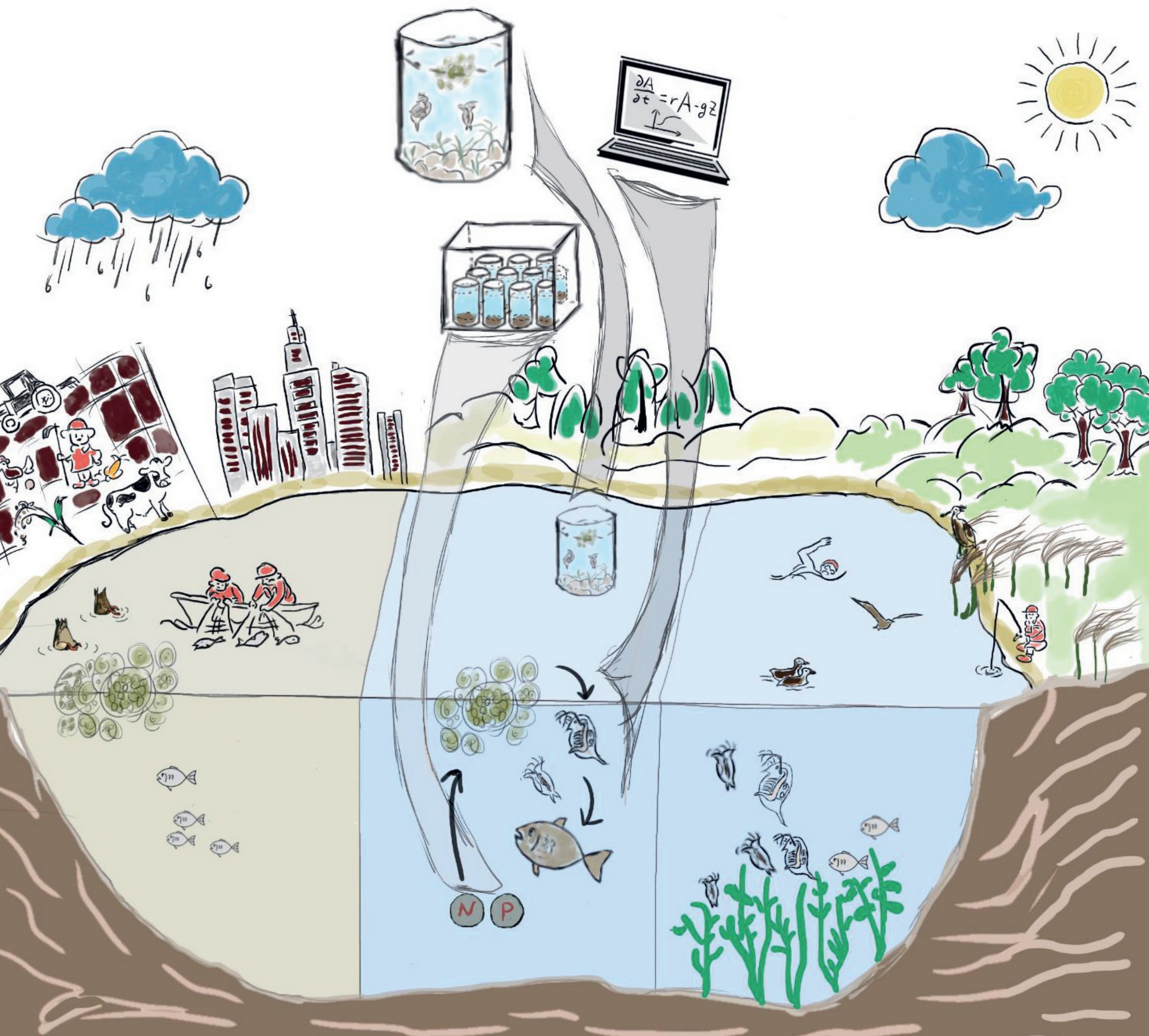

Propositions

1. Climate change is hampering the success of eutrophication control measures.
   (this thesis)
2. More is not necessarily better in lake restoration.
   (this thesis)
3. Models are either overestimated or underestimated in terms of their significance.
4. Solutions to environmental problems are hampered by disciplinary boundaries.
5. The Declaration on Research Assessment (DORA) inhibits excessive competitiveness among researchers.
6. To achieve a diverse and inclusive society, dialogue with marginalized groups is crucial.
7. Criticism without constructive suggestions is not helpful.

Propositions belonging to the thesis, entitled

Towards climate-robust aquatic ecosystem restoration: lessons learned from controlled experiments and modeling

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Towards climate-robust aquatic ecosystem restoration: lessons learned from controlled experiments and modeling

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Qing Zhan

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TABLE 1-1

Glossary	
Ecosystem	A dynamic complex of plant, animal and microorganism communities and their non-living environment, interacting as a functional unit.
Ecosystem structure	The composition of the ecosystem (i.e., its various parts) and the physical and biological organization defining how those parts are organized
Ecosystem states	Specific attributes or characteristics of an ecosystem (Cook et al., 2014)
Ecosystem function	The ecological processes that take place in an ecosystem, including primary production, decomposition, nutrient uptake, and population processes at all trophic levels.
Ecosystem stressor	Any natural or anthropogenic pressure that causes a quantifiable change, whether positive or negative, in biological response.
Extreme Climatic Events	The occurrence of a value of a weather or climate variable above (or below) a threshold value near the upper (or lower) ends of the range of observed values of the variable (typically 5% or 10%)
Biogeochemistry	Processes driving the concentration, fate, and transport of nutrients, contaminants, and other constituents.
Nutrient retention	Nutrient retention is defined as the temporary/permanent removal of nutrients from the water column via storage in macrophyte tissues, sediments binding agents, and denitrification, etc.
Biodiversity	The variability among living organisms from all sources including, inter alia, terrestrial, marine and other aquatic ecosystems and the ecological complexes of which they are part; this includes diversity within species, between species and of ecosystems. Defined here following the 1993 Convention on Biological Diversity (CBD) (http://www.cbd.int/convention/articles). (Note: the CBD formally defines 'Biological Diversity', which we assume to be equivalent to 'Biodiversity'.)
Functional diversity	Biodiversity at functional group level. Species are grouped based on their shared traits in ecosystem functions. Phytoplankton can be divided into three main functional groups: green algae, diatom, and cyanobacteria.
Ecosystem assessment	A systematic evaluation of what is known about the status, trends and future trajectories of ecosystems focusing on the benefits that they deliver to people. Similar to other global environmental assessments, an ecosystem assessment is a collective deliberative process by which experts review, analyze, and synthesize scientific knowledge in response to users' information needs relevant to key questions, uncertainties or decisions, and should be credible, legitimate and salient.
Ecosystem service	An activity or function of an ecosystem that provides benefits (or occasionally disbenefits) to humans.
Final ecosystem service	An ecosystem service that directly underpins or gives rise to a good.

CHAPTER I

Chapter I – General Introduction

1.1 Aquatic ecosystems in the Anthropocene

Our planet has entered an era in which humans have a substantial impact on Earth's geology and ecosystems, called the Anthropocene (Prillaman, 2022). Almost all kinds of ecosystems are undergoing accelerated degradation, with biodiversity loss and impaired ecosystem functioning (Hooper et al., 2005). In comparison to terrestrial and marine ecosystems, freshwater systems encounter the largest biodiversity loss, with a decline rate of 50% since 1970 (Duraiappah et al., 2005). This vulnerability may be attributed to the limited dispersal ability of aquatic organisms and the prevalence of stressors and pollutants specific to freshwater environments. Adding to their challenges, freshwater ecosystems are often embedded in heavily urbanized areas, with high demands on ecosystem services. Despite their relatively small contribution to the global water pool (0.01% of the World's water and ca. 0.8% of the Earth's surface), freshwater systems however provide crucial drinking water resources to all living life, and they are hotspots for biological processes, supporting over million species - almost 6% of all described species (Dudgeon et al., 2006).

1.2 Climate change and extreme climatic events impacts

'Human influence has been the dominant cause of the observed warming since the mid-20th century' (Stocker, 2014), as a consensus statement articulated by the Intergovernmental Panel on Climate Change (IPCC) assessment. Cook et al. (2013) has quantified the consensus on anthropogenic global warming in the scientific literature (N=211944 papers from 1991-2011) and found that 97.1% endorsed the consensus. Climate change is associated with changes in almost all climatic variables including air temperature, precipitation, solar irradiances, and wind velocity. Globally, the average temperature has increased by 1.1 °C since 1880 (Hansen et al., 2010). Higher temperatures lead to greater evaporation and thus increase the intensity and duration of drought (Samaniego et al. 2018; Trenberth et al. 2014). On the other hand, the water vapor in the atmosphere increases with warming, as the water holding capacity of air increases by ca. 7% per 1°C warming. While total precipitation is decreasing, more intense precipitation events are observed to be widely occurring: 'it never rains but it pours!' (Trenberth, 2011).

One of the most important facets of climate change is increased frequency and intensity in extreme climatic events (ECEs) (Stott, 2016). As per the climatological definition by IPCC (Change, 2022), ECEs are characterized by weather or climate variables exceeding or falling below a threshold value near the upper or lower ends of the observed range (typically 5% or 10%). Figure 1-1 shows the trend in Google™ searches using the search terms "heatwave" and "storms", which both exhibit clear increasing trends. ECEs differ from climate trends by their very nature: their effects are out of proportion to their duration (Jentsch et al., 2007). ECEs can have serious implications for ecosystem structure and function including freshwater ecosystems (Change, 2014). For instance, the anticipated increase in lake heatwaves, defined as periods of extremely water surface water temperature (Woolway et al., 2021), can lead to stronger bottom water anoxia (Jankowski et al., 2006) and blooms of harmful cyanobacteria (Joehnk et al., 2008). The increase in storm frequency, intensity, and duration due to climate change, associated with extreme run-off and wind, can significantly influence phytoplankton community dynamics (Stockwell et al., 2020). The impact is attributed to its effects on nutrient inputs and stratification regime. While extreme weather events are becoming the new "Normal" (Lewis et al., 2017), it is of crucial importance to study in order to be able to counter the negative impacts of climate change and ECEs.

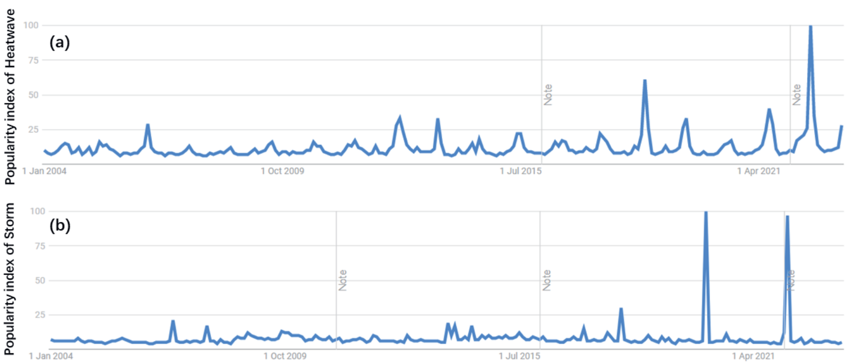

Figure 1-1. *"Popularity index" of the search terms "Heatwave" (upper panel, a) and "Storm" (lower panel, b) over time using Google Trends since 2004 worldwide. The popularity index is scaled to the maximum number of hits, set as 100.*

At the same time regional projections may differ depending on socio-economic developments, emission scenarios and regional climate factors. For example, the Royal Meteorological Institute (KNMI, https://www.knmi.nl/nederland-nu/klimatologie) has developed four scenarios for the Dutch future climate around 2050 and 2085, forming the boundaries of the probable future climate changes in the Netherlands. The four scenarios differ in the amount of global warming (Moderate or Warm) or possible changes in the air circulation pattern (Low or High). In brief, predictions of the main climate variables include: increases in temperature, precipitation, sea level, solar radiation; decreases in wind and fog. In addition, the likelihood for extreme climatic events including heatwave, storms and hail will increase. Figure 1-2 summarized the main results of each Dutch climate scenario around 2050 and 2085, which are the basis of the climate scenario used in my thesis.

KNMI'14 Key figures

Variabele	Indicator	Climate 1981-2010	Scenario changes for the climate around 2050				Scenario changes for the climate around 2085				Natural variations averaged over 30 years
			G_L	G_H	W_L	W_H	G_L	G_H	W_L	W_H	
Global temperature rise:			+1 °C	+1 °C	+2 °C	+2 °C	+1.5 °C	+1.5 °C	+3.5 °C	+3.5 °C	
Change in air circulation pattern:			low value	high value	low value	high value	low value	high value	low value	high value	
Sea level at North Sea coast	absolute level	3 cm above NAP	+15 to +30 cm	+15 to +30 cm	+20 to +40 cm	+20 to +40 cm	+25 to +60 cm	+25 to +60 cm	+45 to +80 cm	+45 to +80 cm	±1.4 cm
	rate of change	2.0 mm/yr.	+1 to +5.5 mm/yr.	+1 to +5.5 mm/yr.	+3.5 to +7.5 mm/yr.	+3.5 to +7.5 mm/yr.	+1 to +7.5 mm/yr.	+1 to +7.5 mm/yr.	+4 to +10.5 mm/yr.	+4 to +10.5 mm/yr.	±1.4 mm/yr.
Temperature	mean	10.1 °C	+1.0 °C	+1.4 °C	+2.0 °C	+2.3 °C	+1.3 °C	+1.7 °C	+3.3 °C	+3.7 °C	±0.16 °C
Precipitation	mean amount	851 mm	+4 %	+2.5 %	+5.5 %	+5 %	+5 %	+5 %	+7 %	+7 %	±4.2 %
Solar radiation	solar radiation	354 kJ/cm²	+0.6 %	+1.6 %	-0.8 %	+1.2 %	-0.5 %	+1.1 %	-0.9 %	+1.4 %	±1.6 %

Royal Netherlands Meteorological Institute, 2015
Contact: klimaatdesk@knmi.nl

Do you want to know more about the KNMI climate scenarios?
www.climatescenarios.nl

Figure 1-2. *Climate scenario changes for future climate in the Netherlands (source: Royal Netherlands Meteorological Institute, www.climatescenarios.nl).*

Freshwater ecosystems are embedded in larger scale watersheds, airsheds, and landscapes, making them intricately connected to their surrounding environment. The effects of climate change on aquatic ecosystems often result from the cumulative impacts of warming and other stresses, such as nutrient loading, induced by human activities in the catchments. As a consequence, many aquatic ecosystems, act as important "sentinels" within their catchments (Adrian et al., 2009), and are experiencing a trend of increasing eutrophication amid ongoing climate change (Hallegraeff et al., 2021; Ho et al., 2019; Matzinger et al., 2007).

Given the importance of freshwater ecosystems, different legislations are established for protection and sustainable management of aquatic ecosystems. For instance, the Water Framework Directive (WFD) is a key piece of European directive that was adopted in 2000. The WFD aims for 'good ecological status' for all water bodies. It is imperative that management strategies consider the expected future impacts of climate change. The necessity for adaptation has been underscored in the

White Paper on “Adapting to climate change: towards a European Framework for action” (Biesbroek et al., 2010), and this approach has played a crucial role in shaping policy implementations over recent decades (Giakoumis and Voulvoulis, 2018). To successfully achieve climate change adaptation ambitions, scientists need to provide robust evidence regarding the impacts of climate change on aquatic ecosystem functioning and services. Furthermore, the scientific knowledge needs to be translated into actionable suggestions for the preservation and restoration of freshwater ecosystems.

1.3 Aquatic ecosystem restoration: eutrophication control measures

Eutrophication is recognized as a prominent driver of water quality deterioration worldwide (Ho et al., 2019; Moss et al., 2011; Smith et al., 2006). The term “Eutrophication”, originating from Greek, denotes an aquatic ecosystem’s transition from lower to higher levels of primary productivity. While it can be a natural process as aquatic ecosystems mature and experience increased primary productivity over time, human activities, such as intensive agriculture and urbanization, have accelerated this aging process (Smith et al., 2006). The consequences of eutrophication are manifested in various water quality issues (see Table 1-2 for a summary), including proliferation of phytoplankton biomass, malodors, and oxygen depletion resulting in fish kills (Smith et al., 2006). Additionally, certain cyanobacterial species, a functional group of phytoplankton, can produce toxins -Cyanotoxins- that pose direct health risks to animals and humans (Chorus et al., 2000). Cyanotoxins are one of the strongest natural poisons that can cause respiratory and liver failure, which may result in fatalities (Ilieva et al., 2019). In 2020, a mass die-off of more than 330 African Elephants in Botswana was attributed to their consumption of pond water contaminated with toxic cyanobacterial blooms (Wang et al., 2021).

Table 1-2. *Potential effects of eutrophication on freshwater ecosystems (adapted from Smith et al. 2006).*

- Increased biomass of phytoplankton and macrophyte vegetation
- Increased biomass of consumer species
- Shifts to bloom-forming algal species that might be toxic or inedible

- Increased biomass of benthic and epiphytic algae
- Changes in species composition of macrophyte vegetation
- Increased incidence of fish kills
- Reductions in species diversity
- Reductions in harvestable fish and shellfish biomass
- Decreases in water transparency
- Taste, odor and drinking water treatment problems
- Oxygen depletion
- Decreases in perceived aesthetic value of the water body

Research on eutrophication processes gained momentum in the 1960s and 1970s. Initial understanding of the links between nutrient enrichments and primary productivity emerged in Europe in the early 1990s, leading to significant advancements in our comprehension of eutrophication over the past half-century (Smith et al., 2006). Nitrogen (N) and Phosphorus (P) have been identified as the key nutrients contributing to eutrophication. While consensus exists that reducing nutrients can lead to a decline in phytoplankton blooms and improve water clarity, there has been an ongoing debate about whether one or both nutrients should be controlled (Cotner, 2017; Paerl et al., 2016; Schindler et al., 2016).

On the one hand, numerous case studies, including a long-term whole-lake experiment conducted at Lake227 in Canada's Experimental Lakes Area (D. W. Schindler, 1974), have suggested that abating eutrophication can be achieved by solely reducing Phosphorus (P), and nitrogen (N) control can be less stringent (Carpenter, 2008; Schindler et al., 2016; Wang and Wang, 2009). On the other hand, the idea of focusing solely on reducing P in restoration has faced criticism on several aspects (Lewis Jr. and Wurtsbaugh, 2008; Lewis et al., 2011; Paerl et al., 2016), including: 1) under high nitrogen conditions, any addition of P can boost phytoplankton growth (Cotner, 2017); 2) mounting evidence indicates that excess N can enhance the toxin production of harmful cyanobacteria (Burson et al., 2016; Horst et al., 2014); 3) N originates from both watersheds and airsheds, and given its harmful effects on climate (greenhouse effect; Kim and Dale, 2008) and ecosystems in watershed (e.g., biodiversity loss; de Vries et al. 2011), reducing N is essential, subsequently decreasing N loading into water bodies. Considering the significant nutrient-eutrophication relationship, it is imperative that any measures aimed at controlling eutrophication through interventions in nutrient levels are supported by robust evidence and a thorough mechanistic understanding, as explored in this Thesis.

In addition to addressing the negative effects of increased nutrient loading on aquatic ecosystems, there is an urgent need for further advancements in understanding the impacts of multiple climate stressors on eutrophication, considering the rapidly changing climate. Figure 1-3 provides a summary of potential relationships between climate change stressors to eutrophication symptoms. Warmer temperatures may exacerbate harmful phytoplankton bloom (Sarian Kosten et al., 2012; Paerl and Huisman, 2008), and future climate conditions may favor cyanobacterial taxa (Carey et al., 2012). Additionally, alternations in precipitation patterns induced by climate change may exacerbate eutrophication by increasing nutrient loading through enhanced runoff (Sinha et al., 2017). However, few studies have focused on the combined effect of extreme events and mean climate change on phytoplankton dynamics (e.g., Bergkemper et al. 2018; A. D. Richardson et al. 2019). In Chapter II, my coauthors and I conducted a controlled experiment to test whether the combined impacts of climate stressors are consistently synergistic, as suggested by Moss et al. (2011). Understanding how these stressors interact is crucial for developing robust management strategies and ensuring the effectiveness of eutrophication control measures in the face of ongoing climate change challenges.

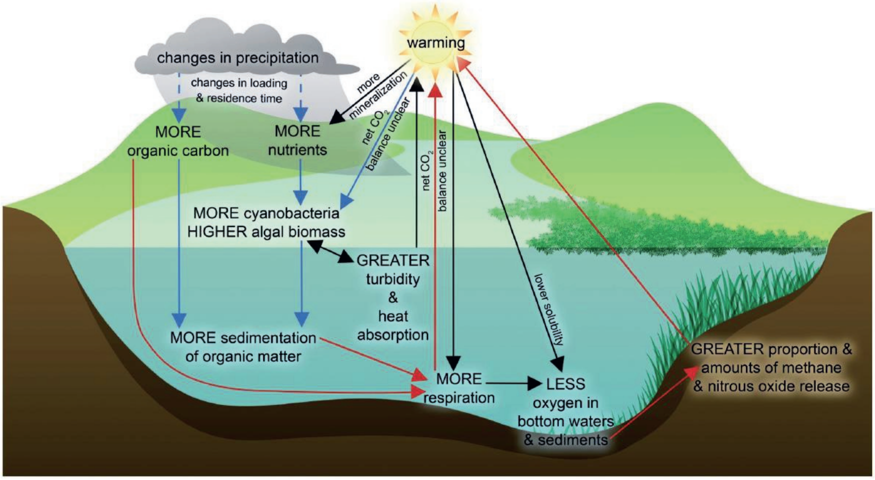

Figure 1-3. *The effects of warming climate on lake ecosystems (infographic from Moss et al. (2011).*

One of the most important steps in controlling eutrophication is to reduce nutrient loads from the watershed, also known as "external loading", by reducing fertilizer application, improving wastewater treatment, etc. Despite these efforts, nutrient release from nutrient-enriched sediments can still lead to internal loading under certain environmental conditions (Søndergaard et al., 2013), resulting in delayed responses of aquatic ecosystems to reductions in external nutrient loading, which may extend up to decades (Schindler, 2006). Many measures have been developed to directly target the eutrophication in the lake itself rather than its surrounding watershed, also known as "in-lake measures" (Lürling and Mucci, 2020). Examples of in-lake measures include geoengineering techniques that target internal loading by precipitating and inactivating nutrients into sediments (e.g., Phoslock®), dredging of nutrient-rich sediments, and aeration for artificial oxygenation.

These in-lake eutrophication measures can be generally grouped into two types: source-oriented, that are designed to reduce internal nutrient loading, and symptom-oriented measures, that are aiming at diminishing eutrophication symptoms (Figure 1-4). Examples of source-oriented measures include external loading reduction, geoengineering techniques, and sediment dredging. Symptom-oriented measures include technical and physical measures (e.g., aeration and flushing), and algicides. I refer to (Drabkova, 2007; Nienhuis et al., 2002; Waajen, 2017) for a review of existing eutrophication control measures and their success or failure factors.

Restoration projects in the Netherlands have historically followed a 'trials and errors' strategy (Nienhuis et al., 2002). Based on the results obtained, the 'bottom-up' approach, specifically nutrient reduction, has been favored, while the 'top-down' measures, such as fish stock removal (mainly bream), are seen as complementary. In this thesis, I assess several commonly used in-lake measures by lake managers in the Netherlands (e.g., geoengineering in Chapter III, geoengineering, dredging and aeration in Chapter IV) to acquire a deeper insight in the potential effects of climatic stressors on our restoration efforts.

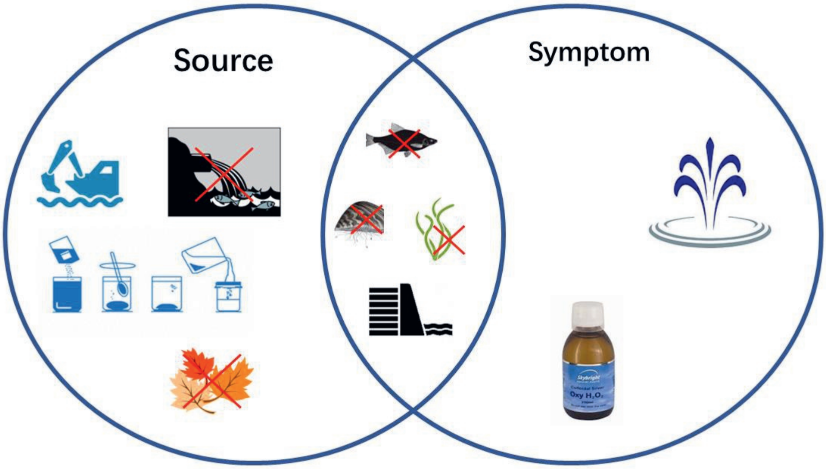

Figure 1-4. *Types of eutrophication control measures based on their targeting elements (Picture modified from Lisette).*

Some of the restoration measures mentioned earlier rely on man-controlled engineering techniques, while another category of measures emphasizes the use of natural processes to restore degraded ecosystems - known as Nature-based Solutions (NBS). NBS is a relatively emerging concept that builds upon earlier concepts such as ecological engineering, catchment systems engineering, green-blue infrastructure, natural infrastructure, ecosystem approach, ecosystem-based adaptation/mitigation, ecosystem services, renaturing, and natural capital (Thinknature et al., 2019). A noteworthy example of NBS in aquatic ecosystem restoration is wetland construction, which utilizes the purification processes in wetlands to eliminate water quality deterioration (Janse et al., 2001; Vymazal, 2007). The adoption of NBS has gained significant political traction due to its potential to enhance the resilience of ecosystems in the face of climate change (Faivre et al., 2017; Kabisch et al., 2016). However, our current understanding of the overall effectiveness of NBS remains limited (Chausson et al., 2020; Seddon et al., 2020a). In chapter V, we aim to assess the effectiveness of wetland construction, as opposed to a technology-based measure.

By conducting this evaluation, we seek to advance our comprehension of the benefits and drawbacks of NBS.

1.4 Ecosystem service for evaluating restoration success

How should we assess the success of ecological restoration projects? While measuring changes in ecosystem functions, such as primary production and nutrient release, remains the most common approach for assessing the effectiveness of restoration (Chapter III and IV) (Wortley et al., 2013a), there has been an increasing interest in using the concept of ecosystem services due to its ability to convey the benefits and costs of restoration measures in a common currency to managers and stakeholders (Boyd and Banzhaf, 2007; Haines-Young and Potschin, 2012; Seppelt et al., 2011). Ecosystem services, defined as "the benefits that people obtain from ecosystems", provide a conceptual framework for assessing the socioeconomic outcomes of ecological restoration (Bullock et al., 2011; Palmer and Filoso, 2009).

The idea of ecosystem service dates back to the concept of nature's services (Westman, 1977), where attempts were made to measure the social benefits of ecosystem functioning (see definition in Table 1-1). The Millennium Ecosystem Assessment (MA) elevated the prominence of ecosystem services (ES) to conceptualize the connection between human well-being and ecosystem functioning, emphasizing the importance of maintaining and managing ecosystems in a sustainable manner (Assessment, 2005). Ever since, the concept of ES has become an important methodology in the policy and scientific communities for sustainable management of human-environment systems (Brück et al., 2022; Seppelt et al., 2011; Vihervaara et al., 2010). This significance is visualized by the short distance between "ecosystem services" and "management" as well as "restoration" in the scientific landscape map (Figure 1-5). There are numerous ESs that ecosystems can provide to our societies, for instance, freshwater ecosystems provide services such as drinking water, swimming, fishing and habitats for flora and fauna. The Millennium Assessment categorized ESs into four main types (Assessment, 2005):

1. Provisioning services: These are the tangible goods that ecosystems provide, such as food, water, timber, fiber, and medicinal plants. Ecosystems are the source of many essential resources that support human livelihoods and economic activities.
2. Regulating services: Ecosystems play a vital role in regulating natural processes and mitigating environmental risks. They help regulate climate by sequestering carbon dioxide, regulate water flow and quality, control erosion, pollination by insects, natural pest control, and disease regulation. These

services are crucial for maintaining the balance and stability of ecosystems and preventing the negative impacts of environmental changes.

3. Supporting services: Ecosystems provide the necessary functions for the production of all other ecosystem services. These include soil formation, nutrient cycling, primary production (photosynthesis), and habitat provision. Supporting services are the foundation upon which other services rely.
4. Cultural services: Ecosystems hold significant cultural, aesthetic, and spiritual values for human societies. They provide recreational opportunities, inspire artistic and intellectual pursuits, and offer a sense of place and connection to nature. Cultural services contribute to the overall well-being and quality of life for individuals and communities.

There are various perspectives on how to describe and quantify the connection between people and nature. Many efforts has been made to quantify ecosystem services through monetization of ES (Costanza et al., 2014, 1997; Gómez-Baggethun et al., 2010) in an attempt to inform policy makers of the benefit-to-cost ratio of ES monetary values resulting from their actions. However, this method has faced criticism on different aspects (Gómez-Baggethun et al., 2014; Palmer and Filoso, 2009; Silvertown, 2015): 1) not each service has a monetary value; 2) our knowledge of the full range services that can be provided by ecosystem is often inadequate, leading to incorrect benefit-to-cost ratio. Decisions on compensating for some service losses can result in unpredictable and potentially damaging consequences for the ecosystem; 3) The value of ecosystems to future generation is difficult to be adequately considered; 4) Monetization of ES has a deeply rooted origin in anthropocentrism, assuming that the human being has the exclusive right to use and manipulate nature in order for their own purposes.

In freshwater ecosystems, numerous studies have demonstrated the linkages between ecosystem conditions and ecosystem service provisioning (Grizzetti et al., 2019; Janssen et al., 2021; Seelen et al., 2021a). However, the assessment of water quality-related ecosystem services is not fully integrated into current ecosystem service modeling tools (Keeler et al., 2012). This is partly due to the complex interactions regulating water quality dynamics and the oversimplified empirical relationships used in large-scale system models (Polasky et al., 2011).

In chapter IV, we adopted a semi-quantitative approach to assess the suitability of provisioning of ecosystem services (ES) based on their required ecosystem states, following (Seelen et al., 2021a), without considering monetization of the ecosystem service. In this framework, threshold values were determined for ecosystem states required for each ecosystem service. For example, low phytoplankton biomass, high transparency and sufficient macrophyte-free zone are considered to be suitable conditions for provisioning the ES "swimming". The "suitability" for each ES range between 0 and 1, depending on the dynamics of ecosystem states. This framework enables us to illustrate the competing requirements for ecosystem conditions and to assess the gains or losses of ESs that do not necessarily have a monetary value (e.g., nutrient retention, habitat).

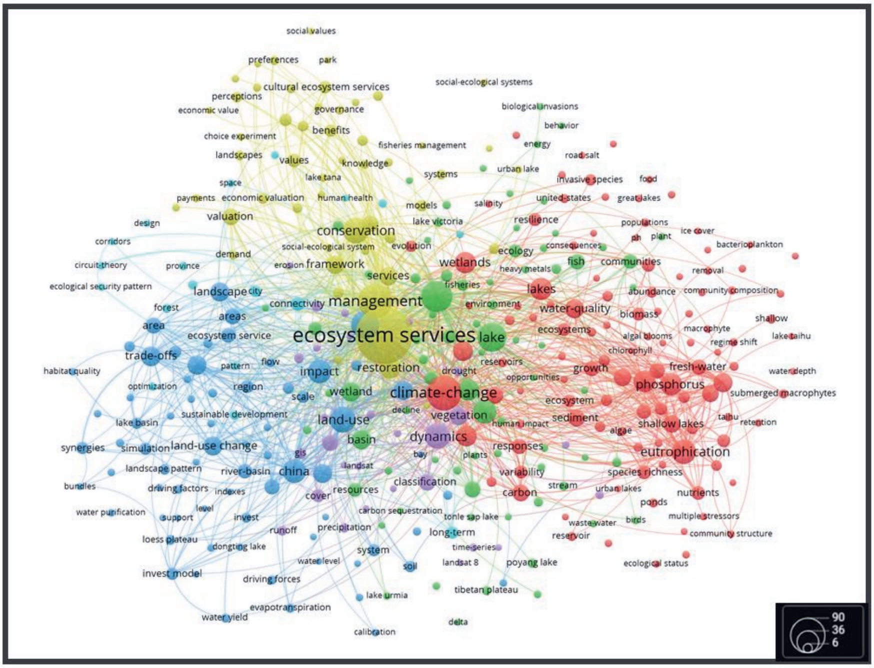

Figure 1-5. *Network map of key words using search criterium: "Ecosystem service*", "Lake*" and publications since 2020 in the Web of Science using the software VOSviewer (Interactive version: https://tinyurl.com/2xp6uvvf). This gives 884 results. Keywords were filtered with a minimum number of occurrences of 5 (354 out of 5236) and manually filtered to remove less informative keywords. The sizes of circles were scaled by occurrences. The distance between two circles in the visualization approximates the relatedness of the words in terms of co-occurrences.*

1.5 Aims and outline of this thesis

This thesis aims at contributing to the establishment of a climate-robust aquatic ecosystem restoration strategy. Restoration should aim at improvement of the whole ecosystem (Bradshaw, 1996), instead of a single component or attribute of the ecosystem. I tried to align with this principle and propose a framework (Figure 1-6) that integrates factors that are crucial for a successful aquatic ecosystem restoration. This integrative framework involves physical processes (climate), biogeochemistry (e.g., nutrient cycling), biological systems (e.g., primary production, food web), and socio-economics (e.g., ecosystem services).

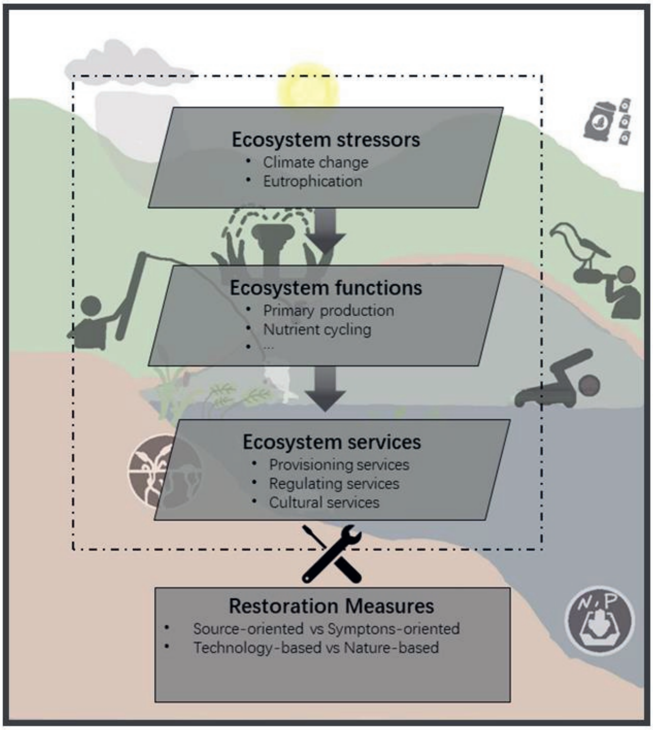

Figure 1-6. *An integrative framework for aquatic ecosystem restoration.*

The thesis is outlined in the manner of this integrative framework: I started with studying how climate stressors influenced our freshwater ecosystem functions (Chapter II). Afterwards, I addressed the influences of climate stressors on some of the commonly used restoration measures (Chapter III, VI, V). The effectiveness of restoration measures is assessed by changes in ecosystem functions (Chapter III and VI) and ecosystem services (Chapter V). The main objectives of the thesis:

- To study the cause-effect relationship between multiple extreme climatic stressors and an ecosystem function (**Chapter II);**
- To test to what extent a commonly-used nutrient-intervention measure can remain effective under disturbance by an extreme heatwave (**Chapter III**);
- To test the efficacy of several commonly-used restoration measures in controlling eutrophication under heatwave conditions (**Chapter VI**);

- To evaluate the success of lake restoration under climate change using the concept of ecosystem service (**Chapter V)**.

The following paragraphs will shortly introduce the research questions and different methods adopted in each chapter.

Chapter II: my co-authors and I studied how two climatic stressors influence ecosystem functioning and phytoplankton functional diversity. A microcosm experiment was carried out with full factorial design with four treatments: two run-off scenarios (normal precipitation and extreme precipitation) and two temperature scenarios (normal and warming). A series of water quality parameters were measured as indicators of ecosystem functioning, including nutrient dynamics and biomass of functional phytoplankton groups. A linear mixed effect model - was used for testing the treatment effects. This chapter improves our mechanistic understanding of the extreme climatic events impacts on ecosystem functioning and functional diversity.

In **chapter III**, a commonly used geoengineering nutrient intervention measure was evaluated regarding its effects on ecosystem functioning, upon exposure to an extreme climatic event - heatwave. This intervention consists of the application of lanthanum-modified bentonite, a compound that is designed to bind soluble reactive phosphorus forming chemical complexes that become biologically unavailable. A three-weeks sediment core experiment was carried out in the laboratory, with a one-week heatwave exposure during the mid of the week. Dynamics of nutrients and greenhouse gasses were measured throughout the experiment as indicators of ecosystem functioning. This study provides implications on whether this nutrient intervention measure's effectiveness will be hampered by heatwaves which are predicted to increase in frequency and intensity during future climatic conditions.

In **Chapter IV**, my co-authors and I investigated results from an in-situ mesocosm experiment carried out in a Dutch urban canal in the summer of 2018, when a summer heatwave swept northern Europe (Kueh and Lin, 2020). In this experiment, five commonly used eutrophication control measures were compared, including two geoengineering measures, aeration, dredging, and fish removal. At the middle of our experiment, an extreme heatwave event was recorded, which was the highest recorded Dutch heatwave temperature since 1901 according to the measurements by Royal Netherlands Meteorological Institute. We evaluated the heatwave impacts on the effectiveness of these measures on controlling nutrient cycling and primary production.

In **Chapter V**, we evaluated how ecosystem services provisioning can be influenced by two types of restoration measures under two different climate scenarios.

We used PCLake+, a process-based ecological model that can explicitly model nutrient cycles and food web groups including primary producers at a functional level. An ecosystem service module was built into this model, to translate the ecosystem state indicators into ecosystem services provisioning, following an ES assessment framework by Seelen et al. (2021a). PCLake+ was manually coupled to a Lake physic model - FLake. This modeling framework enables us to simulate alternative climate scenarios and restoration measures. We simulated two climate scenarios: current and 2050 Dutch climate conditions. In addition, we simulated a technology-based restoration measure - phosphorus reduction, and a nature-based solution - wetland purification. Inclusion of the concept "ecosystem service" into evaluation of restoration effectiveness, can enable us to communicate with lake managers and other stakeholders in a more intuitive way.

In the General Discussion - **Chapter VI**, I summarize the highlights of **Chapter II to V** to put forward several aspects that I think are significant for a successful restoration of our freshwater ecosystems. Furthermore, I provide my future perspectives on how to move forward towards climate-robust aquatic ecosystem restoration and ecosystem services provisioning.

CHAPTER II

Chapter II:

Stressors in a bottle: a microcosm study on phytoplankton assemblage response to extreme precipitation event under climate warming

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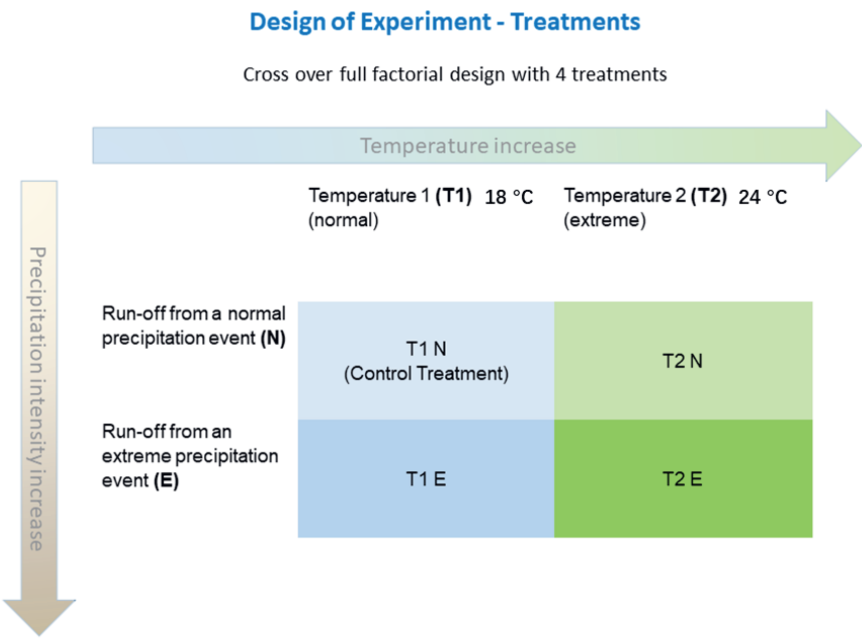

Summary

1. The climatic stressors that are affecting lake ecosystems, especially phytoplankton, are projected to become more intense with continued climate change (e.g., heatwaves, precipitation events). Concerns over the combined effects that multiple, coinciding stressors can have on phytoplankton necessitates investigating the impacts of different regional climate scenarios.
2. A microcosm study was conducted to assess the responses of a phytoplankton assemblage containing a cyanobacterium (*Anabaena flos-aquae*), a green alga (*Chlorella vulgaris*) and a diatom (*Synedra*) to a Northwestern European summer scenario. Eutrophic microcosms were exposed to a full-factorial design including a press temperature treatment scenario (ambient or warm) and a pulse precipitation treatment (no runoff simulation or runoff simulation).
3. Warming scenarios had significant effects on the phytoplankton assemblage biomass, which supports our first hypothesis (H1: higher water temperatures under eutrophic conditions will support larger phytoplankton biomasses, especially cyanobacteria). In contrast, the extreme precipitation event had minimal and short-lived effects on the microcosm assemblage.
4. Overall, the interaction between the two climate stressors was antagonistic. In contrast with our second hypothesis (H2: nutrient additions from extreme precipitation event will promote more productivity in higher temperature microcosms), the precipitation runoff event was not amplified by temperature.
5. Our results indicate that the combined effect of two climate stressors on a phytoplankton community are not necessarily synergistic or multiplicative. Our findings on antagonistic interactions between climatic stressors necessitate future studies assessing variations of intensity and duration of the climatic stressors.

2.1 Introduction

As sentinels within catchments, lakes can be particularly susceptible to climate change (Adrian et al. 2009, p. 201; Stelzer et al. 2022). Along with shifts in the average climate, this also includes the increasing intensity and frequency of extreme climatic events ("ECEs"). Although the implications of ECEs and long-term changes in average climate have been assessed in laboratory settings (e.g., microcosms; Bergkemper et al. 2018), controlled environments (e.g., mesocosms; A.

D. Richardson et al. 2019) and from observation data (e.g., modeling; Joehnk et al. 2008), there are knowledge gaps on how different aspects of climate change interact and how these multiple climatic pressures will affect lakes. Understanding the biotic and abiotic pathways in which these compound pressures occur in combination with prolonged anthropogenic-driven stressors has been highlighted as a critical knowledge gap in the recent IPCC report (Change, 2022). Our study addresses this gap through analyzing the impact of an extreme precipitation event in conjunction with temperature rise on phytoplankton performance in a controlled setting mimicking Northwestern European climate scenarios, as regional projections anticipate increases in extreme precipitation events (Madsen et al., 2014) and extreme summer heatwaves (McGregor et al., 2005; Woolway et al., 2021). As outlined by the Royal Dutch Meteorological Institute, an increase in higher intensity precipitation events during summer will track with higher temperatures (Klein Tank and Lenderink, 2009), thus supporting the potential of multiple extreme climatic events occurring simultaneously and necessitating research studying the potential effects.

2.1.1 Abiotic responses

Changes to lake chemical processes as a consequence of climatic stressors have the potential to instigate ecosystem disruptions (Calderó-Pascual et al., 2020). Between extreme precipitation and warming events, there can be abiotic ramifications such as nutrient loading, turbidity and water temperature change. The positive or negative outcomes of the stressors are dependent upon the local situation, such as regional location, antecedent lake conditions, the hydro-morphology, time of year and event severity amongst other factors. Occurrences of extreme precipitation can lead to increased runoff (Jennings et al., 2012), such that runoff from a single extreme precipitation event could account for a significant portion of the total annual nutrient loading (Zwart et al., 2017). Conversely, precipitation events could cause nutrient depletion from flushing of a system (Ho and Michalak, 2020) or dilution (Cobbaert et al., 2014). Similarly, turbidity could be altered from the re-suspension of *in situ* sediments (Kasprzak et al., 2017), in turn decreasing water transparency (Kasprzak et al., 2017) and light availability (Stockwell et al., 2020). Warming of water systems from climatic-influenced events can also impact abiotic aspects of systems, as evidenced through strengthening stratification in water columns and the subsequent effect this has on biogeochemical processes (De Senerpont Domis et al., 2013; Velthuis et al., 2017; Wagner and Adrian, 2009).

2.1.2 Biotic responses

Phytoplankton biomass can be positively or negatively affected by the occurrence of climatic events depending upon how these events manifest in the water system. For example, extreme precipitation can instigate phytoplankton growth with nutrient loading from runoff (De Senerpont Domis et al., 2013) or thermal pollution from impervious surfaces increasing the temperature of runoff water (Van Buren et al., 2000). Heatwaves can similarly contribute to phytoplankton growth with warming the water to temperatures more favorable for some species such as cyanobacteria, particularly when warming is also paired with a nutrient-rich environment (Lurling et al., 2018). However, the occurrence of climatic events can also negatively affect phytoplankton biomass through the abiotic changes. For example, phytoplankton can be placed at a disadvantage when nutrients become diluted (Cobbaert et al., 2014), lower temperatures create unsuitable conditions (Wood et al., 2017) and phytoplankton are flushed from the system (Stockwell et al., 2020). Shifts in light availability due to alterations of turbidity (Bergström and Karlsson, 2019; Perga et al., 2018) can also select for phytoplankton species with a competitive advantage (Ekvall et al., 2013; Feuchtmayr et al., 2019), such as for cyanobacteria with the capacity for vertical movement (Walsby et al., 1991). Species that are outcompeted due to turbidity as well as temperature, nutrients and flushing may lead to a decrease in overall phytoplankton biomass as well as shifts in community composition favoring harmful cyanobacterial blooms.

2.1.3 Multiple stressors

Pulse-press disturbance categorization (Bender et al., 1984) can be applied to climatic stressors with short, intense extreme events being “pulse” disturbances and prolonged climatic pressures being “press” disturbances (Harris et al., 2018). The combination of these two stressors can have notable implications on biological communities such as shifts in community richness and species dominance (Graham and Vinebrooke, 2009; Harris et al., 2018). At present, few studies have focused on the combined effect of an extreme event (pulse disturbance) and mean climate change (press disturbance) on phytoplankton (Bergkemper et al., 2018; A. D. Richardson et al., 2019), particularly with combined stressors of allochthonous materials and temperature (Graham and Vinebrooke, 2009). Elucidating the mechanisms behind interactive effects of climatic stressors requires experiments in a controlled setting.

2.1.4 Experiment

We carried out a microcosm study with three phytoplankton populations (i.e., cyanobacteria, diatom and green algae), mimicking the primary food web base of a typical eutrophic Dutch lake under two climate scenarios (ambient summer water temperature and +6 ºC summer water temperature). Half of the microcosms were also exposed to an extreme precipitation event. We tested two hypotheses with the full-factorial treatment design. First, under eutrophic conditions, the higher water temperature microcosms will support a larger phytoplankton biomass than the ambient temperatures. Previous studies have illustrated the implications of heatwaves on the proliferations of algal blooms (e.g., Urrutia-Cordero et al. 2020), particularly with the presence of heat-adapted species such as cyanobacteria (e.g., Filiz et al., 2020). Second, upon exposure to the runoff event, we predict that there will be a larger difference in productivity in the warmer versus ambient climate treatments, thus creating more competitive advantages for cyanobacteria. Such productivity can result when higher temperatures instigate more phytoplankton primary production activity and, in combination with access to readily available nutrients, can support significant growth (Paerl and Paul, 2012). This is in line with studies regarding the effect of eutrophication in supporting phytoplankton proliferation (Hansson et al., 2013; Schindler, 1978) .

2.2 Methods and materials

2.2.1 Experimental design

We carried out a full-factorial microcosm experiment where an artificial phytoplankton assemblage was exposed to an ambient and regional warming scenario for a period of 23 days. Both ambient (18 ºC) and warm (24 ºC) microcosms were exposed to a runoff event on day 13 to test whether the microcosm response to an extreme precipitation event was amplified or controlled by temperature. Each treatment had six replicates, resulting in a total of 24 microcosms (6 replicates x 2 temperature treatments x absence/presence of runoff event). Each microcosm was inoculated with a phytoplankton assemblage consisting of cyanobacterium *Anabaena flos-aquae* (CCAP 1446/1C), green alga *Chlorella vulgaris* (UTEX 26) and diatom *Synedra sp.* (from a 2009 field isolate from Lake Maarsseveen, The Netherlands, 52°08’32.2” N 005°04’53.7” E). These species were chosen for the simplified assemblage as they are common in eutrophic systems throughout The Netherlands and represent the dominant cyanobacteria, green algae and diatoms of our reference Omloop Lake (The Netherlands, 51.79242 N, 4.95114 E). Additionally, these three species exhibit differing traits and preferences that can assist in testing the implications that the experimental treatments had on their competitive ability. The microcosms were sampled at a 2-3 day interval, with six samplings occurring before the day 13 runoff event and five happening after.

2.2.2 Reference Omloop Lake

Our experimental phytoplankton species and their relative abundance, the temperature treatments and the precipitation runoff simulation were based on the conditions present in Omloop Lake, which is a hydrologically isolated, moderately deep (6.8m) and eutrophic lake system located in the southwest of the Netherlands (51.79242 N, 4.95114 E). The summer conditions of this lake are representative of many of the anthropogenically-created water bodies in the country. In line with regional trends, land-use induced nutrient enrichment is leading to the eutrophic state of water bodies and an abundance of cyanobacteria.

2.2.3 Microcosm design

The microcosms consisted of 10 L Nalgene containers (Nalgene, Rochester, United States of America) filled with 3.5 L autoclaved COMBO medium (Kilham et al., 1998). Algal trace element solution stocks for $Na_2EDTA{\cdot}H_2O$ and $FeCl_3{\cdot}H_2O$ were stored and added separately to the Nalgene microcosms to avoid crystallization. At the start of the experiment (day 0) the microcosms were inoculated with 540 mL of the algae stock. The introduced biomass was composed of 24% *Anabaena flos-aquae*, 50% *Chlorella vulgaris* and 26% *Synedra sp*. This biomass distribution was chosen to emulate a typical eutrophic Dutch lake system under summer conditions with green algae dominance following the phytoplankton seasonal succession (De Senerpont Domis et al., 2007). Incident light was set at 24.91 ± 4.74 µmol photons m^{-2} s^{-1} integrated over PAR (TL Osram 18w/840, Berlin, Germany) programmed for 16 h light and 8 h dark (Theben selecta 170 top 2 digital astronomical switch set, Haigerloch, Germany). This light intensity is around the critical light intensity of the phytoplankton types involved (e.g., Huang et al. 2018; Shi et al. 2015; Shu et al. 2012). The microcosms were closed off with a silicone stopper to prevent contamination by air and evaporation losses. This stopper contained an air vent with a filter and a tubing system through which an air flow was administered to prevent oxygen depletion and to create a subtle mixing of the water column. Microcosm water columns were homogenized three times per week through manual perturbation to prevent phytoplankton adherence to surfaces.

2.2.4 Treatment scenarios

2.2.4.1 Temperature

Water temperature scenarios were based on average and extreme summer temperatures using hourly air temperature data records (1951-2017) of the Royal Dutch Meteorological Institute's de Bilt weather station. Air temperatures were converted to water temperatures with the Dutch surface water model developed by (Mooij et al., 2008b), yielding 18 ºC and 24 ºC for ambient and warm scenarios, respectively. Temperature treatments were administered through water baths containing a heating element (EHEIM 3619 300W heater, Deizisau, Germany) and an underwater pump (EHEIM compactON 1000, Deizisau, Germany). Water temperature was controlled with a custom climate control system (SpecView, Uckfield, United Kingdom) at +/- 0.5 ºC.

2.2.4.2 Precipitation

The extreme precipitation-induced runoff event was based on daily precipitation values from the de Bilt weather station's 1906-2017 summer precipitation records. To attain a realistic scenario of soil runoff volumes we performed rainfall simulations with the Wageningen University + Research Soil Physics and Land Management Group rainfall simulator (Lassu et al., 2015); Supplement Information SI 2.2). Soil samples from the shore of Omloop Lake were taken to simulate particulate material in overland runoff. Based on these rainfall simulations, precipitation treatments were represented in the microcosms through introduction of a soil runoff solution (2.9 g soil dissolved in 600 mL demi water, equaling to approximately 15% microcosm volume dilution) to the extreme precipitation-assigned microcosms. To mimic the increased water volume that takes place after intense precipitation for lakes with no outflow, the total volume of the precipitation-treated microcosms increased to approximately 4.6 L in the 10 L containers, and maintained the higher volume (as compared to the non-precipitation-treated microcosms) for the remainder of the experiment. As such, dilution of dissolved nutrient concentrations in the microcosms occurred with the application of the rainfall simulation due to the added runoff increasing the total microcosm volume. During the experiment, removed sample volumes were replaced with equivalent amounts of COMBO medium following every sampling (approximate 2% dilution rate). The nutrient composition in the runoff was 125 mg/L particulate carbon, 12 mg/L particulate nitrogen and approximately 0.08 mg/L mobile phosphorus, of which 0.004 mg/L was the readily available phosphorus fraction, 0.06 mg/L was the redox sensitive phosphorus fraction and 0.01 mg/L was the organic phosphorus fraction as was determined through an adjusted version of the Psenner soil analysis (Cavalcante et al., 2018), with details on measurements in SI 2.3, Table SI 2-2. Carbon, nitrogen and phosphorus were measured as these values will provide insight into potential macronutrient limitations, while other nutrients such as silica and iron were not measured as they are perceived to be sufficiently provided through the quantity and frequency of COMBO medium that was added into the microcosms (SI 2.1, Table SI 2-1). The runoff event was applied to microcosms on day 13 of the experiment.

2.2.5 Sample analysis

2.2.5.1 Sample collection

To account for vertical heterogeneity in phytoplankton abundance, samples were collected from microcosms using sampling tubes. During experiment days 0-12, approximately 170 mL of sample volume was collected from each microcosm. After day 13, microcosms treated with runoff had approximately 230 mL collected during sampling. All sampled volumes were replaced with equivalent amounts of COMBO medium to compensate for the loss in water as well as nutrients.

2.2.5.2 Phytoplankton

The microcosm phytoplankton assemblage composition was quantified during each sampling event using a PhytoPAM fluorometer (WALZ, Effeltrich, Germany). This method was used as it has been considered more reliable than microscopic counting methods (Lurling et al., 2018). Before the onset of the experiment, we conducted a regression analysis of PhytoPAM measurements versus Coulter counter counts of the individual phytoplankton cultures which yielded high agreement between these two measurements (*Anabaena flos-aquae* R^2 = 0.96, *Chlorella vulgaris* R^2 = 0.97, *Synedra* R^2 = 0.94, see SI 2.4, Figure SI 2-1 A-C; Beckman Coulter Nederland BV, Woerden, the Netherlands). Calculated dilution concentrations are shown for Total Chlorophyll a in SI 2.5, Figure SI 2-2.

2.2.5.3 Abiotic

To determine dissolved and particulate nutrient fractions, samples were filtered with Aquadest washed glass microfiber filters (Whatman GF/F, Maidstone, United Kingdom). Filters were dried for 24 h at 60 °C before being stored in a desiccator. Filters for particulate phosphorus were incinerated at 550 °C for 20 minutes then autoclaved with a 2% potassium persulfate solution at 121 °C for 30 minutes. Resulting solutions were analyzed for phosphorus concentrations with a

Quaatro segmented flow analyzer (Seal Analytical, Beun de Ronde, the Netherlands). Particulate carbon and nitrogen fractions were determined from filter samples with a FLASH 2000 organic elemental analyzer (Interscience B.V., Breda, the Netherlands). Filtrate samples were stored at -20 ºC until run through an ASI-L Auto Sampler (Shimadzu, Kyoto, Japan). Dissolved phosphate, total oxidized nitrogen, nitrite, nitrate and ammonium concentration were quantified with a Quaatro segmented flow analyzer. Dissolved organic carbon and dissolved inorganic carbon were measured weekly in a TOC-L Total Organic Carbon Analyzer (Shimadzu, Kyoto, Japan). Phosphorus and nitrogen were calculated through summation of the measured dissolved and particulate nutrient fractions. Calculated dilution concentrations are shown for dissolved phosphate and dissolved nitrogen in SI 2.5, Figures SI 2-3.

Prior to sampling, a WTW Multi 350i Field Meter (WTW, Weilheim, Germany) measured water temperature, pH and dissolved oxygen of the microcosms. Turbidity was measured weekly with a WTW Turb430IR Meter (WTW, Weilheim, Germany).

2.2.6 Statistics

Linear mixed-effect models (“LME”; Lindstrom and Bates, 1988a) were used to analyze the effects of our experimental treatments on the phytoplankton and nutrients. Precipitation treatment runoff (RUNOFF), temperature (TEMP) and time (TIME) were integrated as fixed factors. Data were analyzed for the full time period, as well as for the before and after runoff periods separately. For the latter, we divided the dataset into a before runoff period (0–12 days), where only temperature and time effects were evaluated, and an after-runoff period (14–23 days), where the effect of the precipitation treatments was also assessed. We opted to only present and discuss the analyses of the dataset in two time periods as, upon the application of the runoff treatment, the microcosms exhibited contrasting trajectories relative to before runoff periods, i.e., changed slope and intercept. To account for the variation in initial states among microcosms for both before runoff and after runoff periods, we included the individual microcosms as a random term in the LME model. A metric called intraclass correlation (ICC) was used for evaluation of the significance of random effects. The ICC, by calculating the ratio of between-cluster variance to total variance, can be helpful in determining whether random effects are needed (Theobald, 2018). For completeness, we document both the analysis of the full time period as well as the separate analyses of the two time periods in SI 2.6, Tables SI 2-3, 2-4, 2-5, 2-6, 2-7, 2-8, 2-9, 2-10, 2-11, and 2-12. The Shapiro Wilk test (Ghasemi and Zahediasl, 2012a) was used to check for normality. If normality assumptions were violated, we transformed the data through a logarithm, square root or reciprocal transformation. If transformed data still did not meet the assumption of normality, we chose to show the model outcome on the untransformed data but associated the p-values with a more conservative probability cut-off (i.e., only factors with very small p-value were considered significant; (Fowler-Walker and Connell, 2002). In addition, we used the Breusch Pagan test (Waldman, 1983a) to check for data heteroscedasticity and a weighted linear mixed-effect model was applied if necessary. Additionally, the interaction term was calculated for the total chlorophyll a, individual phytoplankton species, phosphorus and nitrogen LME models to evaluate the potential interactive effects of multiple stressors (Tables SI 2-3, 2-4, 2-5, 2-6, 2-7, 2-8, 2-9, 2-10, 2-11, and 2-12).

Principal response curve analysis ("PRC"; Paul J. Van den Brink and Braak, 1999), a multivariate statistical method, was carried out on multiple parameters to determine the system responses of the four different treatments over time and the weights of different parameters. In our study, we set the ambient temperature (18 ºC) and non-runoff-treated microcosms as the reference (baseline) to compare other treatments against. Data were standardized prior to the PRC analyses. All statistical analyses in this study were performed in R (Team, 2019a) with the packages *lubridate* (Grolemond and Wickman, 2011a), *ggplot2* (Villanueva and Chen, 2019a), *nlme* (Pinheiro et al., 2019a) and *vegan* (Oksanen et al., 2019b).

2.3 Results

2.3.1 Biotic response

The runoff and temperature effects were assessed for the total phytoplankton biomass (Figure 2-1 A) and for the three species individually (Figures 2-1 C-E) through a linear mixed effect model (LME). Temperature had a significant positive effect on total chlorophyll-a concentrations throughout the duration of the experiment ($F_{1,118} = 5.09$, $p <0.05$, days 0-12, TEMPxTIME; $F_{1,92} = 7.35$, $p <0.05$, days 14-23, TEMPxTIME). The runoff event resulted in a significant lowering of total phytoplankton biomass ($F_{1,92} = 4.55$, $p <0.05$, days 14-23, RUNOFFxTIME; Figure 2-1 A). However, there was no significant interaction detected between both climatic events ($F_{1,92} = 0.02$, $p = 0.89$, days 14-23, TEMPxRUNOFFxTIME). To explore the dilution aspect of the runoff event, we calculated changes in total chlorophyll a of the non-runoff event exposed treatments (18 ºC & 24 ºC) due to dilutions. These graphs are provided in SI 2.5, Figure SI 2-2 A-B.

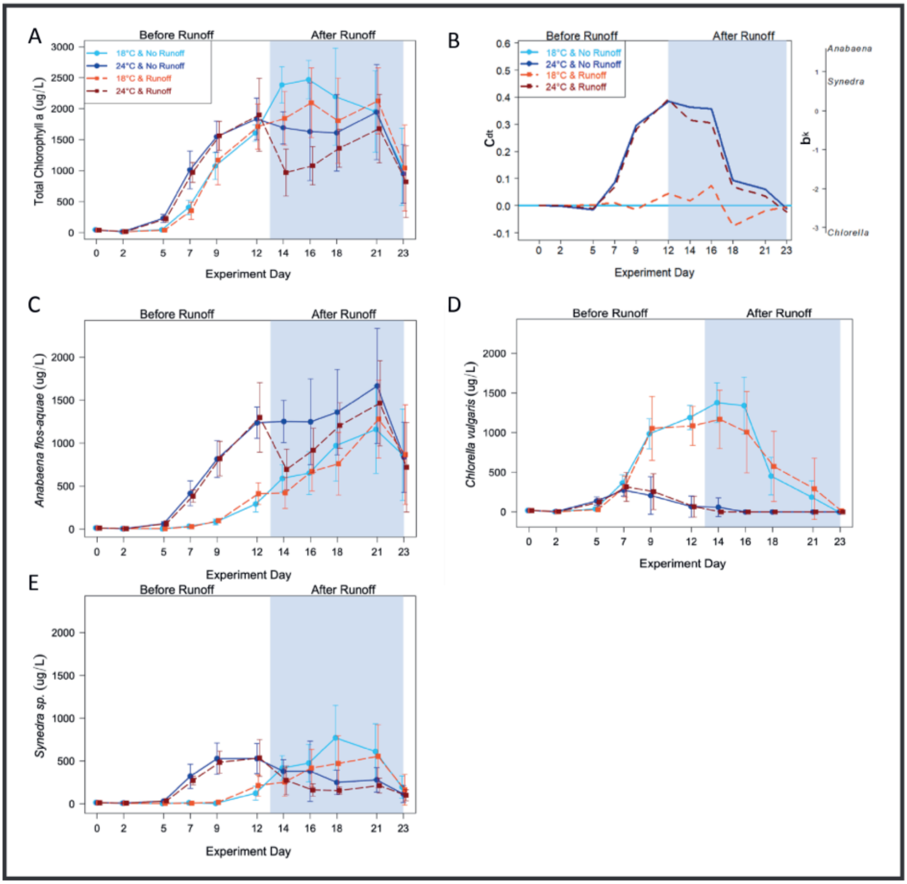

Figure 2-1. *Overall phytoplankton biomass (chlorophyll a concentration) presented by microcosm treatment (**A**) and with principal response curves ("PRC") of phytoplankton species, as expressed by coefficient effects for the control and each experimental treatment (**B**). The PRC figure visualizes the multivariate response of the microcosm assemblage (expressed in canonical regression coefficient Cdt, left y-axis) over time (x-axis) in the different treatments relative to the control (the baseline) and to what extent this response was influenced by the individual phytoplankton species concentrations (expressed in the species weight bk, right y-axis). A positive weight on the right y-axis for a specific parameter indicates that this parameter is positively correlated with the observed patterns. Conversely, a negative weight on the right y-axis indicates that a specific parameter is negatively related with the observed patterns. Individual algal species concentrations measured with PhytoPAM of chlorophyll a for each experimental treatment and control treatment are presented for Anabaena flos-aquae (**C**), Chlorella vulgaris (**D**) and Synedra sp. (**E**). The light blue solid line represents ambient temperature (18 ℃) & no runoff, the dark blue solid line represents higher temperature (24 ℃) & no runoff, the light red dashed line represents ambient temperature (18 ℃) & runoff, and the dark red dashed line represents higher temperature (24 ℃) & runoff. In Figure 2-1 B, the flat light blue line is the control treatment and the other three lines are the experimental treatments. These lines apply the same color key scheme as illustrated in Figure 2-1 A.*

The dynamics of phytoplankton biomass in response to experimental treatments were shown in principal response curves (PRC, Figure 2-1 B), with the weight of each species indicating their influence on the overall dynamics. The cyanobacterium *Anabaena flos-aquae*, and to a lesser extent the diatom *Synedra*, showed opposing influences on the principal responses in comparison with the green alga *Chlorella vulgaris*. This differential response becomes apparent only at day 6, with higher temperatures resulting in higher cyanobacteria ($F_{1,118} = 116.66$, $p < 0.0001$, days 0-12, TEMPxTIME; Figure 2-1 C) and diatom concentrations ($F_{1,22} = 25.96$, $p < 0.0001$, days 0-12, TEMP; Figure 2-1 E) as well as lower green algal concentrations ($F_{1,118} = 41.92$, $p < 0.0001$, days 0-12, TEMPxTIME; Figure 2-1 D).

Following the runoff event on day 13, recipient microcosms had a short-term but non-significant decline in cyanobacteria and diatom biomass ($F_{1.92} = 1.74$, $p = 0.19$, day 14-23, RUNOFFxTIME; $F_{1.92} = 1.79$, $p = 0.18$, day 14-23, RUNOFFxTIME), and a non-significant increase in green algal biomass ($F_{1.92} = 3.10$, $p = 0.08$, day 14-23, RUNOFFxTIME). Within the warmer microcosms, such a decline in biomass occurred on day 14 and recovered to levels equivalent to non-runoff-treated microcosms by day 16 (Figure 2-1 B). Ambient temperature microcosms had a delayed effect with the decline visible starting at day 18 and reaching biomass levels equivalent to the non-runoff-treated microcosms on day 23 (Figure 2-1 B). Temperature did not amplify or control the response of the phytoplankton assemblage to the runoff event and remained significant in determining cyanobacterial ($F_{1,92} = 5.56$, $p < 0.05$, days 14-23, TEMPxTIME; Figure 2-1 C), diatom ($F_{1,20} = 4.62$, $p < 0.05$, days 14-23, TEMP; Figure 2-1 E) and green algal biomass ($F_{1,92} = 146.85$, $p < 0.0001$, days 14-23, TEMPxTIME; Figure 2-1 D). The runoff effect (RUNOFF or RUNOFFxTIME) was not significant for any of the individual species.

2.3.2 Nutrients

<u>2.3.2.1 Particulate and dissolved nutrients</u>

The concentrations of particulate and dissolved phosphorus (particulate phosphorus + soluble reactive phosphorus (“SRP”)) in warmer microcosms were significantly higher than that in ambient microcosms during the first half of the experiment. Distinct differences between the warmer and ambient microcosms are visible on day 12 of the experiment. This trend, however, was lost after the application of the runoff event ($F_{1.92} = 1.86$, $p > 0.05$, days 14-23, TEMPxTIME). Following the runoff event, there was a nearly significant effect of precipitation on the particulate and dissolved phosphorus content of the microcosms ($F_{1,92} = 3.43$, $p = 0.07$, days 14-23, RUNOFFxTIME). Throughout the duration of the experiment, temperature had a significant positive effect on particulate and dissolved nitrogen concentrations (particulate nitrogen + nitrite + nitrate + ammonia; $F_{1,22} = 11.34$, $p<0.005$, days 0-12, TEMP; $F_{1,20} = 5.55$, $p<0.05$, days 14-23, TEMP; Figure 2-2 B).

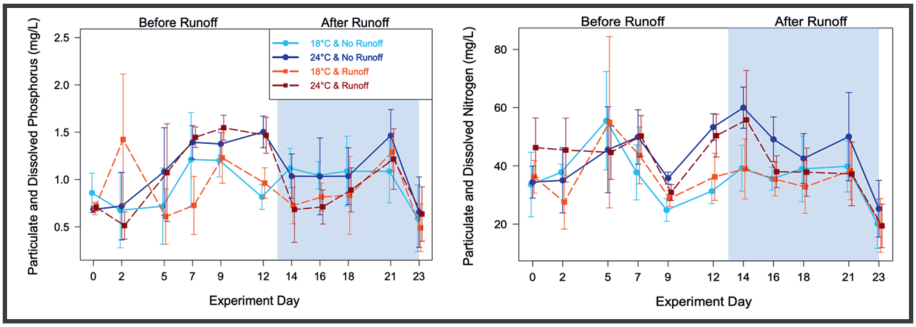

Figure 2-2. *Particulate and dissolved phosphorus (**A**) and nitrogen (**B**) by treatments. The light blue solid line represents ambient temperature (18 ℃) & no runoff, the dark blue solid line represents higher temperature (24 ℃) & no runoff, the light red dashed line represents ambient temperature (18 ºC) & runoff, and the dark red dashed line represents higher temperature (24 ℃) & runoff.*

2.3.2.2 Dissolved, particulate nutrients

Initial average phosphate concentrations were recorded at 0.66 mg/L (day 1, Figure 2-3 A). Microcosms maintained high concentration levels until day 7, after which there was a decline. The change in phosphate levels closely coincides with the increase of total chlorophyll a across all microcosm treatments (Figure 2-1 A). Following day 12, phosphate remained at near non-detectable levels regardless of the treatment ($F_{1,92} = 1.32$, $p >0.05$, days 14-23, TEMPxTIME; $F_{1.92} = 2.88$, $p >0.05$, days 14-23, RUNOFFxTIME). To explore the dilution aspect of the runoff event, we calculated changes in phosphate of the non-runoff event exposed treatments (18 ºC & 24 ºC) due to dilutions. These graphs are provided in Figure SI 2-3 A-B.

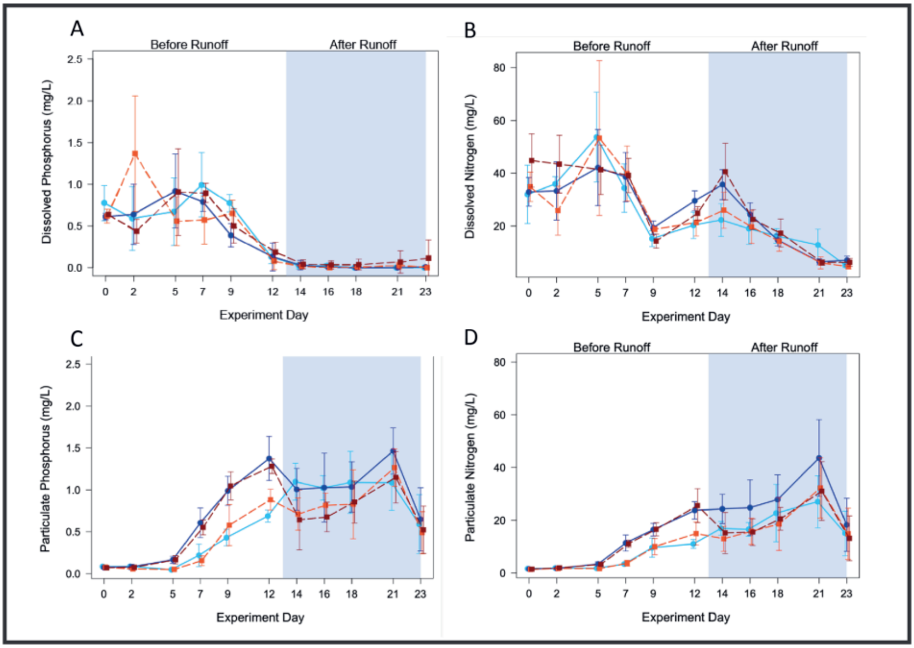

Figure 2-3. *Experimental treatments and control treatment are presented for dissolved phosphorus (**A**), dissolved nitrogen (**B**), particulate phosphorus (**C**) and particulate nitrogen (**D**). The light blue solid line represents ambient temperature (18 ºC) & no runoff, the dark blue solid line represents higher temperature (24 ºC) & no runoff, the light red dashed line represents ambient temperature (18 ºC) & runoff, and the dark red dashed line represents higher temperature (24 ºC) & runoff.*

Dissolved nitrogen concentrations (nitrate + nitrite + ammonium) had a similar overall decrease in concentration (Figure 2-3 B) with no temperature effect detected ($F_{1.118} = 0.03$, $p > 0.05$, days 0-12, TEMPxTIME; $F_{1.92} = 0.33$, $p > 0.05$, days 14-23, TEMPxTIME). However, over days 9-14 there was a brief increasing trend for all microcosms, wherein the warmer microcosms displayed sharper concentration increases. In contrast to dissolved phosphate, the dissolved nitrogen did not decrease to near non-detectable levels. During the post-runoff period, the precipitation treatment also had a significant effect on dissolved nitrogen concentrations, as seen on day 14 ($F_{1,92} = 4.71$, $p < 0.05$, days 14-23, RUNOFFxTIME). To explore the dilution aspect of the runoff event, we calculated changes in dissolved nitrogen concentrations of the non-runoff event exposed treatments (18 ºC & 24 ºC) due to dilutions. These graphs are provided in SI 2.5, Figure SI 2-4 A-B.

Particulate phosphorus increased before the runoff event, with the warm microcosms increasing more rapidly than the ambient temperature microcosms ($F_{1,118} = 26.98$, $p < 0.0001$, days 0-12, TEMPxTIME; Figure 2-3 C). However, this significant interaction disappeared following the runoff event ($F_{1.92} = 1.27$, $p > 0.05$, days 14-23, TEMPxTIME). Despite the introductions of sediment-associated nutrients, exposure to the runoff event had a non-significant impact on the phosphorus concentrations ($F_{1,20} = 4.25$, $p = 0.05$, day 14-23, RUNOFF; Figure 2-3 C). Particulate nitrogen showed similar responses with the higher rates of increase in the warmer microcosms versus the ambient temperature microcosms ($F_{1,118} = 20.96$, $p <0.0001$, days 0-12, TEMPxTIME; Figure 2-3 D) before disappearing upon exposure to the runoff event ($F_{1.92} = 0.05$, $p >0.05$, days 14-23, TEMPxTIME).

2.4 discussion

We examined the implications of coinciding climatic stressors on a phytoplankton assemblage within a full-factorial microcosm experiment design. Our study aim was to analyze the effects of runoff and temperature on phytoplankton under typical Northwestern European summer conditions. For this, the microcosms emulated a eutrophic and hydrologically-isolated water system, which is common for deeper lakes throughout the Rhine and Meuse delta (Seelen et al., 2021b). Regional temperature and precipitation data were used to devise the summer ambient and extreme treatments. Within this design, a coinciding chronic press stressor and short-term pulse stressor were administered through a warming event and a precipitation runoff event, respectively. Our study showed that the individual temperature treatments had a more significant effect on the phytoplankton assemblage than the combined treatment. Specifically, this resulted in proliferation of cyanobacteria biomass, and to an extent of diatom biomass, in the warmer treatments and green algae biomass in the ambient treatments. The runoff event, on the other hand, had a transient effect on the phytoplankton dynamics with a short-lived decrease in chlorophyll a measured in the overall phytoplankton and the individual cyanobacteria in the higher temperature treatment. Based on these results, we here discuss the implications of individual versus multiple stressor scenarios, the influence of press and pulse stressors in lake systems as well as suggestions for future studies.

2.4.1 Temperature treatment

In support of our first hypothesis, the observed phytoplankton dynamics highlighted the role of temperature in stimulating biomass growth, with the exception of the green alga *Chlorella vulgaris*. This species has been observed to have a different range of temperatures for promoting growth rather than our temperature treatment. Under controlled conditions, *Chlorella vulgaris* has been observed to achieve high growth rates at 25-30 ºC (Sharma, 2012), though growth has also been observed up to 35 ºC (Lee et al., 1985). However, within our assemblage setting, *Chlorella vulgaris* was unable to outcompete *Anabaena flos-aquae* at the higher microcosm temperature. In comparison, our cyanobacterial species demonstrated the largest growth rate under warm conditions. Previous studies have demonstrated this relationship through laboratory experiments (Sarian Kosten et al., 2012), modeling (Alex Elliott et al., 2005; Mooij et al., 2007) and observations (Konopka and Brock, 1978). Our results are congruent with growing concerns regarding how intensified warming could impact lake ecosystems, especially those in already eutrophic or degraded states. The dominance of cyanobacteria under the warming treatments, relative to the ambient treatments, can cause challenges as these species are capable of disrupting food web dynamics (Bartosiewicz et al., 2019) and causing health concerns with toxin production (Francy et al., 2016). Microcystin in particular has been a prominent toxin of concern in freshwater systems (Faassen and Lürling, 2013). While our study incorporated measurements to evaluate microcystin concentrations, its production was considered absent in our microcosm study as toxin levels were undetectable. However, other cyanobacteria species within the phytoplankton community may be capable of producing toxins under similar experimental conditions (Lürling et al., 2017a).

Additionally, the higher temperature treatment had a significant effect on the measured (dissolved + particulate) phosphorus fractions in the microcosms. A significant difference in phosphorus levels occurred in the time period before the application of the runoff simulation. As the microcosms were closed systems, the difference in phosphorus concentrations could not be accounted for due to removal of phosphorus from the system. Aside from sampling events, the contents of the microcosms were not removed. We hypothesize that the ambient temperature instigated an increase in the quantity of colloidal phosphorus, which would thereby render the nutrient immeasurable in the dissolved and particulate nutrient analysis. We recognize, however, that not all fractions of phosphorus or of nitrogen were accounted for in the sample analysis. Therefore, in future, incorporating additional analyses of other nutrient fractions into the experimental set-up can further elucidate the mechanisms behind the significant difference in nutrient concentrations.

2.4.2 Precipitation runoff treatment

The impact of the runoff event on the phytoplankton was apparent through a significantly lower phytoplankton assemblage biomass, though this effect was not evident for the individual species. As precipitation runoff is capable of instigating a range of disparate effects within the recipient aquatic setting (Feuchtmayr et al., 2019; Kasprzak et al., 2017; Morabito et al., 2018), there could be a number of mechanisms behind the alteration in total chlorophyll a concentration in our experimental microcosms. The increase of the turbidity after the runoff event (SI 2.7, Figure SI 2-5) may have posed a light limitation for the phytoplankton. A visual, short-lived increase in suspended solids following the application of the runoff supports the role of turbidity within our microcosm setting. Continuous measurements of light levels within the water column could assist in further elucidation of the influence of such a runoff event in future experiments. On the other hand, the abrupt addition of 600 mL soil runoff solution into the extreme precipitation-treated microcosms could also have caused a dilution effect. As demonstrated in previous studies, the influx of water from an extreme precipitation event can lead to a decreased biomass through system dilution (Wood et al., 2017).

The calculated dilution from the runoff event (SI 2.5, Figures SI 2-2 A-B) illustrated a relatively small decrease in phytoplankton biomass. The approximation of the dilution aspect of the runoff event of dissolved nutrients (Figures SI 2-2 A-B and SI 2-3 A-B) indicates that the dilution aspect of the runoff event could at least partially be mitigated by the increased availability of nutrients upon runoff exposure. It is likely that these nutrients were rapidly uptaken by the phytoplankton assemblage as phosphate remained at near limiting levels, and dissolved nitrogen levels were only temporarily significantly elevated.

2.4.3 Multiple stressors in freshwaters

Contrary to our second hypothesis, temperature did not amplify or control the impact of runoff on the microcosms. In the second half of the experiment, both the temperature increases as well as runoff seemed to reduce chlorophyll-a concentrations relative to the control conditions. Whereas this effect was subtle but not significant for the runoff only treatment, it was significant for a short time period in both the 24 ºC treatment (day 14) as well as the combined treatment (day 14 and day 16). Following the classification of potential interaction types between multiple stressors by Piggott et al. (2015), the conditions wherein an interaction may occur include when 1) two single stressor effects oppose each other, 2) act in the same direction, 3) when both stressors have no effect individually and 4) when one single stressor has a significant effect and the other stressor does not have a significant effect. In our study during the period just after exposure to the runoff treatment (day 14), simultaneous exposure to runoff and 24 ºC temperature resulted in stronger negative impact on chlorophyll-a biomass levels than the effect of the single stressors, thereby demonstrating a negative synergistic effect (based on a negative (24 ºC)-neutral (runoff) interaction type) according to Piggot et al.'s classification. For the precipitation simulation, this could be due to the runoff treatment having mainly had a hydrological diluting effect rather than a biogeochemical effect. As for temperature, the 24 ºC microcosms exhibited trends of *Anabaena* growth briefly leveling off, *Chlorella* crashing and *Synedra* having peaked around day 14. In comparison, the phytoplankton in the 18 ºC microcosms exhibited steady growth around the period of the runoff application. Regardless of the mechanism, the two treatments did not have the anticipated effect of increasing phytoplankton biomass.

Comparably designed microcosm experiments have found other effects when multiple climatic stressors were combined into one treatment; previous microcosm studies utilizing heating and nutrient addition treatments have found that there was a positive effect on phytoplankton abundance when the treatments were individually applied, yet a lesser effect occurred when the two treatments were applied together (A. D. Richardson et al., 2019). A meta-analysis of multiple stressor freshwater studies by Jackson et al. (2016) indicated that multiple stressors predominantly (48%) had an antagonistic impact on the functional performance of freshwater ecosystems, rather than an synergistic (28%) or additive interaction (16%). This antagonistic interaction phenomenon in freshwater systems has been theorized to be rooted in these systems' potential to acclimate to pressures quickly due to environmental variability, specifically with co-adaptation in the systems dampening multiple stressor effects (Jackson et al., 2016). In future controlled system studies, particularly those with more complex food webs, these patterns of antagonistic or synergistic interactions can be more directly observed. Further, the upscaling of mechanistic findings such as those from this experiment can be tested.

2.4.4 Press and pulse stressors in freshwaters

In situations where press and pulse pressures are paired, the press stressors can be indicative of the overall effect. As witnessed in our study, the effects of temperature on the phytoplankton community eclipsed those of the runoff event in magnitude of change, effectively accounting for the majority of the significant effects. Similar press events have been noted to present a larger effect on lake systems as compared to coinciding pulse events. For instance, the coinciding long-term heatwave and the short-term storm events observed in Lough Feeagh during summer 2018 instigated different effects on the system. On a time scale perspective, the implications of the heatwave persisted in the lake longer than those of the storm event (Calderó-Pascual et al., 2020).

However, pulse stressors also contribute to the cumulative effect of multiple stressors. By their nature, pulse stressors can stimulate intense responses in a system over a short period of time (Harris et al., 2018). The capacity of lakes to quickly mitigate a pulse stressor may provide an opportunity for the system to recover the pre-disturbance functions, but the shortening return period of these events can hamper the resilience of lakes. Further, lags or legacy effects from the pulse events can cause complications (Harris et al., 2018), such as mitigation measures not being implemented or the delayed effect coinciding with another stressor.

2.4.5 Caveats and future steps

We studied the combined effect of a climatic press and pulse stressor on an experimental phytoplankton assemblage. Over the course of the experiment, the microcosms exhibited significant effects due to the applied treatments. Of interest is that all of the microcosm assemblages exhibited a decline towards the end of the experimental period. We hypothesize that a limitation of resources, particularly of nutrients, became unsustainable and led to an observed decrease in total phytoplankton biomass levels following day 21. Further, the presented methods could be improved upon for evaluating assemblages. For instance, our approach of utilizing PhytoPAM for measuring phytoplankton biomass was proven as effective as more traditional counting methods. However, calibration of the PhytoPAM throughout the experiment could accommodate shifting experimental conditions.

While experimenting with such an assemblage lacks the environmental realism of a natural aquatic food web, it does permit us to gain a deeper mechanistic understanding of cause-and-effect relationships. With the increasing likelihood of multiple and compound climatic pressures (e.g., IPCC, 2022), such experimental approaches can be key for elucidating relevant, underlying mechanisms of ecosystem processes. While experimental studies have demonstrated both antagonistic and (negative) synergistic climatic stressor interactions, phytoplankton communities may react differently when different climate scenarios are applied (Bergkemper et al., 2018; A. D. Richardson et al., 2019). Additionally, studies must incorporate geographic differences that will influence the form, frequency and severity in which stressors will manifest (Donat et al., 2016). Accounting for regional projections will guide what climatic scenarios are appropriate for assessing the probable pressures and reactions of a lake ecosystem.

Further research should focus on validating these mechanisms in more complex environmental settings, e.g., by using a mesocosm approach (Pace et al., 2019). Establishing this baseline understanding of coinciding climatic stressors on phytoplankton communities can support and inform the potential scenarios in real lake systems.

Chapter II

Acknowledgements

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Data availability statement

The R scripts and data used in the analyses are available at DOI: 10.5281/zenodo.4816237.

Supplementary information

CHAPTER III

Chapter III:

Effectiveness of phosphorus control under extreme heatwaves: implications for sediment nutrient releases and greenhouse gas emissions

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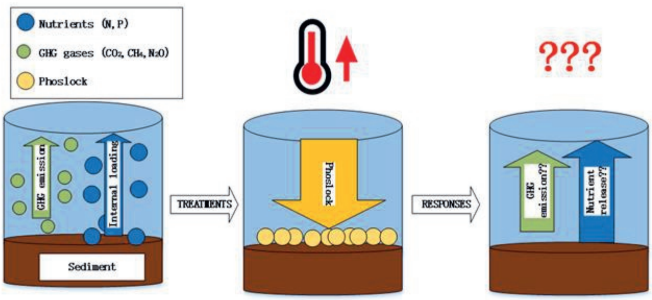

Abstract

Eutrophication has been identified as the primary cause of water quality deterioration in inland waters worldwide, often associated with algal blooms or fish kills. Eutrophication can be controlled through watershed management and in-lake measures. An extreme heatwave event, through its impact on mineralization rates and internal nutrient loading (phosphorus – P, and nitrogen – N), could counteract eutrophication control measures. We investigated how the effectiveness of a nutrient abatement technique is impacted by an extreme heatwave, and to what extent biogeochemical processes are modulated by exposure to heatwaves. To this end, we carried out a sediment-incubation experiment, testing the effectiveness of lanthanum-modified bentonite (LMB) in reducing nutrients and greenhouse gas emissions from eutrophic sediments, with and without exposure to an extreme heatwave. Our results indicate that the effectiveness of LMB may be compromised upon exposure to an extreme heatwave event. This was evidenced by an increase in concentration of 0.08 ± 0.03 mg P/L with an overlying water volume of 863 ± 21 mL, equaling an 11% increase, with effects lasting to the end of the experiment. LMB application generally showed no effect on nitrogen species, while the heatwave stimulated nitrification, resulting in ammonium loss and accumulation of dissolved oxidized nitrogen species as well as increased dissolved nitrous oxide concentrations. In addition, carbon dioxide (CO_2)-equivalent was more than doubled during the heatwave relative to the reference temperature, and LMB application had no effect on mitigating them. Our sediment incubation experiment indicates that the rates of biogeochemical processes can be significantly accelerated upon heatwave exposure, resulting in a change in fluxes of nutrient and greenhouse gas between sediment and water. The current efforts in eutrophication control will face more challenges under future climate scenarios with more frequent and intense extreme events as predicted by the IPCC.

3.1 Introduction

Eutrophication has been identified as the primary cause of water quality deterioration in inland waters worldwide across decades (David W Schindler, 1974; Smith et al., 2006). Eutrophication is caused by the over-enrichment of nutrients in surface waters, such as nitrogen (N, Howarth and Marino, 2006) and phosphorus (P, Carpenter 2008), resulting in increased primary productivity. The nutrients that originate from external sources in the catchment and from weathering of lake sediments stimulate autochthonous organic matter production (Smith et al., 1999), which may accumulate in lake sediments. This internal nutrient storage, mostly P due to denitrification driven N losses, may periodically be recycled in the water column (Søndergaard et al., 2013). A key symptom of eutrophication is the development of algal blooms (Kalff and Knoechel, 1978) that may hamper provisioning of ecosystem services such as drinking water and recreation, resulting in economic losses as well as negative impacts on quality of human life (Bruna Grizzetti et al., 2016). A consequence of eutrophication-related organic matter deposition is oxygen depletion that may influence global warming potential by increasing methane emissions from lakes and impoundments (Jake J Beaulieu et al., 2019; DelSontro et al., 2018).

To counter environmental degradation, there is a need to control eutrophication and reduce nutrient loading. Apart from catchment-level nutrient abatement techniques such as wastewater treatment and control of fertilizer application, in-lake measures are becoming an effective tool for minimizing algae nuisance (Lürling and Mucci, 2020). In-lake restoration measures can generally be divided into two categories: symptom-oriented, i.e., not directly targeting nutrients but rather targeting the nuisance associated with water quality deterioration, and source-oriented mitigation, i.e., directly targeting nutrients. Examples of the former are aeration/mixing that improves hypolimnetic oxic conditions and hampers surface accumulations of algae (Beutel and Horne, 1999; Visser et al., 2016), coagulation of algae cells (Liu et al., 2013), fish-stock reduction that improves clarity and sediment resuspension (Hosper and Meijer, 1993). Examples of source-oriented mitigation are dredging of nutrient-enriched sediments (Zhang et al., 2010) or the application of phosphorus locking agents that precipitate and immobilize phosphorus (Lurling et al., 2016). Phosphorus locking agents that reduce P availability for organism growth provide a promising avenue for in-lake measures. A widely used P fixative is lanthanum-modified bentonite (LMB), sold under the Phoslock® trademark (Douglas, 2002), which is designed to remove dissolved reactive phosphorus from the water column and to block P release from the sediment by forming an insoluble lanthanum-phosphate complex ($LaPO_4$). LMB settled at the sediment can thus provide an active barrier for P fluxes from the sediment, promoting oligotrophication. In comparison with many other chemical locking agents, LMB can keep P locked under a wide range of environmental conditions, such as under high pH, unlike iron and aluminum based products (Mucci et al., 2018); under low pH, unlike calcium-bound P (D. Copetti et al., 2016; Lin et al., 2015); and under low redox conditions, unlike iron- and manganese-bound P) (Mucci et al., 2018). Binding/complexation with other oxyanions/humid substances is only a kinetic hindrance of LMB (Lurling et al., 2014). A laboratory study by Zamparas et al. (2012) showed that the P-adsorption capacity by LMB can be enhanced with increased temperature (from 5 to 35 ^{o}C) due to the enlargement of pore size and/or activation of the bentonite surface.

Lake heatwaves (periods of extremely warm lake surface temperatures) are reaching higher temperatures and are lasting longer under climate change (Woolway et al., 2021), which, through subsequent impacts on mineralization rates and internal nutrient loading, could potentially counteract the current efforts in lake restoration. Heatwaves enhance thermal stability, resulting in deep-water anoxia (Jankowski et al., 2006). As a consequence, under anoxic conditions iron- and manganese-bound P in lake sediments can be released and become bioavailable (Beutel et al., 2008). Rising water temperatures can also increase internal loading by enhancing carbon (C) mineralization rates (Gudasz et al., 2010a) and liberating nutrients. Moreover, heatwaves could reinforce global warming regimes through greenhouse gas (GHG: carbon dioxide – CO_2, methane – CH_4, nitrous oxide – N_2O) emissions from lake sediments (Bartosiewicz et al., 2016). Although studies on combined effects of nutrients and warming show strong interactive effects on GHG emission (Aben et al., 2017; Davidson et al., 2018, 2015a), little is known about specific effects of heatwaves and restoration measures. Microbial processes like mineralization, nitrification and denitrification are all temperature dependent (de Klein et al., 2017; Veraart et al., 2011), while restoration measures may modulate these processes by reducing C, N and P availabilities needed for microbial activities (Redfield, 1958). As a result, the nutrient cycling and GHG emission can be largely changed by the altered microbial processes due to restoration and climate change even without considering the role of primary producers.

Most experimental studies on the efficacy of eutrophication control measures under climate change to date used continuous warming temperature scenarios (Cabrerizo et al., 2020a), while few have investigated sudden and large temperature boosts (i.e., heatwaves) and the potential for post-heatwave recovery in lakes. Given its rather sudden and short-term characteristics, the heatwave impacts may be transient rather than long-lived. In our study, we conducted an exposure scenario where we exposed our systems to a heatwave, with prior- and post-heatwave monitoring of water quality, enabling us to study the potential for post-heatwave recovery in lakes. We investigated if the effectiveness of the well-established nutrient abatement technique Phoslock® (hereafter LMB) is impacted by an extreme heatwave, and how this affects potential lake GHG emissions. We measured sediment nutrient release and dissolved GHG concentrations at the sediment-water interface in a three-week sediment incubation experiment. We used unmodified bentonite as a control treatment to account for the potential effects of bentonite clay in the LMB treatment.

We tested three hypotheses: 1) Heatwaves will enhance sediment nutrient releases by increasing mineralization rates and decreasing oxygen concentrations; 2) LMB can reduce the potential heatwave-induced P-release by reducing P-availability in the sediments; and 3) GHG emissions in LMB treated systems will be mitigated due to a reduction in nutrient availabilities.

3.2 Materials and methods

3.2.1 Experimental design

Pre-treatment. On 21 June 2018, sediments were collected in 39 cores (60 cm in length and 6 cm in diameter) with overlying water column at a depth of 1.85 m from a eutrophic Dutch pond (52°02'20.6"N, 5°38'51.4"E) using a UWITEC gravity core sampler. Pond water was sampled from three depths of the water column (0 m, 0.5 m, 1.5 m). Three of the 39 sediment cores were selected for analyses of P pools in the sediments, whereas the remaining 36 cores were designated for the experiment.

On these 3 cores, we carried out a P fractionation method following (Cavalcante et al., 2018) for the top 10 cm sediment to determine loosely bound P (H_2O-P), redox-sensitive P (BD-P), metal oxide-bound P (NaOH-P), Calcium-bound P (HCl-P) and residual P (residual-P). Each fraction of P consists of soluble reactive P (SRP) and non-reactive P (NRP) that represents the organic part. The sediment pools of mobile P, which can be released in anoxic conditions or by organic matter degradation and become bioavailable, was determined by the sum of the SRPs of the H_2O-P and BD-P fractions and the NRP of the NaOH-P fraction (Cavalcante et al., 2018). The sum of other P forms represents the non-mobile sediment P pool, i.e., the difference between the sum of all P forms and the above-mentioned mobile P forms. In our treatments, we determined LMB doses based on the mobile sediment P pool.

Upon transportation into the laboratory, the undisturbed sediment cores were placed in a temperature-controlled water bath at 20 °C. 20 °C is regarded as a baseline temperature for the experiment, similar to the pond water temperature during core collection. Water temperature was continuously recorded during the course of the experiment. The cores were open to the air throughout the experiment and were kept dark most of the time to prevent algal growth. The cores were exposed to light during the sampling events of around one hour, when the light ranged between 0.01 and 104.0 µmol photons m^{-2} s^{-1}. Sediments were acclimatized to the laboratory conditions for 5 days prior to the experiment.

Treatment. LMB was obtained from Phoslock® Europe GmbH (Manchester, UK). To test the effectiveness of LMB under a heatwave scenario, we split the 36 sediment cores into three groups such that 12 cores were treated with LMB, 12 cores were treated with bentonite (Bent) and the other 12 cores were left untreated (Ctrl) (Figure 3-1). We made a slurry of 380 mg LMB resuspended in water from each LMB treatment unit and added the slurry at the top of the core, targeting the amount of potential releasable P in the top 3.3 cm of the sediment to achieve an LMB:P ratio of 100:1 (see Table 3-1 for details on calculation of LMB dose). The same dose of bentonite was added to the 'Bent' treatment to control for potential physical capping of sediment in the LMB treatment.

Table 3-1. *Calculation of Phoslock® (LMB) dose*

Step	Calculation	Unit	Value
1. Target sediment depth		cm	3.3
2. Target sediment volume	Target sediment depth × core area	cm^3	93.31
3. Potentially available P of the sediment	Sum of mobile P forms × target sediment volume	mgP	3.8
4. La:P weight ratio	molar mass of La (= 138.9) ÷ molar mass of P (= 31)	-	4.48:1
5. Amount of La needed for target volume	Available P × La:P weight ratio	mg	17.024
6. Phoslock® (LMB) applied	Amount of La needed for target volume ÷ La content (=4.5%, Lurling et al., 2014)	mg	380

All of the 36 sediment cores were kept at 20 °C during the first week (Figure SI 3-1). During the second week, a heatwave scenario was simulated by exposing half of the cores of all P control treatments (i.e., LMB, Bent and Ctrl, 18 cores in total) to a temperature of 30 °C, whilst half of the cores of all P control treatments (LMB, Bent and Ctrl) were kept at 20 °C, yielding 6 replicates in each treatment unit (Figure 3-1). After one week at 30 °C, the heatwave cores were all returned to the baseline temperature of 20 °C. The heatwave scenario is similar to the recent summer conditions (2015-2020) in the Netherlands where the average temperature during heatwave that lasted weeks was around 30 °C (KNMI data, https://data.knmi.nl/). In the experimental heatwave scenarios, the heating and cooling of the water columns were realized within one day to simulate a sudden temperature boost scenario. As a result, we were able to monitor the dynamics of different water quality parameters before, during and after the heatwave in different treatment units.

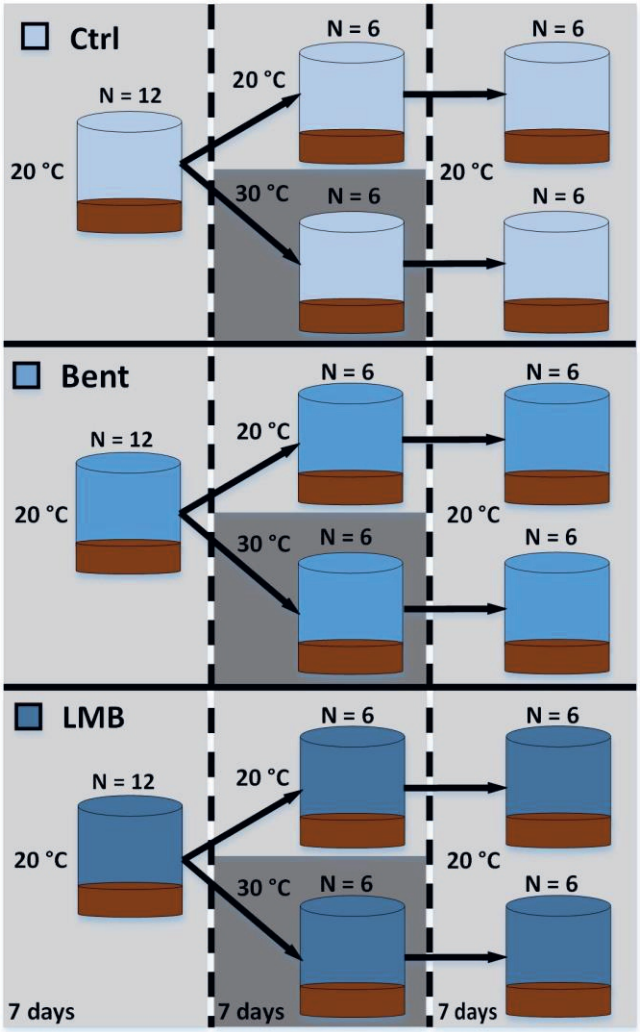

Figure 3-1. *Experimental design: 'Ctrl' represents control without adding P-binding materials; 'Bent' represents bentonite treatment; 'LMB' represents Phoslock® treatment. Shaded boxes represent sediment cores exposed to heatwaves.*

3.2.2 Water and sediment measurements

We sampled a suite of water quality variables including dissolved oxygen concentrations (O_2), pH, conductivity, dissolved inorganic nutrients and dissolved GHG at 10 cm above the sediment surface of each of the experimental units. We sampled SRP, NO_3-N + NO_2-N and NH_4-N, and carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) in total eight times along the course of the experiment (2-3 times/week). Metals, i.e., lanthanum (La), calcium (Ca), iron (Fe), aluminum (Al) and manganese (Mn) were sampled three times during the experiment (1 time/week). We used handheld sensors to instantaneously measure O_2 (HQ40d Portable probe, Hach, Colorado, US), pH and conductivity (WTW Multi 350i, Geotech Environmental Equipment Inc., Colorado, US). After filtration of water samples over prewashed GF/F filters (Whatman, Maidstone, U.K.) we analyzed the filtrate for SRP, NO_3-N + NO_2-N and NH_4-N, using an QuAAtro39 Auto-Analyzer (SEAL Analytical Ltd., Southampton, U.K.). In addition, we measured concentrations of La, Ca, Fe, Al and Mn in the filtrate by inductively coupled plasma optical emission spectrometry (iCAP6500 Duo, ThermoFisher, U.K.).

The concentrations of GHGs in the water column were determined by a headspace equilibration technique described in Magen et al. (2014) and Halbedel (2015). Briefly, water samples were introduced in a syringe, where air was introduced and the dissolved GHGs were equilibrated with the headspace by shaking the syringe vigorously for two minutes. Afterwards, the equilibrated headspace gas was collected and analyzed for GHG concentrations in a Gas Chromatography (TRACE™ 1300 GC, ThermoFisher, U.K.) machine equipped with a Flame Ionization Detector (FID) and an Electron Capture Detector (ECD). Calculations for the water column concentrations were based on Halbedel (2015), in which we used parameters from Weiss (1974) for CO_2, Yamamoto et al. (1976) for CH_4, and Weiss and Price (1980) for N_2O. Note that the CO_2 concentrations in our system were far beyond atmospheric CO_2 equilibrium ($\approx$ 412 ppm), therefore the limits of the headspace method to analyze the partial CO_2 concentration in water discussed in Koschorreck et al. (2021) is not relevant in our case.

To gain a close understanding of the anoxic conditions in the sediments in addition to the O_2 concentrations measured in the overlying waters, 12 cores (2 cores randomly chosen from each of the six treatment groups) were equipped with redox probes. Redox potential dynamics were continuously recorded (time interval of 10 minutes) at 12 different depths above and/or below the sediment water interface (max = 14 cm depth below the sediment surface).

After the experiment was completed, the P-fractions in 24 out of 36 cores (the ones without a redox probe, i.e., 4 cores from each treatment) were determined using the same method described for the three initial cores above. Besides the mobile P, their non-mobile P (i.e., the sum of the NRPs of the H_2O-P, BD-P fractions, the SRP from NaOH-P fraction and HCl-P and residual-P fractions) was also determined.

3.2.3 Statistical analysis

The effects of the experimental treatments on the dynamics of different variables including O_2, pH, SRP, NH_4-N, NO_3-N + NO_2-N, CO_2, CH_4, and N_2O were analyzed by a linear mixed-effect model (LME; Lindstrom and Bates, 1988), with each of the variables as the univariate response variable. The P treatments (Ctrl, Bent, or LMB) and temperatures were included as fixed effects. Day in the experiment was taken as an additional fixed effect to evaluate the changes in response variables through time. Differences among subjects (cores) were taken as a random effect in the LME model. The LME model corresponds to:

$$y_{ik} = \beta_0 + \sum_{m=2}^{3} \beta_{1mk} \times I[P]_{imk} + \beta_{2k} \times Temp_{ik} + \beta_{3k} \times Time_{ik} + b_{0k} + \varepsilon_{ik}$$

Where $i = 1,2, \ldots ,288$, index $k = 1, 2, \ldots ,36$ corresponds to the 36 cores, $m = 2,3$ corresponds to the P control measures. β are the fixed-effects coefficients. $I[P]_{im}$ is the dummy variable representing the level m of the P treatments. $Temp_{ik}$ stands for temperature, and $Time_{ik}$ stands for time. b_{0k} is the random effect for level k of cores, and ε_{ik} is the observation error for observation i. The random effect has the prior distribution,

$$b_{0k} \sim N(0, \sigma_b^2),$$

And the error term has the distribution,

$$\varepsilon_{ik} \sim N(0, \sigma^2).$$

We analyzed three phases in the experiment separately. First, we analyzed the period before the heatwave (days 1 – 7), where we only evaluated the effects of the P treatments and time. Second, we analyzed the period during the heatwave (days 8 – 14), where we evaluated the effect of the different temperature treatments (heatwave vs non-heatwave exposed treatments) in addition to the effects of P treatments and time. Finally, we analyzed the post heatwave period (days 15-21), where we evaluated the effects of P treatments and the recovery from the heatwave over time. The normality and heteroscedasticity of the residuals were tested by

Shapiro Wilk test (Ghasemi and Zahediasl, 2012b) and Breusch Pagan test (Waldman, 1983b), respectively. For the data that did not pass the test for normality, we applied a data transformation method (i.e., square root transformation for O_2, pH, NO_2 and NO_3, and logarithm transformation for CH_4). To account for heteroscedasticity, we deployed a weighted linear mixed-effect model (Zuur et al., 2009).

Determination of differences between the sediment P forms after the experiment were performed through two-way analysis of variance (ANOVA) with heatwave and LMB/Bent treatments as factors. In addition, we carried out two-way ANOVA analyses to determine the differences between metal concentrations in the heatwave phase as well as in the post-heatwave phase. All statistical analyses in this study were performed in R language (Team, 2019b). We used the packages *lubridate* (Grolemond and Wickman, 2011b), *ggplot2* (Villanueva and Chen, 2019b), *nlme* (Pinheiro et al., 2019b) and *vegan* (Oksanen et al., 2019a).

3.3 Results

3.3.1 Pre-treatment conditions

At the moment of field-sampling, water transparency measured with a Secchi disc was 0.54 m, pH was 7.52 ± 0.0, temperature was 19.5 ± 0.0 °C and O_2 concentration was 3.8 ± 0.1 mg/L and no apparent water stratification was observed. The soluble reactive phosphorus (SRP) concentration was 0.14 ± 0.02 mg P/L, the ammonium (NH_4-N) concentration was 0.56 ± 0.13 mg N/L, and the sum of nitrate and nitrite (NO_3-N + NO_2-N) was 0.04 ± 0.08 mg N/L. The total dissolved carbon (TDC) averaged 49.1 ± 3.1 mg/L, with an inorganic dissolved carbon (IDC) concentration of 36.9 ± 0.4 mg/L and a dissolved organic carbon (DOC) concentration of 12.2 ± 3.0 mg/L.

The sediment layers in the cores were at least 15 cm deep. The sediment was very fluffy with an average water content of 90.7 ± 1.5%, a dry weight (DW) density of 0.10 ± 0.02 g/mL, and an average organic matter (OM) amount of 0.022 ± 0.001 g/mL wet sediment.

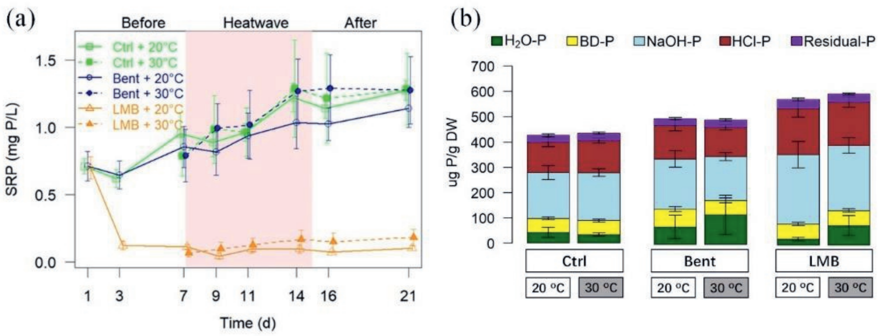

Figure 3-2. Panel (a): Dynamics of soluble reactive phosphorus (SRP) in the water column. Error bars indicate the standard error. The pink shading indicates exposure to different temperature regimes (20 °C in solid lines and 30 °C in dashed lines); before and after the pink shading shows all P-treatments (Ctrl, Bent and LMB) at 20 °C. Panel (b): Phosphorus (P) fractions in sediments (µg P/g DW). The labels on the x-axis illustrate treatment units: 'Ctrl' for no P treatments (i.e., no LMB/bentonite), 'Bent' for bentonite and 'LMB' for Phoslock®; '20 °C' for non-heatwave exposed groups and 30 °C for heatwave exposed groups.

3.3.2 Nutrients and metals dynamics and responses

In all treatments the initial SRP concentration in the water columns started at a similar level of 0.71 mg P/L (SE = ± 0.06) and changed significantly throughout the experimental periods (Figure 3-2 a). After LMB application the amount of SRP in the water column of our experimental units dropped by 83% within two days, whereas in the non-LMB groups (i.e., Ctrl and Bent treatments) a continuous increase in the SRP concentrations was observed along the entire course of experiment, up to 1.24 ± 0.10 mg P/L. No significant difference between Ctrl and Bent treatments were detected, with SRP concentrations increasing at a similar rate over time in both groups regardless of heatwave treatment (effect of increasing rate = 0.027 mg P/L/day, $F_{1, 162}$ = 117.5, $p < 0.001$). In contrast, in LMB-exposed groups, upon exposure to the heatwave, SRP concentrations were significantly increased compared to the non-heatwave exposed treatments (estimate of difference = 49%, $F_{1, 58}$ = 14.20, $p < 0.001$), with effects lasting to the end of the experiment. The heatwave-induced elevation of SRP concentrations in LMB exposed treatments ranged between 0.05 and 0.08 mg P/L.

After completion of the experiment, the sediment P fractionation analyses showed different P pools among different P-binding treatments, with Ctrl treatments of 430.3 ± 81.6 µg P/g DW, Bent treatments of 494.6 ± 198.1 µg P/g DW and LMB treatments of 590.9 ± 177.9 µg P/g DW (Figure 3-2 b). According to the two-way ANOVA test of different P pools, heatwave exposure resulted in a significantly lower redox sensitive P pool (BD-P) than the non-heatwave treatments (estimate of difference = 7%, $F_{1, 113} = 12.2$, $p < 0.001$). Such heatwave-induced decrease in BD-P was not observed in the LMB addition groups. Other sediment P forms showed no significant heatwave effects, but LMB addition led to significantly higher contents of metal oxide-bound P (NaOH-P, estimate of difference = 86%, $F_{2, 114} = 7.9$, $p < 0.001$) and calcium-bound P (HCl-TP, estimate of difference = 42%, $F_{2, 114} = 7.9$, $p < 0.001$).

We analyzed NH_4-N and NO_3-N + NO_2-N as indicators of N dynamics in the water columns (Figure 3-3). In all treatments NH_4-N had a slight increase in the first week from 3.54 ± 0.25 to 4.58 ± 0.29 mg N/L, and then decreased to approximately 0.55 ± 0.34 mg N/L by the end of the experiment. The NH_4-N concentrations for cores subjected to the heatwave were lower (estimate of difference = 27%, $F_{1, 249} = 117.5$, $p < 0.001$) than those not subjected to a heatwave. The NO_3-N + NO_2-N concentrations started to increase from the second week. The NO_3-N + NO_2-N concentrations for treatments subjected to the heatwave were higher compared to the non-heatwave groups in the second week, with a decline after the heatwave leading to a lower concentration relative to the non-heatwave groups at the end of the experiment (estimate of difference = 8%, $F_{1, 174} = 18.88$, $p < 0.001$). No effects of LMB/Bent additions on NH_4-N or NO_3-N + NO_2-N were detected.

Dissolved La concentrations in the LMB-exposed groups were much higher in the pre-heatwave and during the heatwave phases (estimate of difference = 91%, $F_{2, 33} = 35.1$, $p < 0.001$), and decreased through time, with an end concentration of 1.50 ± 0.30 µg La/L, which is below the Dutch La standard for surface water (= 10.1 µg La/L). A decreasing trend of La was also observed in the treatments without LMB additions (Figure SI 3-2 a), without significant differences between LMB/Bent/Ctrl treatments in the post-heatwave phase. Dissolved Fe concentrations decreased through time (Figure SI 3-2 b), with heatwave exposure leading to higher Fe concentrations during and after heatwave phases (estimate of difference = 103%, $F_{1, 68} = 9.9$, $p = 0.003$), whereas no effects from LMB/Bent treatments were detected. Of other metals including Ca, Al, Mn and S we detected no effects from heatwave or LMB/Bent treatments (Figure SI 3-2 c). Both Ca and S concentrations decreased over time with a high correlation between them (Pearson correlation coefficient = 0.84, t = 19.3, df = 105, $p < 0.001$, Figure SI 3-3).

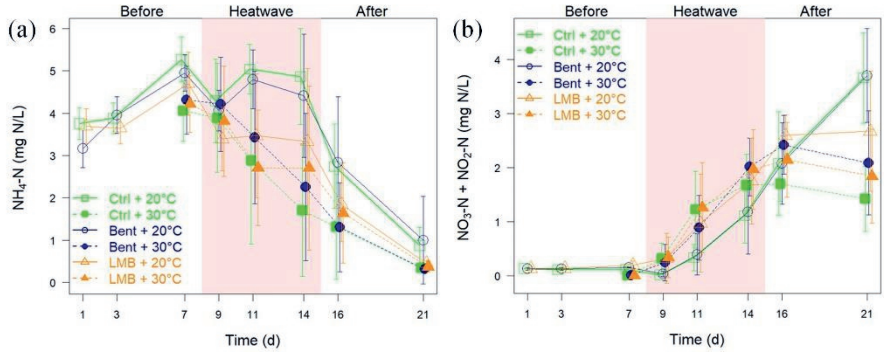

Figure 3-3. *Dynamics of (a) ammonium (NH_4-N) concentration, (b) dissolved oxidized nitrogen (DON = NO_3-N + NO_2-N) concentration in the water column. Error bars indicate the standard error. The pink box indicates exposure to different temperature regimes (20 °C in solid lines and 30 °C in dashed lines); before and after the pink box indicates all P-treatments (Ctrl, Bent and LMB) at 20 °C.*

Chapter III

3.3.3 Oxygen dynamics

In all treatments the oxygen concentrations significantly increased from 0.42 ± 0.16 to 3.01 ± 0.43 mg/L with time (Figure 3-4, $F_{1, 239} = 98.6$, $p < 0.001$), with no effects from LMB/Bent additions detected. This was reflected by the redox dynamics (Figure SI 3-4) which indicated reducing conditions in the water column of the cores in the starting phase, with the systems becoming more redox potential-positive towards the end of our experiment, irrespective of the treatments. In contrast to observations in the water column, redox potentials in the sediments were descending along the experiment period.

Our linear mixed effect model (LME), however, revealed a temporal reduction of oxygen concentrations during the heatwave in the heatwave treatments (estimate of difference = 16%, $F_{1, 34} = 4.9$, $p = 0.03$), with a maximum deviation by 0.87 mg/L at day 11. This heatwave effect disappeared after the heatwave. By the end of our experiment, the oxygen concentrations were still unsaturated (saturation concentration at 20 °C = 9.03 mg/L).

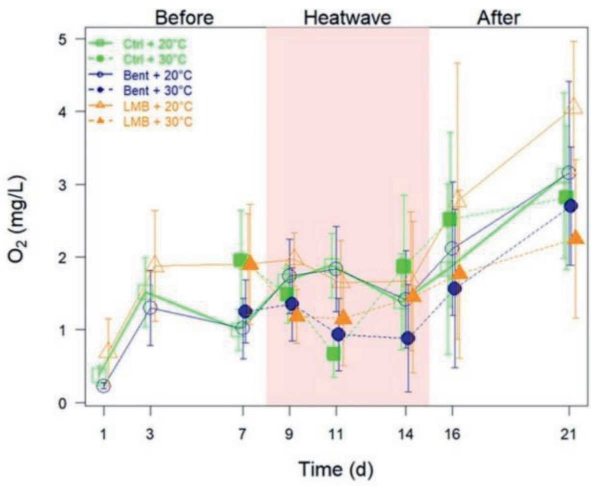

Figure 3-4. Dynamics of dissolved oxygen concentration (O_2) in the water column. Error bars indicate the standard error. The pink shading indicates exposure to different temperature regimes (20 °C in solid lines and 30 °C in dash lines); before and after the pink shading indicates all P-treatments (Ctrl, Bent and LMB) at 20 °C.

3.3.4 Dissolved greenhouse gasses

We measured concentrations of dissolved greenhouse gasses CO_2, CH_4 and N_2O, as a proxy of their emission potential. Among the three gasses, CO_2 concentrations were the highest, followed by CH_4 and N_2O, with respectively a factor 10 and 100 lower levels. All three gas concentrations in the water column of the cores changed significantly over time, with significant increase during the heatwave phase (Figure 3-5 a for CO_2, estimate of difference = 15%, $F_{1,243} = 27.9$, $p < 0.001$; Figure 3-5 b for CH_4, estimate of difference = 21%, $F_{1,243} = 20.4$, $p < 0.001$; Figure 3-5 c for N_2O, estimate of difference = 536%, $F_{1,243} = 116.6$, $p < 0.001$), equaling an increased CO_2-equivalent by 106%. No effects from LMB or Bent treatments on the greenhouse gas dynamics were detected.

CO_2 concentrations decreased from $7.3 \pm 0.3 \times 10^3$ to $6.4 \pm 0.3 \times 10^3$ ppm in the before-heatwave phase, whereas during the heatwave phase in the heatwave-exposed treatments the CO_2 concentrations rose up to $8.4 \pm 0.5 \times 10^3$ ppm. In the post-heatwave phase, CO_2 concentrations in the heatwave groups dropped to the same levels as the non-heatwave treatments, resulting in an average of $6.0 \pm 0.5 \times 10^3$ ppm by the end of the experiment.

CH_4 concentrations dropped from 391.98 ± 123.98 ppm to 62.70 ± 45.74 ppm in the pre-heatwave phase. During the heatwave phase, the heatwave-exposed cores were observed with higher CH_4 concentrations (mean = 47.38 ± 3.21 ppm) than the non-heatwave treatments (mean = 26.69 ± 1.87 ppm). However, in the post-heatwave phase (days 15 – 21), the CH_4 concentrations in the non-heatwave treatments surpassed that in the heatwave-exposed groups and reached a high average level of the same magnitude as that measured in the beginning of the experiment (mean = 174.25 ± 57.39 ppm), whereas the CH_4 concentrations in the heatwave-exposed cores had a relatively low-end concentration (mean = 23.40 ± 5.84 ppm).

N_2O concentrations stayed at a rather low level (mean = 0.15 ± 0.02 ppm) in the before-heatwave phase. During the heatwave phase, N_2O emissions started to increase in all treatments, with N_2O concentrations in heatwave-exposed cores increasing at a much higher rate than in non-heatwave groups. In the period after the heatwave (days 15-21) the non-heatwave groups showed a relatively stable N_2O concentration (mean = 15.16 ± 2.52 ppm) until the end of the experiment. N_2O concentrations in the heatwave groups increased to 72.84 ± 26.53 ppm during the heatwave, but in the post-heatwave phase, the concentrations dropped to 38.10 ± 19.14 ppm, which is, however, a still higher level than the observed N_2O emission in the non-heatwave groups.

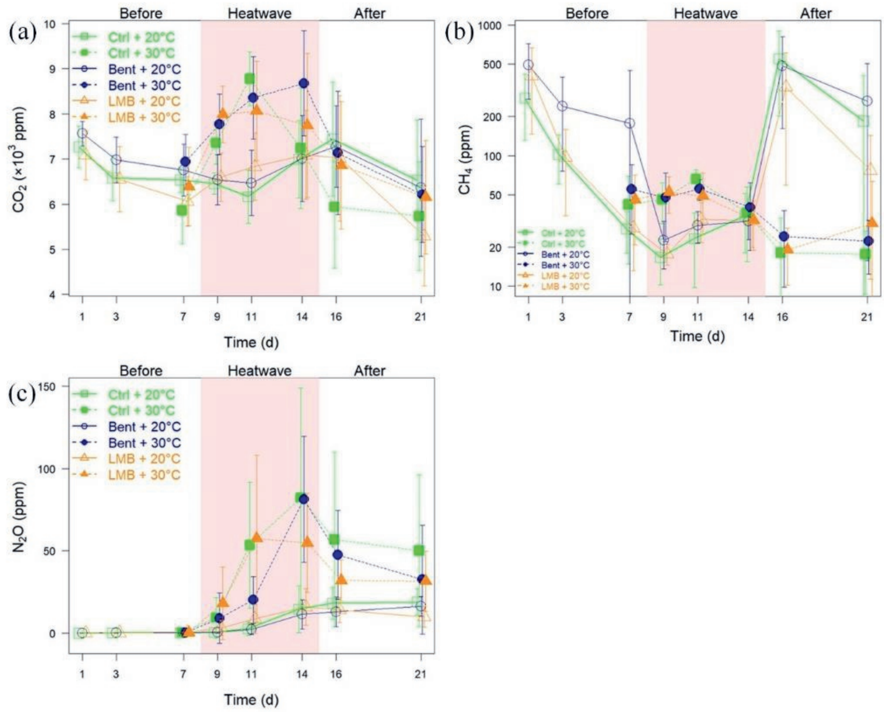

Figure 3-5. *Dynamics of (a) dissolved carbon dioxide (CO_2), (b) dissolved methane (CH_4) and (c) dissolved nitrous oxide (N_2O). Error bars indicate the standard error. The pink shading indicates exposure to different temperature regimes (20 °C in solid lines and 30 °C in dashed lines); before and after the pink shading indicates all P-treatments (Ctrl, Bent and LMB) at 20 °C.*

3.4 Discussion

Using a full-factorial design, we investigated the combined effects of phosphorus control by lanthanum-modified bentonite (LMB) and exposure to an extreme heatwave event on the biogeochemistry at the sediment-water interface and the resulting fluxes between sediment and water. For shallow waters, one of the most abundant water types (Verpoorter et al., 2014), such fluxes between water and sediment play an important role in the phosphorus, nitrogen and carbon cycling. Despite the observation that LMB was able to reduce phosphorus levels in the water column up to 91% in comparison to the control groups by the end of our experiment, LMB effectiveness was hampered upon exposure to a heatwave, resulting in increasing P concentrations with 11%, persisting until the end of the experiment. There was no significant effect of LMB addition on nitrogen dynamics. Under low oxygen conditions (O_2 < 4.8 mg/L in all treatments), nitrification was stimulated by increased oxygen and temperature, resulting in an accumulation of nitrate + nitrite and nitrous oxide. In addition, our results suggest that GHG dynamics were impacted upon heatwave exposure, but LMB did not affect this pattern.

3.4.1 The impact of heatwaves on phosphorus and nitrogen dynamics: eutrophic vs oligotrophic sediments

The continuous P-release in controls, leading to concentrations as high as 1.2 mg P/L towards the end of our experiment, could be explained by the large pool of bioavailable phosphorus in sediment (see Figure 3-2 b). This pool of bioavailable phosphorus consists of phosphorus in the pore water, redox-sensitive P (BD-P), and organic P which can be mobilized under anoxic conditions (Cavalcante et al., 2018). LMB strongly reduced phosphorus concentrations in the water column and kept those persistently low until the end of our experiment, which indicates that LMB both stripped the water column P and hampered sediment P release, as was expected from its well-documented performance (D. Copetti et al., 2016). The bentonite-only treatment did not have any impact on P dynamics relative to our controls, which further underpins that the LMB effect was a result of the P inactivation and not caused by depositing a thin clay layer on top of the sediment. Some studies reported a P abatement capacity of unmodified bentonite (Zamparas et al., 2012), but the bentonite used in our study had no P-binding capacity (Mucci et al., 2018) and the layer was evidently too thin to act as a passive barrier (Kim et al., 2007).

When we exposed the LMB-treated sediments to a one-week heatwave, phosphorus concentrations increased by 0.08 ± 0.03 mg P/L (the overlying water volume = 863 ± 21 mL) in the water column at the end of our three-week experiment (see Figure 3-2 a), equaling an 11% increase compared to the non-heatwave exposed group. In an earlier study, however, higher P-adsorption capacity by LMB was observed under increased temperature due to the enlargement of pore size and/or activation of the bentonite surface (Zamparas et al., 2012). It is noteworthy that Zamparas et al. (2012) used a rather simple environment (3 hours of experimental time, heavy mixing of the slurry with solution), whereas the static sediment in our experiment is a much more complex matrix with biogeochemical processes playing an important role in determining the LMB capacity. Earlier model simulations indicate that concentrations of 0.05 mg P/L, similar to the increase in SRP concentrations observed at the end of this experiment, could cause systems to shift from transparent to turbid states (Janse et al., 2008). However, this has not been observed in whole lakes that have undergone LMB additions; for instance, the LMB-treated shallow Lake Barensee in Germany did not develop any blooms during heatwaves (Epe et al., 2017).

The discrepancy between our lab study and the field observations might be caused by a larger dilution effect in lakes compared to the small water volumes in the cores, by not all binding sites of LMB being rapidly available, by a possible under-dosing in our experimental treatments, or erratic sediment-water transport through ebullitive processes in our cores. The P inactivation by LMB is a kinetic process, which means that it takes a certain time before all binding sites are occupied (Dithmer et al., 2016a), especially in the presence of high DOC (Lurling et al., 2014) as was the case in our system. However, despite the notion that binding sites were potentially not all occupied, LMB was only partially able to counteract the temperature-enhanced P release in the week after the heatwave exposure, an observation that has been confirmed by an in-situ months-long enclosure experiment (Zhan et al., 2022). Furthermore, we may have potentially under-dosed LMB our experimental treatments, as we did not include the BD-NRP fraction which may also contain organic P (Jan et al., 2015) in our dose estimates. The microbial breakdown of organic matter results in release of organic phosphate to pore waters and can be considered one of the most important sources of phosphate (Föllmi, 1996). As organic matter breakdown is expected to be enhanced by increased temperature (Gudasz et al., 2010a), part of the liberated P is taken up by the decomposing bacteria, and part will enter the overlying water column. In addition, the ebullition that transports sediment-P might be enhanced under heatwave conditions (Aben et al., 2017). Therefore, inclusion of the BD-NRP and targeting also deeper layers of the sediment in dose estimations are highly recommended for lake managers applying LMB as a eutrophication control measure, especially to counteract the heatwave impacts.

Our results showed that the rates in the N-cycle processes were significantly changed upon exposure to a heatwave, irrespective of treatment. At the start of our experiment, the sediment incubations were anoxic, with NH_4-N as the dominant nitrogen form accumulating in the overlying water. As dissolved oxygen concentrations rose over time, nitrification became a more dominant process, decreasing ammonium accumulation and leading to increased oxidized nitrogen concentrations (Figure 3-3). Rysgaard et al. (1994) demonstrated that nitrification is stimulated by increasing O_2 in the O_2 range of 0-9.6 mg/L, which was the case in our experiment. Upon exposure to a heatwave (30 °C), the oxidation of NH_4-N was accelerated, indicating a positive response of nitrification to increasing temperature. Thamdrup and Fleischer (1998) demonstrated that the optimum temperature for nitrification in warm temperate sediment was near 40 °C. The decline of oxidized nitrogen concentrations (NO_3-N + NO_2-N) in the heatwave groups during the post-heatwave phase could be associated with the depletion of ammonium. Nitrification can operate at low ammonium concentration but at low rates (Dodds and Jones, 1987).

Moreover, denitrification is expected to be stimulated with increasing temperature (Veraart et al., 2011). Though we did not measure denitrification directly, denitrification was plausibly leading to an increased consumption of NO_3-N and NO_2-N, therefore decreasing N-release into the overlying water. The LMB treatment showed no effect on N-dynamics, which supports our conclusion that LMB acted as a chemical binding compound of DRP rather than a physical barrier for nutrient release from the sediments. A recent study by Zeller and Alperin (2021), however, showed that LMB can act as NH_4-N source with an increase in NH_4-N concentration by 10 to 275%. This difference between our results and Zeller and Alperin (2021) might be attributed to the fact that their LMB dose was more than double of ours (0.029 compared to 0.013 g LMB/cm^2 sediment) and the overlying water volume was much smaller in their experiment (150 mL compared to 863 mL), resulting in higher LMB concentrations.

3.4.2 Heatwave effects on greenhouse gas emissions

In our experimental system, regardless of the treatments, concentrations of greenhouse gasses (GHG) initially decreased (CO_2 and CH_4), or were close to zero (N_2O). Earlier studies on freshwater ecosystems demonstrate increased GHG emissions under warming scenarios (Aben et al., 2017; Bartosiewicz et al., 2016; Bergen et al., 2019). In our experiment, exposure to a heatwave did lead to increased concentrations of CO_2 and N_2O. For CH_4, however, after an initial short-lived increase during the heatwave itself, the heatwave-exposed treatments had lower CH_4 concentrations relative to the non-heatwave exposed group towards the end of the experiments (Figure 3-5). A potential explanation for this might be that on the longer term, substrate limitation for methanogens (Duc et al., 2010) may play a stronger role in the heatwave exposed cultures, potentially due to the short-lived increase in methane production during the heatwave. Note that our sediment incubation was conducted under dark condition, different patterns might emerge in real lakes in the presence of primary producers, which points to the importance of validating our results with field observations.

Previous studies on shallow aquatic systems demonstrated that greenhouse gas emissions are higher in eutrophic systems than in more oligotrophic systems (Davidson et al., 2015a; Peacock et al., 2019). We therefore hypothesized that LMB treatments, by reducing nutrient availability, would inhibit bacteria growth and subsequently reduce GHG productions. In disagreement with our hypothesis, our results showed that addition of LMB, although effective in blocking sediment P-release, did not affect the GHG emissions from the sediments. Previous studies (Dithmer et al., 2016a) demonstrated that LMB needs time (up to months) to bind all available P in sediments. Another potential cause may be that our doses applied theoretically can only target top 3.3 cm sediment, which is about 20-25% of the sediment column, leaving ample space for bacterial activity and methanogenesis in deeper layers. Under warmer conditions the sediment layers available for bacterial activity and methanogenesis may be located deeper, because anoxia is expected to be stronger (Jankowski et al., 2006), associated with enhanced methanogenesis (Schulz et al., 1997). Nonetheless, our results indicate that LMB might not be an effective method in controlling GHG emissions, at least in the short term. For reduction of carbon associated GHG emissions (CH_4 and CO_2) measures that directly target the reduction of organic matter inputs into sediments, such as an improvement of water treatment in the catchment (Jones et al., 2016) and control of bank soil erosion (Rickson, 2014), may be more favorable.

N_2O is typically derived during nitrification of NH_4-N under oxic conditions and from the coupled nitrification-denitrification reactions under suboxic conditions, which explains the increase in N_2O coinciding with the NH_4-N decrease. Both nitrification and denitrification are strongly temperature-dependent (de Klein et al., 2017; Veraart et al., 2011). Heatwave treatments in our experiment had higher N_2O concentrations, coinciding with a drop in O_2 concentrations, which further indicates that freshwater N_2O emissions can be strongly temperature dependent and can be boosted under climate change (Parton et al., 2001; Veraart et al., 2011). The decline in N_2O concentrations in the post-heatwave phase in heatwave-treated groups could be because NH_4-N for nitrification became limiting, while denitrification in deeper sediment layers increased in efficiency, reducing the N_2O:N_2 ratio in the final product (Leemput et al., 2011). Conventional biological denitrification requires low oxygen concentration less than 0.2 mg/L (Seitzinger et al., 2006). Even when the water column was oxygenated, these concentrations still occurred in anoxic microsites in the sediments of our experimental cores (Figure SI 3-4). In addition, aerobic denitrification has also been observed in freshwater sediments (Lv et al., 2017; Rysgaard et al., 1994; Trevors and Starodub, 1987) as well as in coastal sediments (Marchant et al., 2017). Moreover, the pathway of dissimilatory nitrate reduction to ammonium (DNRA) could also contribute to part of the production of N_2O (Sun et al., 2016). A ^{15}N tracing technique (Müller et al., 2014) is needed to determine which pathway is mainly responsible for the production of N_2O.

3.5 Conclusions and recommendations

Our sediment incubation experiment indicates that the rates of biogeochemical processes can be significantly accelerated upon heatwave exposure, resulting in a change in fluxes of nutrient and greenhouse gasses between sediment and water column. The current efforts in eutrophication control will face more challenges under future climate scenario with more frequent and intense extreme events as predicted by the IPCC.

The effectiveness of widely established eutrophication control measure LMB was, at least temporarily, impaired upon exposure to an extreme heatwave, with an increase in concentration of 0.08 ± 0.03 mg P/L with an overlying water volume of 863 ± 21 mL, equaling 50% increase relative to non-heatwave treatments. Although the effect of the heatwave on P-release of LMB treated sediments persisted until the end of the experiment, long term studies should address whether the P-concentrations eventually return to lower pre-heatwave levels. In addition, further research is needed to explore whether increased LMB dosage can mitigate the negative impacts of a heatwave. Nonetheless, our study does suggest that our current abatement efforts may be hampered under climate change, which calls for consideration of more climate-robust measures, such as through revisiting dose-response relationships in the development of rehabilitation plans.

Exposure to a heatwave resulted in higher dissolved GHG concentrations with an increased CO_2-equivalent by 106%, showing potential for increased emissions relative to non-heatwave exposed treatments. Our experiment showed that LMB addition did not lead to lower GHG concentrations, which implies that inhibiting microbial GHG production by creating a P-limiting environment through LMB is ineffective. Thus, alternative strategies directly targeting reduction in organic load such as sludge removal or erosion control should be explored to effectively mitigate greenhouse gas emission.

Acknowledgement

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Supplementary information

CHAPTER IV

Chapter IV:

Towards climate-robust water quality management: testing the efficacy of different eutrophication control measures during a heatwave in an urban canal

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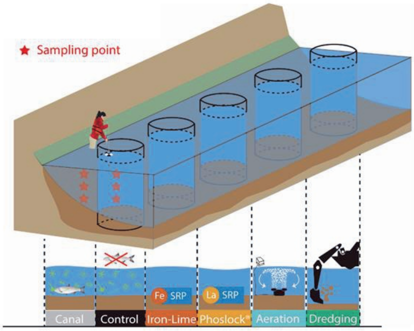

Abstract:

Harmful algal blooms are symptomatic of eutrophication and lead to deterioration of water quality and ecosystem services. Extreme climatic events could enhance eutrophication resulting in more severe nuisance algal blooms, while they also may hamper current restoration efforts aimed to reduce nutrient loads. Evaluation of restoration measures on their efficacy under climate change is essential for effective water management. We conducted a two-month mesocosm experiment in a hypertrophic urban canal focusing on the reduction of sediment phosphorus (P)-release. We tested the efficacy of four interventions, measuring phytoplankton biomass, nutrients in water and sediment. The measures included sediment dredging, water column aeration and application of P-sorbents (lanthanum-modified bentonite - Phoslock® and iron-lime sludge, a by-product from drinking water production). An extreme heatwave (with the highest daily maximum air temperature up to 40.7 °C) was recorded in the middle of our experiment. This extreme heatwave was used for the evaluation of heatwave-induced impacts. Dredging and lanthanum modified bentonite exhibited the largest efficacy in reducing phytoplankton and cyanobacteria biomass and improving water clarity, followed by iron-lime sludge, whereas aeration did not show an effect. The heatwave negatively impacted all four measures, with increased nutrient releases and consequently increased phytoplankton biomass and decreased water clarity compared to the pre-heatwave phase. We propose a conceptual model suggesting that the heatwave locks nutrients within the biological P loop, which is the exchange between labile P and organic P, while the P fraction in the chemical P loop will be decreased. As a consequence, the efficacy of chemical agents targeting P-reduction by chemical binding will be hampered by heatwaves. Our study indicates that current restoration measures might be challenged in a future with more frequent and intense heatwaves.

4.1 Introduction

Eutrophication, defined by over-enrichment of nutrients resulting in increased primary production, is identified as one of the key drivers of water quality deterioration in inland waters across the globe (Carpenter et al., 1999). Eutrophication of a water body can hamper provisioning of ecosystem services by a series of symptoms, e.g., accumulation of phytoplankton biomass in the water column, malodor, and oxygen depletion resulting in fish kill (Smith and Schindler, 2009). Furthermore, some cyanobacterial species can produce toxins, which pose a direct health risk to animals and humans (Chorus et al., 2000). From previous experimental and modeling studies it has been well-established that through reduction of nutrient loading degraded systems can be restored to a clear water state (Janse, 2005; Waajen, 2017).

Nutrient loading (nitrogen and phosphorus) can originate from external sources in the watershed as well as from internal lake sediments. Lakes sediments are often enriched with nutrients after years of accumulation and under certain conditions these sediment nutrients will be released into the water column (Søndergaard et al., 2013). While external loading can be controlled through e.g., watershed management and water treatment, in-lake measures that target sediment nutrient release are becoming inevitable as many studies have demonstrated that a sole reduction of external loading without control of internal loading is not efficient (Lürling and Mucci, 2020; Spears et al., 2016).

While external load control will mostly reduce both nitrogen (N) and phosphorus (P), in-lake nutrient reduction often focuses on P, as P can be made limiting more easily than N (Schindler et al., 2008). It has increasingly been accepted that drastic reduction of P release from sediments is critical for long-lasting eutrophication control (Carpenter, 2008). Bio-availabilities of phosphorus differ among various sediment P forms (Cavalcante et al., 2018). In general, the mobile P pool is comprised of forms that are easily available, such as P dissolved in pore water (measured as Soluble Reactive Phosphorus, i.e., SRP), P loosely adsorbed to FeOOH and $CaCO_3$ surfaces, P that can become available rapidly under anoxic conditions (i.e., redox-sensitive P bound to oxidized Iron and Manganese), and P that will gradually become available due to mineralization of organic matter (Hupfer et al., 2009). P adsorbed to aluminum (Al) and Iron (Fe) oxy/hydroxides and P in Al and Fe (hydroxy) phosphates will only become available when phosphate is exchanged with hydroxyl ions at high pH (Boström, 1984). Acid-soluble and refractory organic P, P in calcium-phosphate minerals, and non-extractable mineral P are viewed as non-available (Hupfer et al., 2009).

In this study, we investigated four promising measures for their potential in mitigating internal eutrophication, including lanthanum-modified bentonite (LMB) and removal of the nutrient-rich top soil (dredging), as well as aeration and iron-lime sludge amendment. The four restoration measures have variable modes of actions to control eutrophication. Lanthanum-modified bentonite (LMB, also called Phoslock®), a well-established eutrophication control technique that has been applied to over 200 water bodies across a wide geographic distribution (Diego Copetti et al., 2016), is developed to immobilize P by forming a La-P complex. This complex has proven to be poorly soluble under anoxic conditions and under a wide range of pH (6-10 tested in Kang et al. 2021; Mucci et al. 2018). This compound has been compared with other P adsorbents with respect to their P adsorption capacity and often performs better (Lin et al., 2015; Mucci et al., 2018). Some studies have evaluated it against dredging, a commonly used measure that removes the organic- and nutrient-rich top sediment layer. The results are not conclusive, as one study observed that LMB was less effective in removing P compared to dredging (Lürling and Faassen, 2012), whereas another study found that LMB was more effective than dredging (Yin et al., 2021). However, dredging in general is more expensive than the application of LMB (Lürling and Faassen, 2012). Aeration, as a measure of artificial oxygenation of the water column, aims at enhancing the natural capacity of the system in binding phosphorus through reduction in the concentrations of reduced forms of iron and manganese (Cowell et al., 1987; Yuan et al., 2020). Iron-lime sludge, a by-product from drinking water production, has P-adsorption capacity through the presence of iron (Fe) and calcium (Ca) (Babin et al., 1994; Golterman, 1997; Smolders et al., 2008). P bound to oxidized iron is redox-sensitive and can be remobilized under anoxic condition (Gächter and Müller, 2003), and P bound to reduced iron is suffering from sulfide which binds more strongly to reduced iron than to P (Geurts et al., 2010). The Ca in the iron sludge may bind P under elevated pH. These Ca-P minerals are stable under most natural conditions, but P bound by Ca can be released under acidic conditions (Huang et al., 2005). As a waste product from water treatment this sludge is economically favorable compared to dredging and lanthanum modified bentonite (LMB).

To compare the efficacy of these four measures in a near-realistic environment, we conducted a two-month mesocosm experiment in a hypertrophic urban canal. Such mesocosm experimental settings have proven to be a valuable approach for testing the efficacy of various ecological restoration measures in urban waterways in previous studies (Waajen et al., 2017). Mesocosm studies represent a near-realistic level of environmental complexity while allowing for a replicated design with well-defined treatments. Shallow water bodies are the most abundant freshwater ecosystems (Verpoorter et al., 2014) and provide important ecological and societal services including recreation, water and nutrients retention, microclimate regulation and biodiversity reservoir (Biggs et al., 2017; Bolund and Hunhammar, 1999). Urban canals and ponds are examples of such shallow freshwater ecosystems that, due to their close proximity to humans, are both valuable for ecosystem service provisioning as well as exposed to high levels of anthropogenic stressors (Noble and Hassall, 2015; S. Teurlincx et al., 2019). They are often nutrient-rich and regularly suffering from blooms of nuisance algae (Waajen et al., 2014).

The main objectives of this study are: (i) comparing the efficacy of four intervention measures in reducing nutrient releases and controlling eutrophication; (ii) evaluating the heatwave impacts on the efficacy of these four intervention measures; (iii) proposing a conceptual model that provides routes through which measures to mitigate sediment phosphorus release might be affected by heatwaves. We propose the following hypotheses regarding the efficacy of the four measures: Hypothesis 1) Dredging and lanthanum modified bentonite (LMB), via reducing mobile P effluxes from the sediments, will be the most effective measures in reducing phytoplankton biomass; Hypothesis 2) Iron-lime sludge will be less effective in reducing sediment P release because it is both redox-sensitive and pH-sensitive; Hypothesis 3) Aeration -although widely used- is not effective for P-reduction as in such a shallow system air pumping can lead to enhanced sediment resuspension promoting nutrient release (Visser et al., 2016).

In future climate conditions the efficacy of the current restoration measures might be hampered by extreme climate events posing a sudden and severe disturbance to lakes (Stockwell et al., 2020; Woolway et al., 2020). For instance, lake heatwaves, defined as periods of extremely warm surface water temperature, are anticipated to increase both in frequency and intensity in future (Woolway et al., 2021). The heatwave impacts are expected to be especially relevant to shallow water systems as their temperatures are highly related to the air temperature (Mooij et al., 2008a). Release of organic P can be enhanced with increasing temperatures owing to accelerated decomposition rates, whereas the redox sensitive P will be rapidly freed under anoxia. Such conditions, higher temperatures, and stronger bottom water anoxia (Jankowski et al., 2006) are consequences of climate change. In addition, warming is also seen as an important factor that promotes algal blooms (Paerl and Huisman, 2008) and therewith could lead to elevated pH in surface waters. The climate impact-related factors temperature, redox, and pH influence phosphate diagenesis and thus how much P can become available (Holtan et al., 1988). Less evidence, however, is collected from field studies on the impact of heatwaves on the effectiveness of restoration measures. In the middle of our two months mesocosm experiment we recorded an extreme heatwave, which provided the opportunity for evaluation of heatwave impacts on the efficacy of the four restoration measures.

We hypothesize that this heatwave, through its impacts on the oxygen content of the water body (Jeppesen et al., 2021), could hamper the efficacy of iron-lime sludge (Hypothesis 4). As a previous short-term laboratory experiment demonstrated that the efficacy of Lanthanum modified bentonite can be hampered upon exposure to a heatwave (Zhan et al., 2021a), we hypothesize that the induced P-release will compromise the efficacy of Lanthanum modified bentonite (Hypothesis 5). Since dredging is designed to remove the nutrient-rich top layer of the sediments, we expect no effect of the heatwave on the efficacy of the dredging treatments (Hypothesis 6).

4.2 Methods and materials

4.2.1 Experimental set-up

A mesocosm experiment was carried out in a shallow urban canal (max depth ca 3 m) situated in the South of the Netherlands in the municipality of Geertruidenberg (coordinates in DMS: 51°42'12.0"N, 4°51'40.8"E). The canal has a stable water level owing to regulation of inlet waters (full capacity = 0.06 m^3/s) by local water managers. Drought is therefore not considered a problem for this system throughout the year. The sediments at this study site were sampled and analyzed in September of 2018 (one year prior to the experiment) for determination of the chemical adsorbent dosages applied in the mesocosm experiment. The P fractions in the top 20 cm sediments (communicating depth) were determined by a sequential P-fractionation analysis (Hupfer et al., 2009; Psenner et al., 1984), where the following fractions were determined: the P dissolved in the pore water (SRP), the redox-sensitive bound P (bound to Iron or Manganese), the organic P, the acidity-sensitive P (bound to aluminum or Calcium) and the refractory P.

The mesocosm experiment was carried out from 25-06-2019 to 19-09-2019. In total, 20 mesocosms (clear Perspex cylinders with height: 2.25 m; diameter: 1.05 m) were exposed to four measures and one control treatment, yielding 5 treatments · 4 replicates. To allow for air-water interactions and sediment-water interactions, the mesocosms were open at the top and bottom, see Fig. 1a. The treatments were assigned randomly to the mesocosms to account for the heterogeneity of sediment and water conditions. The mesocosms were inserted ca. 30 cm deep in the sediment, with an overlaying water layer of ca. 1.6 m. The four measures tested include: iron-lime sludge (drinking water production by-products), lanthanum modified bentonite

(LMB), aeration and dredging. The doses and/or application of these four measures are introduced in section 4.2.2 below.

At the mid of our experiment (22th of July – 27th of July), an extreme heatwave event –maximum air temperature 25.0 °C or higher– was recorded by Royal Netherlands Meteorological Institute (KNMI, https://www.knmi.nl/nederland-nu/klimatologie/lijsten/hittegolven). This heatwave had 4 tropical days (maximum temperature 30.0 °C or higher) with a maximum of 40.7 °C (from the nearby weather station Gilze-Rijen, https://www.knmi.nl/nederland-nu/klimatologie/daggegevens), which was the highest recorded heatwave temperature since 1901 (the average Dutch summer temperature ≈ 21.0 ºC). During each sampling event we monitored the water temperature, recording a time series of water temperature dynamics at a time interval of 2-3 weeks. In addition to the measurements, we ran FLake (http://www.flake.igb-berlin.de/), an open-resource model, specifically designed to evaluate climate scenario's influences on inland waters and numerically predict water temperature and mixing regime (Shatwell et al., 2019). This process-based model has a high level of parametrization, is well validated for inland waters and thus allowed us to simulate water temperature dynamics on a daily basis. Details on how we configured the FLake model for the Geertruidenberg canal system can be found in the supplemental information section SI 4.1. All the model parameters are summarized in Table SI 4-1. Based on the measured and simulated temperature dynamics (Figure 4-1 b), we incorporated the sampling event prior (12th of July) and post heatwave (7th of August) in our analysis of the impacts of an extreme heatwave. In such a way we included both the rising and falling limb of the extreme heatwave. We refer to this period as the 'heatwave phase' from hereon. Note that this heatwave phase differs from the definition of heatwave period by KNMI, which is defined as a succession of at least 5 summer days (maximum air temperature 25.0 °C or higher) in De Bilt (the headquarters of KNMI), of which at least three are tropical (maximum air temperature 30.0 °C or higher).

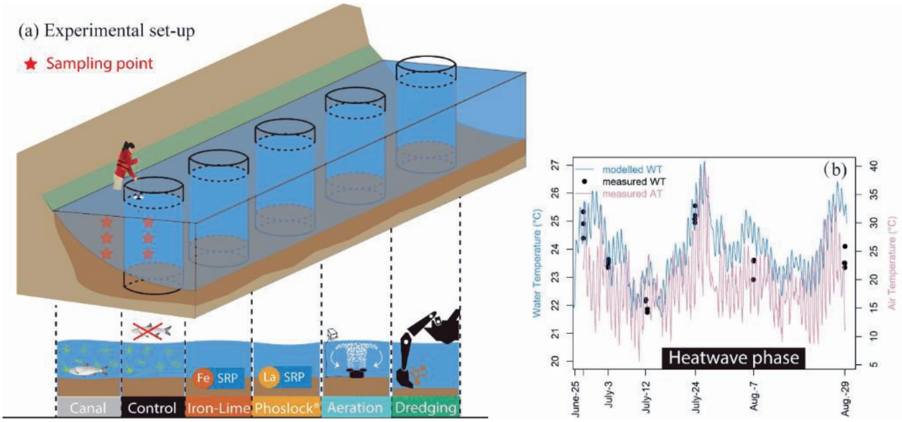

Figure 4-1. *(a) Experimental set-up; (b) Dynamics of monitored air temperature (AT; in purple line) and modelled water temperature (WT; in blue line) and measured water temperature (WT; in black points). As we observed no difference in the water temperature in the mesocosms and the surrounding canal water, we proceeded with displaying the mean of the measured temperatures.*

4.2.2 Restoration treatments

The sediment was characterized as fluffy with a density of 1.21 ± 0.04 kg/L. The sediment P fractionation analysis showed that the sediment is nutrient-rich. This analysis showed that the P pool available for growth of primary producers (the sum of pore-water P, redox-sensitive P, and organic P) was 234.15 ± 9.88 μg P/g. When taking the acidity-sensitive P that becomes bio-available at very high or low pH, the mobile P averages to 291.32 ± 10.43 μg P/g. The amount of P in pore water was marginal. The redox sensitive P and organic P were the most abundant P species in our sediments.

<u>Lanthanum modified bentonite</u> (also called Phoslock®): The dosage of lanthanum modified bentonite (LMB) was based on the amount of potentially releasable P (=291.32 ± 10.43 μg P/g, including pore-water P, redox-sensitive P, organic P, and pH-sensitive P) in the top 5 cm layer of the sediment (as in Lürling et al. 2017c; Yin et al. 2021), and weight ratio of LMB:P of 230:1 (as based on Lürling et al. 2014). The water column total P (= SRP + particulate P) was assumed to be negligible compared to the sediment P pools and thus not included into the determination of LMB dose. As such, we added 1.35 kg of LMB as a slurry to the bottom of each of the four mesocosms using a 1.5 m tube in a rotating motion in two doses on 25-06-

2019 (by 89% = 1.2 kg LMB) and 26-06-2019 (by the remaining 11% = 0.15 kg LMB), forming a layer of approximately 1 cm thick of LMB on the top of sediments.

Iron-lime sludge: On 25-06-2019, 13.4 kg of iron-lime sludge, collected from drinking water treatment plant Veghel, was applied as a slurry via a 1.5 m tube onto the sediments of each of the four mesocosms, resulting in a layer of approximately 1 cm thick of sludge. Measured concentrations of various elements in the iron-lime sludge can be found in supplemental Table SI 4-2. Our dose resulted in an approximate addition of 495.4 g of Calcium, 215.0 g of Iron, 21.8 g of P, and 1.1 g of Sulphur to the treated mesocosms. The P present in the iron-lime sludge has proven to not hamper eutrophication control in previous experiments (Remke et al., 2018), owing to its favorable Fe/P and Ca/P ratios. Note that phosphorus adsorption capacity of this material is not only dependent on sludge composition (i.e., Ca/Fe, Fe/S) but also on other environmental conditions including redox conditions and pH levels, resulting in a contextual dose-response relationship. As a compromise, we followed the dosage that has proven to be successful in locking P in previous experiments implemented in two eutrophic Dutch ponds (Remke et al., 2018).

Dredging: On 25-06-2019, for dredging treatments ca. 30 cm of the silt layer of the sediments were mechanically removed with an excavator on a pontoon, before four mesocosms were pushed into the dredged sediments. This method was applied in another mesocosm experiment testing the effect of dredging and Lanthanum modified bentonite in controlling phytoplankton nuisance in a hypertrophic pond (Lürling et al., 2017c). Removal of top sediments resulted in the top edge of the four dredged mesocosms being slightly lower relative to the non-dredged mesocosms (< 30cm). At all times during the experiment, there was sufficient headspace in the dredged mesocosms to prevent exchange with the surrounding canal water.

Aeration: Aeration tiles (AIRDisc 250®) with a fixed airflow of 250 L h^{-1} were placed on the sediment and turned on at 26-06-2019, enriching the water column with pressurized air. The aeration rate was set to allow for sufficient oxygenation whilst not creating air bubbles which can negatively impact zooplankton (Cowell et al., 1987).

4.2.3 Water & sediment Sampling

We sampled each mesocosm and the canal water 6-7 times at a time interval of 2-3 weeks over the experimental period for a suite of water quality parameters, including analyses of phytoplankton (green algae, diatoms and cyanobacteria), macronutrients (phosphorus and nitrogen), water transparency (Secchi depth) and metals (manganese-Mn, aluminum-Al, lanthanum-La, iron-Fe). All sampling events were conducted at midday between 12pm and 14pm, such that our oxygen results did not reflect differences in primary productivity taking place over the course of the day, which can be substantial in a hypertrophic system such as ours. A sample of the top 50 cm of the water layer was taken for measurements of chlorophyll-a fluorescence using a Phyto-PAM fluorometer (Walz, Effeltrich, Germany), as a proxy of the phytoplankton biomass (Lürling et al., 2018), with the chlorophyll-a fluorescence of cyanobacteria, green algae and diatoms differentiated by blue, green and brown signals in emission lights, respectively (Cabrerizo et al., 2020b). After water samples were filtered over prewashed GF/F filters (Whatman, Maidstone, U.K.), dissolved phosphorus (SRP), nitrite (NO_2-N), nitrate (NO_3-N) and ammonium (NH_4-N) were determined in the filtrate using a QuAAtro39 Auto-Analyzer (SEAL Analytical Ltd., Southampton, U.K.). The filters containing the residue were further used for determination of particulate phosphorus (PP) using a digestion step. In short, we incinerated the filters at 550 ºC for 20 minutes, after which the filters were autoclaved with a 2% potassium persulfate solution at 121 ºC for 30 minutes. The resulting solutions were analyzed for PP concentrations using a QuAAtro39 Auto-Analyzer (SEAL Analytical Ltd., Southampton, U.K.). The SRP and PP added up to be the total phosphorus (TP). The transparency of the water column was determined on site with a Secchi disc. We used inductively coupled plasma - optical emission spectrometry (ICP-OES, Thermo ICAP 6500-duo ICP) for measurement of total filterable metals, including Ca, Al, La, Fe. In addition, we measured depth profiles of dissolved oxygen (DO), pH using a Hydrolab multi-sensor probe (Hydrolab DS 5, Ott Hydromet, Colorado, United States). To control for the impact of mesocosms on the water quality, all of the above measurements were also carried out in the canal outside of the mesocosms (ca. 1 m distance).

In addition, an extra sampling of the pore water of the top 10-15 cm sediment was done using a Rhizon® soil sampler at the end of the mesocosm experiment (19-09-2019). Porewater samples were analyzed using the same method and instruments described above for determination of the water concentrations of dissolved nutrients and metal elements. In addition, to gain further insight into the effect of our treatments on microbial activity and their greenhouse gas production, we followed a headspace equilibration technique (Halbedel, 2015; Magen et al., 2014) for determination of concentrations of dissolved carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) in the water column. GC-FID (Gas Chromatography-Flame Ionization Detection) was used for determining the headspace gas concentrations, and the gas concentrations in the water column were calculated based on the equilibrium

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relationship between water column and headspace (Zhan et al., 2021a). Note that in this approach the gas fluxes through bubbling are not included.

4.2.4 Statistical analysis

We used a multivariate analysis method, i.e., principal response curve (PRC; Paul J Van den Brink and Braak, 1999), to visualize the overall responses (principle response) in different restoration treatments over time. In this approach, a principle variable for each restoration treatment was produced summarizing the variation in a set of response variables including Secchi depth, dissolved oxygen (DO), pH, total phosphorus (TP) and dissolved phosphorus (SRP), total chlorophyll-a (sum of chlorophyll-a of cyanobacteria, green algae, and diatoms) and cyanobacterial chlorophyll-a, which are the most relevant response variables regarding our research questions. The weights of individual response variables on the principle response curve are represented on the extra right y-axis (b_k) in the PRC diagram, indicating the contributions of individual variables to the principle response patterns. The mesocosms without restoration treatments (control) were taken as a reference line, with its principal trajectory set to zero. As a result, the deviations of other treatments from the control mesocosms can be interpreted as an overall response to the restoration treatments (represented in the left y-axis of PRC: expressed as the coefficient of treatment response, C_{dt}) over time (x-axis). The canal water was taken as another treatment for evaluation of the potential effects of mesocosms (i.e., isolation of a water volume from the surrounding canal water). Note that the patterns of the overall responses are influenced by selection of the variables. We have selected the water quality variables that are of importance in terms of evaluation of heatwave and treatment impacts.

Further, we used linear mixed effect models to test for significant differences in the response parameters between the treatments over time (LME; Lindstrom and Bates, 1988c). The linear mixed effect model allows for testing both fixed effects as well as random effects. Mesocosm identity was included in LME as a random effect to account for the heterogeneity between different mesocosm sites. To evaluate the treatment-related changes in response variables over the whole experimental period, we included the restoration treatments and the experimental time as fixed effects. In addition, to evaluate the effect of nutrient availability for the dynamics of algal biomass, dissolved phosphorus (SRP) and dissolved ammonium (NH_4-N) were included as predictor variables in the LME model for the response variables total chlorophyll-a and cyanobacteria chlorophyll-a.

To evaluate the effect of occurrence of an extreme heatwave on the efficacy of the different measures, observed water temperature was included as an additional fixed effect during the heatwave phase (12^{th} of July – 7^{th} of August). In this analysis, time was excluded as there were only three sampling points during this period. We regard this as a solution for evaluating heatwave impacts in a field experiment where a control treatment of heatwave is not possible.

We used depth-integrated values for the variables DO and pH in the data analysis, as the depth profiles of these variables showed limited variability with depth. We confirmed this absence of stratification during the experimental period with our FLake simulation results.

We used a Shapiro Wilk test (Ghasemi and Zahediasl, 2012b) to test for normality of model residuals and if needed, different data transformation methods were applied, including logarithmic, reciprocal and square root. Breusch Pagen test (Waldman, 1983b) was used to check for heteroscedasticity of the residuals and if needed, a weighted linear mixed-effect model was carried out to correct for deviations from homoscedasticity.

To evaluate treatment effects on the nutrients in the sediment pore water (sampled at the end of the experiment), we used one-way ANOVAs. Tukey's range test was used to compare the means of Greenhouse Gas (GHG: CO_2, CH_4, and N_2O) concentrations between the different treatments (Tukey, 1949). All statistical analyses and data visualization were performed in R language (Team, 2019b). We used the packages *lubridate* (Grolemond and Wickman, 2011b), *nlme* (Pinheiro et al., 2019b), *dplyr* (Wickham et al., 2019), and *vegan* (Oksanen et al., 2019a). In addition, we used color-blind-friendly color palette for visualizations of our results following (Wong, 2011).

4.3 Results

4.3.1 Intervention treatment effects on water quality

Our PRC model (Figure 4-2) revealed that among the four restoration treatments the Lanthanum modified bentonite (LMB) groups showed the strongest mitigation potential relative to the control treatments, followed by the dredging and iron-lime sludge treatments. The aeration treatment showed the least deviation from the control mesocosms, reflecting its limited potential for water quality improvement. In addition, the principal response curve of the surrounding canal water showed a distinct negative deviation from the control treatment, indicating a strong mesocosm effect on the water quality dynamics.

The response variables Secchi depth, total chlorophyll-a and cyanobacteria chlorophyll-a accounted for the largest contribution to the variation in the principle response variable, with TP, pH and DO only playing a minor role in determining the overall response patterns. Secchi depth and nutrients developed in opposite directions to the chlorophyll-a variables, pH and DO, indicating a negative correlation between these two sets of parameters.

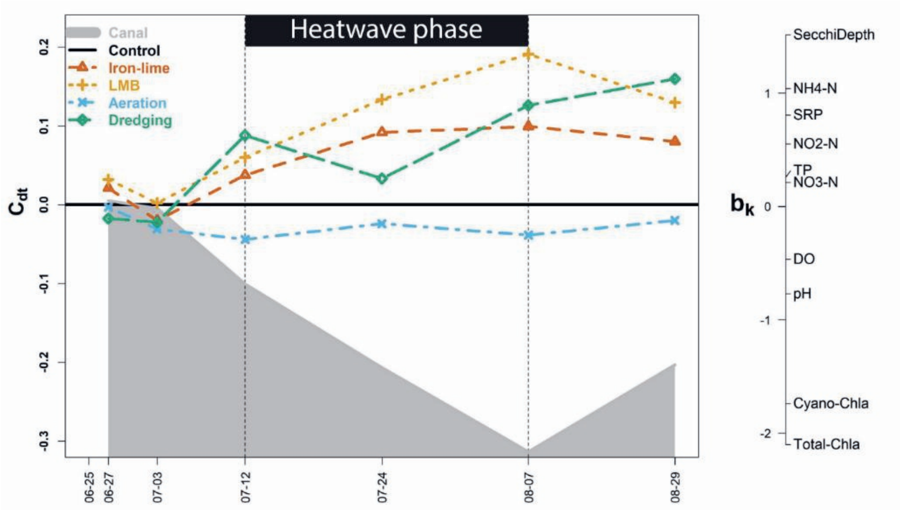

Figure 4-2. *Principal response curve of water quality parameters. The principal response curve model included the parameters Secchi Depth, DO, pH, total chlorophyll-a, cyanobacteria chlorophyll-a, SRP, TP, NH_4-N, NO_2-N and NO_3-N. The PRC shows the trajectory of each treatment response (coefficient of treatment response, C_{dt}) for each restoration treatment on the left y axis, with the control mesocosms trajectory set to 0. The x-axis represents time. The weights of individual water quality parameters (b_k) on the overall system response curves are displayed on the right y-axis.*

Over the course of the experimental period, our LME model detected a significant decrease in dissolved oxygen (DO) concentrations over time, from an initial value of 11.0 ± 0.5 mg/L down to 5.7 ± 0.2 mg/L at the end of the experiment (DO log-transformed: effect of time = -0.12, $F_{1, 111} = 90.0$, $p < 0.001$, Figure 4-3 a). The restoration treatments did not show a significant effect on the DO dynamics.

The LME model detected a significant increase in Secchi depths over the course of the experiment (effect of time = 0.03, $F_{1, 111} = 24.8$, $p < 0.0001$, Figure 4-3 b). The restoration treatments also had a significant impact on Secchi depth relative to the control ($F_{5, 15} = 4.13$, $p = 0.01$), with the largest increases in transparency in the dredging treatment (by 38.5 ± 15.5%), followed by the LMB treatment (by 19.1 ± 15.1%) and the iron-lime sludge treatment (by 11.1 ± 15.0%), whereas the aeration treatment showed a decrease in Secchi depths (by 13.0 ± 15.1%). Secchi depths in mesocosms improved in comparison to the canal water (estimate of difference = -34.3, DF = 15, t-value = -1.83, p = 0.087). The Secchi depth in the canal stayed at low levels (56.9 ± 1.2 cm) over the entire course of the experiment.

The pH levels in the water columns started at high levels (mean = 9.28 ± 0.02) and decreased significantly over time (effect of time = -0.005, $F_{1, 111}$ = 19.46, p < 0.0001; Figure 4-3 c), without significant differences between the different restoration treatments.

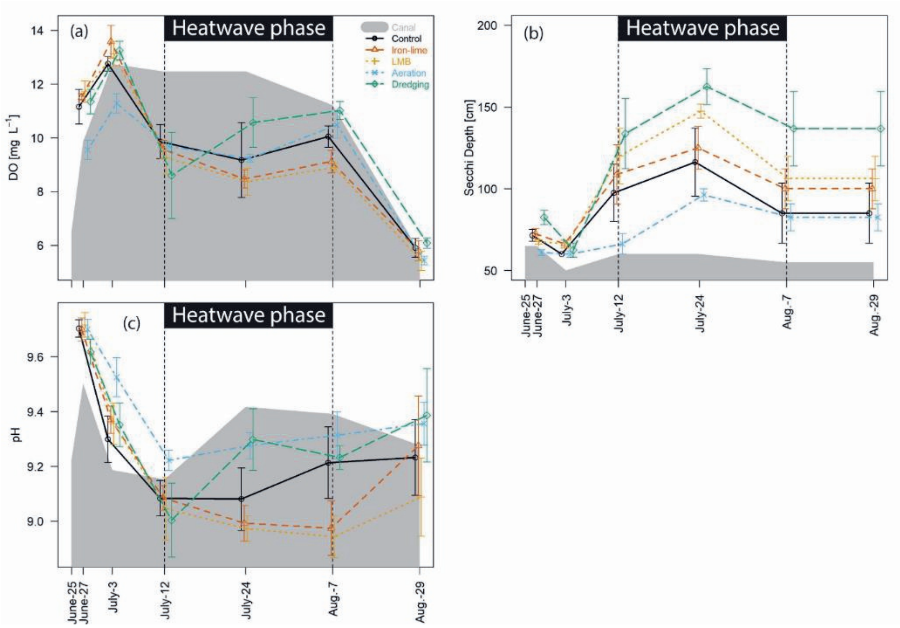

Figure 4-3. *Dynamics of (a) dissolved oxygen (DO), (b) Secchi depth, and (c) pH values in the water column. Error bars illustrate standard errors.*

Over the experimental period, the LME model detected a significant time effect on the dissolved phosphorus levels (SRP, estimate of time effect = 0.0007, $F_{1, 110}$ = 17.82, p < 0.0001, Figure 4-4 a). The mesocosms were SRP-depleted at the start of the experiment (< 0.6 µg P/L), after which the SRP concentrations started to rise, reaching maximum concentrations of 82.2 ± 16.3 µg P/L on 24th of July. In the end of the experiment, the SRP levels decreased to 30.1 ± 5.5 µg P/L. The restoration treatments showed no significant effect on the SRP dynamics. The SRP concentrations in the canal water were lower than in the mesocosms during the experimental period (9.2 ± 2.1 µg P/L), showing no initial increase as observed in the mesocosms. At the end of the experimental period, our one-way ANOVA model detected no significant differences in the pore-water SRP concentrations between restoration treatments ($F_{5, 18}$ = 1.01, p = 0.44; Figure 4-4 b). The SRP concentrations in the pore water were comparable with the maximum water column concentrations as observed on 24th of July with average concentrations of 85.7±15.1 µg P/L.

The total phosphorus concentrations (TP) increased significantly over the experimental period (estimate of time effect by LME model = 0.009, $F_{1, 110} = 31.55$, $p < 0.0001$, Figure 4-4 c). The LME model detected no effect of the restoration treatments on TP levels, and there was no distinct difference between the TP levels in the canal water and the mesocosm water.

The LME model revealed that the lanthanum concentrations (La) in the water column of the LMB treatments were significantly higher relative to the control mesocosms (estimate of difference = 1.8 µg /L, DF = 15, t-value = 2.94, $p = 0.01$; Figure 4-4 d).

Over the whole experimental period, the LME model detected a significant Time × Restoration treatment effect on total chlorophyll-a concentrations ($F_{5,103} = 4.1$, $p = 0.0021$; Figure 4-5 a). Overall, the total chlorophyll-a concentrations started at a high level of 57.7 ± 1.9 µg/L, reaching the lowest level of 14.9 ± 5.4 µg/L at the end of July, which coincided with the peak in nutrients (Figure 4-4, SRP = 82.2 ± 16.2 µg/L; Figure SI 4-1, NH_4-N = 0.91 ± 0.07 mg/L) as observed during the heatwave phase (Figure 4-1 b). After the heatwave phase, the total chlorophyll-a concentrations increased with concentrations at the end of the experiment reaching levels of 44.0 ± 6.1 µg Chl-a/L. Our LME model detected a significant difference between the restoration treatments ($F_{5, 15} = 5.98$, $p = 0.0031$), with the dredging treatment resulting in a 62.5 ± 39.9% reduction in Chl-a levels relative to the control treatment. Compared with the control mesocosm, the LMB treatment reduced Chl-a levels by 48.2 ± 39.5%, while the iron-lime sludge treatment reduced Chl-a levels by 46.2 ± 41.2% by the end of the experiment. The aeration treatment showed no distinct difference with the control treatment. The control treatment had significantly lower total chlorophyll-a concentrations relative to the surrounding canal water, showing a reduction in end concentrations by 82.2 ± 41.2%. In addition, our LME model detected significant effects of nutrient availability on the total chlorophyll-a levels (estimate of SRP effect = -32.46, $F_{1, 108} = 28.94$, $p < 0.0001$; estimate of NH_4-N effect = -32.04, $F_{1, 108} = 27.09$, $p < 0.0001$).

For the cyanobacteria chlorophyll-a, the LME model showed an overall increase during the experimental period (estimate of time effect = 0.13, $F_{1, 108} = 31.93$, $p < 0.0001$; Figure 4-5 b). After an initial decrease from 5.84 ± 1.88 to 0.89 ± 0.15 µg/L the concentrations increased continuously ending with a relatively high level of 10.06 ± 1.32 µg/L. The restoration treatments showed significant effects on the cyanobacteria chlorophyll-a levels ($F_{5, 15} = 5.37$, $p = 0.005$), with the largest reduction relative to the control treatment in the end concentration of cyanobacteria chlorophyll-a by the dredging treatment by 58.5±33.8%, followed by the LMB treatment by 51.6 ± 32.2% and by the iron-lime sludge treatment by 40.8 ± 33.7%, whereas the aeration treatment did not reduce the cyanobacteria chlorophyll-a levels. Similar to the total chlorophyll-a measurements, the cyanobacteria chlorophyll-a concentrations in the control mesocosms had a much lower level compared to the canal water, showing a reduction of 82.8 ± 34.6%. Comparable to the results of the total chlorophyll-a LME model, the cyanobacteria chlorophyll-a LME model also detected significant effects of SRP and NH_4-N on the cyanobacteria chlorophyll-a levels (estimate of SRP effect = 9.31, $F_{1, 108} = 5.28$, $p = 0.02$; estimate of NH_4-N effect = -5.08, $F_{1, 108} = 6.29$, $p = 0.01$).

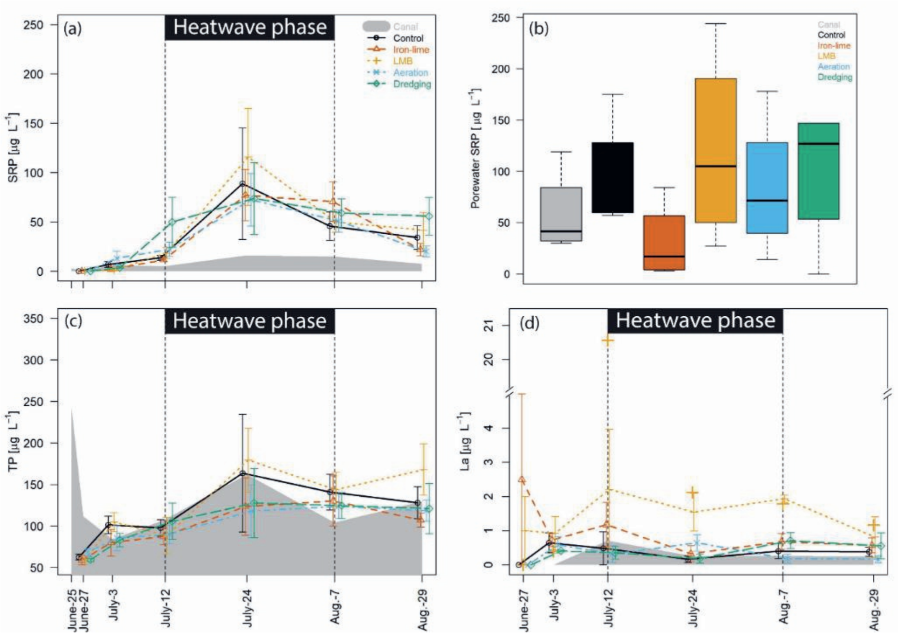

Figure 4-4. *Soluble reactive phosphorus (SRP) in the water column (a) and in the sediment pore water (b), total phosphorus (TP = SRP + particulate P) (c), and Lanthanum (La) concentration (d) in the water column. The La concentrations in one mesocosm ("+" points in orange color) were represented separately, as the observed concentrations in this mesocosm strongly deviated from the rest of levels found in the other mesocosms on 12th of July. Error bars illustrate standard errors.*

4.3.2 The heatwave effects on water quality and intervention treatment efficacy

During the heatwave phase, our LME model did not detect a significant main effect of temperature on DO concentrations. However, during the heatwave phase the restoration treatments showed a significant effect on the DO levels relative to the control treatment ($F_{5, 15} = 5.45$, $p = 0.0047$), with increased DO concentrations in the dredged treatment (by 12.3 ± 6.4%) and decreased DO concentrations in the LMB treatment (by 10.1 ± 6.4%) and iron-lime sludge treatment (by 8.5 ± 6.4%). There was no significant difference in the aeration treatment (by 2.6 ± 6.4%) relative to the control treatment. The control treatment had significantly lower DO concentrations relative to the surrounding canal water (by 19.3 ± 7.4%).

During the heatwave phase, our LME model indicated that Secchi depths increased significantly with water temperatures (main effect of temperature = 7.36, $F_{1, 44}$ = 17.25, p = 0.0001). The main effect of temperature, however, was not treatment-dependent, indicating no treatment effects on the responses in water transparency to heatwave exposure.

The LME model detected a significant difference in the pH dynamics between the restoration treatments ($F_{5, 15}$ = 6.06, p < 0.003) relative to the control treatment, with increased pH levels in the dredging treatment (by 0.77 ± 0.97%) and aeration treatment (by 1.89 ± 0.98%), and decreased pH levels in the LMB treatment (by 1.16 ± 0.97%). The iron-lime sludge treatment showed no distinct difference with the control treatment (by 0.48 ± 0.97%). The control treatment had significantly lower pH levels relative to the surrounding canal water (by 1.53 ± 1.17%). The LME model detected no main effect of temperature on the pH dynamics.

During the heatwave phase, LME model detected a positive main effect of temperature on the SRP levels (SRP log-transformed: estimate of temperature effect = 0.40, $F_{1, 44}$ = 27.11, p < 0.0001), resulting in a mean rise of 37.4 µg P/L compared to the prior-heatwave phase (days 0-16). Similar to the SRP, the TP concentrations increased with water temperatures during the heatwave phase (TP log-transformed: estimate of temperature effect = 0.089, $F_{1, 44}$ = 4.35, p = 0.04).

During the heatwave phase, LME model showed that the total chlorophyll-a levels decreased with the water temperatures (total chlorophyll-a log-transformed: estimate of temperature effect = -0.16, $F_{1, 43}$ = 19.65, p = 0.0001). Similar to the analyses of the entire experimental period (see above), the availability of NH_4-N had a significant effect on the total chlorophyll-a concentrations during the heatwave phase (total chlorophyll-a log-transformed: estimate of NH_4-N effect = -2.21, $F_{1, 43}$ = 4.89, p = 0.03). The availability of SRP, however, had no significant effect on the total chlorophyll-a levels during the heatwave phase.

During the heatwave phase, LME model detected no main effect of temperature on the development of cyanobacteria chlorophyll-a. Regarding the nutrient effects on the cyanobacteria chlorophyll-a, the effect of NH_4-N availability remained (cyanobacteria chlorophyll-a square root-transformed: estimate of NH_4-N effect = -1.34, $F_{1, 43}$ = 8.33, p = 0.006) but the SRP effect disappeared.

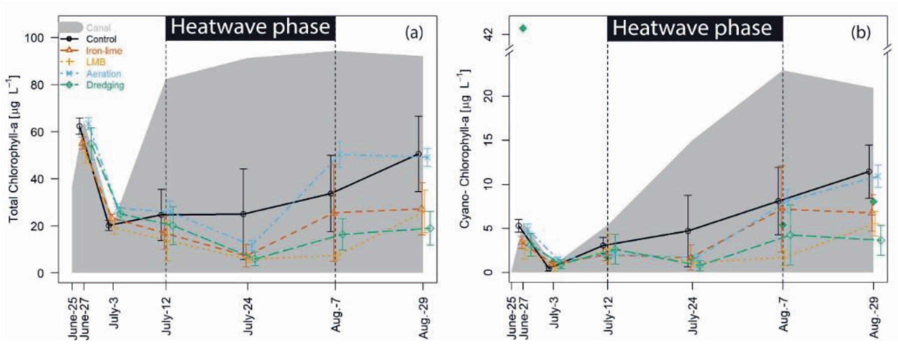

Figure 4-5. *Total chlorophyll-a concentration (a) and cyanobacterial chlorophyll-a concentration (b) in the water column. The cyanobacterial chlorophyll-a concentration concentrations in one mesocosm (blue-bluish green points) were represented separately, as the observed concentrations in this mesocosm strongly deviated from the rest of levels found in the other mesocosms on 27^h of June. Error bars illustrate standard errors.*

4.3.3 Treatment effects on dissolved Greenhouse gas concentrations

The LMB treatment had the highest dissolved GHG concentrations at the end of the experiment, while the aeration treatment had the lowest dissolved GHG concentrations (based on Tukey test, see also Figure 4-6). For instance, the LMB mesocosms had significantly increased dissolved CO_2 values in comparison to the control mesocosms (estimate of difference = 64.0 µmol/L, $p = 0.08$) and to the aerated mesocosms (estimate of difference = 90.2 µmol/L, $p = 0.01$).

With respect to the concentrations of the dissolved CH_4 at the end of the experimental period, the aerated mesocosms showed decreased values in comparison to the control mesocosms (estimate of difference = 4.3 nmol/L, $p = 0.07$) and to the iron-lime sludge mesocosms (estimate of difference = 4.5 nmol/L, $p = 0.06$); The LMB mesocosms had higher dissolved CH_4 values than the aerated mesocosms (estimate of difference = 7.9 nmol/L, $p < 0.005$) and dredged mesocosms (estimate of difference = 4.4 nmol/L, $p = 0.07$).

With respect to the concentrations of dissolved N_2O, the aerated mesocosms had significantly lower values than the control mesocosms (estimate of difference = 19.7 nmol/L, $p = 0.02$), iron-lime sludge mesocosms (estimate of difference = 18.0 nmol/L, $p = 0.05$), and LMB mesocosms (estimate of difference = 34.3 nmol/L, $p < 0.005$). In addition, the LMB mesocosms had higher dissolved N_2O concentrations than the mesocosms that were exposed to the iron-lime sludge mesocosms (estimate of difference = 16.3 nmol/L, $p = 0.08$) and the dredging mesocosms (estimate of difference = 21.8 nmol/L, $p = 0.01$).

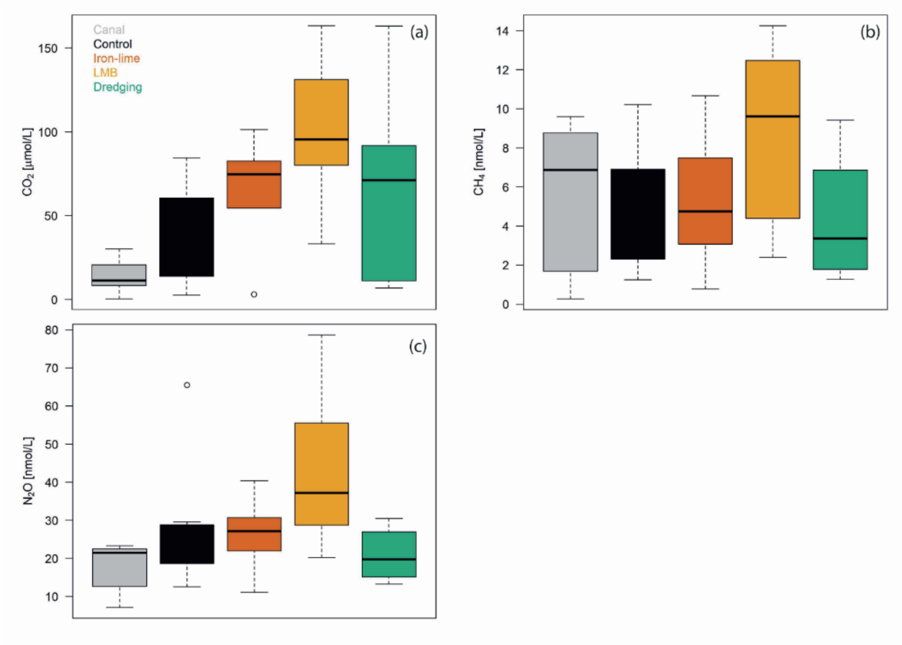

Figure 4-6. *Box plot (10%, 25%, 75% and 90% percentiles) of the concentrations of dissolved methane (a – CO_2), carbon dioxide (b – CH_4), and nitrous oxide (c – N_2O) at the end of the experiment (19-09-2019).*

4.4 Discussion

In this study, we compared four restoration measures with respect to their efficacy of reducing phytoplankton and improving water quality in an urban canal using a mesocosm approach. This type of experiments comparing different intervention measures at a near-realistic level of environmental complexity are few and far between. Here, we also evaluated how the efficacy of these interventions is impacted by exposure to an extreme heatwave in the middle of the experiment. This addressed the knowledge gap we currently face regarding the usefulness of commonly applied restoration measures under future climate scenarios. At the end of this discussion section, we will propose a conceptual model on potential routes through which measures to mitigate water quality deterioration might be affected by heatwaves. To our knowledge, such a comprehensive conceptual model is still lacking in literature and can provide a starting point for future validation.

The study site was a hypertrophic shallow water system according to the Carlson trophic state index (TSI; Carlson, 1977). The experiment focused on the reduction of the internal loading as a means to mitigate water quality deterioration, with most of the external loading effectively blocked in our type of mesocosm. The experiment started at the end of June with rather high phytoplankton biomasses (initial total chlorophyll-a = 57.7±1.3 µg/L) and depleted SRP concentrations (< 0.6 µg P/L), presumably due to high nutrient uptake by phytoplankton. Overall, the dissolved oxygen concentrations in the mesocosms decreased over the lifetime of the experiment, indicating that the systems were shifting from a primary production-dominant to a decomposition-dominant system.

4.4.1 Comparison of intervention measures

Among the tested four restoration treatments, the dredging treatments exhibited the greatest efficacy with respect to reduction of total phytoplankton biomass (evidenced by total chlorophyll-a), cyanobacteria biomass (evidenced by cyanobacteria chlorophyll-a), and improvement on water transparency (evidenced by Secchi depth). The dredging treatments aimed at removing the top nutrient-rich sediments, resulting in newly exposed sediments with lower nutrient release (estimate of the P loading = 0.2-0.7 P/m^2/day; Van Herpen, 2019). While the other three restoration measures only targeted immobilization of inorganic P, dredging of top 30-cm sediments will also result in a reduction of nitrogen (Figure SI 4-1) and assimilable carbon in the organic matter that may facilitate microbial growth leading to oxygen depletion and release of redox-sensitive P (Yin et al., 2021). Moreover, there is increasing evidence that phytoplankton can also uptake organic nutrients for their growth (Bentzen et al., 1992; Boyer et al., 2006; Znachor and Nedoma, 2010). The anticipated decline in organic matter content in the newly exposed sediments may lead to decreased oxygen consumption, supported by the temporally increased DO and pH during the heatwave phase (Figure 4-3). Such an increase of DO concentrations in the dredging treatments disappeared after the heatwave phase, which can be caused by the sedimentation of phytoplankton charging the newly exposed sediments with organic nutrients (Lürling and Faassen, 2012).

The lanthanum modified bentonite (LMB) treatments exhibited comparative efficacy compared with the dredging treatments, confirming the first hypothesis. We expected that the LMB treatments would immobilize SRP from the water columns into the sediments, which was not supported by the observations of SRP concentrations in the water column showing no distinct deviations from the control treatments. A rough estimate of P fluxes using the water column SRP data from July 12th and July 24th resulted in as high as 16 mg P/m^2/d in LMB treatments and 12 mg P/m^2/d in controls, and these estimates were even with uptake by phytoplankton. This level of P loading is much higher than the critical value for this system shifting from a clear state to a turbid state (estimate = 2.2 mg P/m^2/day; Van Herpen, 2019). The high P-fluxes in LMB treatments are probably due to ebullition of gas transporting sediment nutrients into water, evidenced by the relatively high CO_2 and CH_4 gas concentrations in LMB treatments (Figure 4-6). Previous studies indicated that the ebullition of gasses from sediments can be an important mechanism for nutrient transport from the sediment into overlying water in eutrophic lakes (Varjo et al., 2003). This result contrasts other studies that have shown a strong SRP reduction capacity of LMB, also under anoxia (e.g., Funes et al., 2021; Li et al., 2019), but finds support in another mesocosm study that observed hampered SRP binding by LMB (Lürling and Faassen, 2012). There may be several factors responsible for those deviating performances. The high pH at the start of the experiment (pH 9.7) implied strong competition between phosphate and hydroxyl ions for binding sites; the binding capacity of LMB at pH 9.5 is about one-third of the binding capacity at pH 7 (Li et al., 2019). Filterable La in the water column over the course of the experiment did not bind with SRP (Figure 4-4 d), which may be attributed to the presence of high DOC prevailing in eutrophic water bodies (background concentration in the canal = 6.37 ± 1.74 mg/L, unpublished data Water Authority Brabantse Delta), preventing phosphate precipitation by La-clay chelation (Lürling et al., 2014). Field observations from multiple lakes suggest that DOC concentrations negatively influence the efficacy of LMB (Spears et al., 2016) and such negative impacts by DOC will not disappear after one year (Dithmer et al., 2016b). Note that although we observed overall higher La concentrations in the overlying water of the LMB treatments, they are far below the Dutch standard for surface water (10.1 µg La/L; Sneller et al. 2000) during most of the time except for one mesocosm which temporally exceeded the standard reaching 21 µg La/L on 12th of July, but dropped down to 2 µg La/L immediately at the next sampling. Our LMB results were in line with (Li et al., 2019) demonstrating that the presence of phytoplankton can act as a P sink and thus hampering P adsorption by LMB. They found that an intensified dosage of LMB can mitigate such inference from phytoplankton. Moreover, (Lürling and Faassen, 2012) demonstrated that combined sediment dredging and LMB addition is a more promising measure than their treatments alone.

The iron-lime sludge exhibited a moderate efficacy, with a performance better than aeration but worse than dredging and LMB treatments, confirming our second hypothesis that the application of iron-lime sludge on the sediment is less effective in reducing phytoplankton biomass. Fe measurements of the water column as well as pore water (Figure SI 4-2) showed iron-lime sludge did increase the Fe pool. The sediment P-fractionation results (Figure SI 4-3 a) showed that organic P is the second common P fraction after the redox-sensitive P accounting for approximately 35% of the mobile P. Mineralization of organic matter would exhaust the oxygen pool. Thus, the sediments were highly likely to be reducing (also reflected by the decreased DO concentrations in the iron-lime sludge treatments, Figure 4-3 a and Figure SI 4-3 b), leading to an increasing fraction of Fe^{2+} reducing P retention capacity of the sediment (Gächter and Müller, 2003). The optimum pH values for Fe-P binding is 4-5.5 (Kraal et al., 2015), while the Ca-P bond can dissolve under acidic conditions (Gon Kim et al., 2002; Ippolito et al., 2003). We observed no distinct difference in the calcium concentrations in the water column between the iron-lime sludge treatments and other treatments (Figure SI 4-2), suggesting no Ca-P dissolution. Huang et al. (2005) demonstrated that P release in response to pH variations in lake sediments is dependent on a ratio of Fe-P content to Ca-P content, with high Fe-P/Ca-P ratio releasing P under alkaline conditions and low Fe-P/Ca-P ratio releasing more P under acidic conditions. In our Iron-lime sludge, Ca accounted for a larger proportion than Fe (Table SI 4-1), thus, being acidity-sensitive. However, the pH in the water columns remained high in our systems (pH > 8.8, Figure 4-3 c) presumably owing to the presence of a high phytoplankton biomass consuming inorganic carbon. Thus, in this system the efficacy of Iron-lime sludge is more likely to be redox-related than pH-related.

In agreement with our third hypothesis, the aeration treatments were unable to stimulate the iron trap of sediment phosphorus and hinder the growth of phytoplankton, with an end concentration comparable to the control mesocosms (Figure 4-5). Previous studies demonstrated that any form of mixing of water columns in shallow water bodies (< 15 m) can lead to a negative effect on the water quality (Visser et al., 2016). This is because in such shallow water bodies (< 2m), oxygenation by air pumping will inevitably enhance sediment resuspension. The direct consequence of sediment resuspension is decrease in water clarity as reflected by the decreased Secchi depth in comparison to the control mesocosms (see Figure 4-3 b). Another unfavorable consequence of enhanced sediment resuspension may likely be sediment nutrients release, which will fuel the phytoplankton growth in the surface water. The favorable effect of aeration we expected was increased DO in the water columns and in the sediments, preventing release of redox-sensitive P (Cavalcante et al., 2018). Based on the water column DO measurements (Figure 4-3 a, DO concentrations and Figure SI 4-3 b for DO saturation) as well as the pore water nutrient concentrations (Figure 4-4 b for SRP and Figure SI 4-1 for NH_4-N and NO_2-N), we have to reject this hypothesis as we observed no distinct difference between the aeration treatment and the other treatments. This might be related to the large pool of organic matters in the sediments (Remke et al., 2018) and the observation that decomposition of resuspended sediment organic matters can lead to high DO consumption. Gächter and Wehrli (1998) demonstrated that oxygenation was unable to increase the P retention capacity of the sediment in presence of excessive organic matter. In conclusion, aeration is not a suitable measure in eutrophication control in shallow water systems.

In addition to these four measures, the mesocosm treatment itself showed significant effects on water quality (grey area in Figure 4-2). The direct consequences of mesocosm treatments are isolation from the surrounding canal water, which occasionally receives an inlet discharge of 0.06 m^3/s when the inlet was fully operated (Herpen, 2019). This resulted in a dramatic reduction of external nutrient loading (estimate = 2.77 mg $P/m^2/day$; Van Herpen, 2019), absence of fish (estimate = 772.8 kg/ha; Van Herpen, 2019), and shelter from wind resulting in decreased mixing of water and sediment resuspension (indicated by the increased Secchi depth in mesocosms, Figure 4-3 b). Absence of fish will lead to decreased grazing pressure on zooplankton (Jeppesen et al., 1997) and reduced bioturbation of sediments (Adámek and Maršálek, 2013). In a mesocosm experiment by Lürling et al. (2017c) increased Rotifer and Cladocera abundances were observed, supporting this hypothesis. This could partly explain the lower phytoplankton abundance in the mesocosms owing to increased grazing pressure from zooplankton. The higher P loading in canals, however, did not translate to a relatively higher concentration of SRP relative to the mesocosm water. This is likely to be a result of the higher phytoplankton biomass in the canal resulting in larger amounts of P-uptake (Riegman, 1985).

4.4.2 Heatwave impacts on the internal P cycling

During the heatwave phase, we observed in all mesocosm treatments an increase of SRP concentrations in the water column by on average 270.3%, with a mean concentration of 30.1 µg P/L at the end of the experiment. Previous modeling studies (Janse, 2005) demonstrated that an SRP concentration of 50 µg P/L can result in an ecosystem shift from the clear state to the turbid state. This shows that the temperature effect detected in our data (a rise of the SRP concentration of 10 µg P/L/°C) is highly relevant. The increases in SRP concentrations coincided with increased phytoplankton biomass in the last month (Figure 4-5) and decreased water transparency (Figure 4-3 b). However, the increases in phytoplankton biomass showed a lagged response to the increases in nutrient concentrations. This mismatch could be due to the previous depletion of environmental SRP concentrations resulting in a low internal nutrient content (‘cell quota’) in the phytoplankton cells (Droop, 1974). It likely took some time for the organisms to rebalance their cell quota resulting in a delayed response in their biomass. This phenomenon is modelled by the well-known Droop equation in ecological models (e.g., PCLake; Janse, 2005). A potential explanation for our observations is thus that sediment SRP release was taken up quickly once phytoplankton attained sufficient biomasses, resulting in a depleted SRP concentration in the water column until the end of the experiment. Evaluating this hypothesis on the nutrient uptake by phytoplankton is difficult in such *in-situ* mesocosm experimental set-up, where there is unlikely to be a control treatment for primary productivity. Our fourth hypothesis that the efficacy of iron-lime sludge will be hampered by increased water temperature was not rejected as was our fifth hypothesis that heatwave exposure resulted in P-release from lanthanum modified bentonite treated sediments. The heatwave-induced P-release was not re-immobilized despite the presence of available La (Figure 4-4 d), at least at a time scale of months. Similar results were observed in a previous laboratory study (Zhan et al., 2021a), which supported our conclusion that the heatwave-induced P-release is long-lasting and will not disappear immediately post to heatwave. Additional experiments are needed to investigate the changes of La-P binding capacity upon heatwave exposure. Our sixth hypothesis that there is no heatwave effect on the efficacy of dredging is rejected as the dredging was shown to be unable to mitigate the heatwave-induced increases in P-releases. In summary, the efficacy of all the tested measures was reduced during the heatwave phase.

Greenhouse gas (GHG) emission of water bodies is substantial (Li et al., 2021; Rosentreter et al., 2021) and is promoted by eutrophication (Jake J. Beaulieu et al., 2019; Davidson et al., 2015b). Climate change might reduce the efficacy of interventions (Rolighed et al., 2016; Zhan et al., 2021a), as indicated by this study as well. If interventions become less effective, water quality deteriorates even further, resulting in more GHG emissions (Li et al., 2021). These extra contributions to climate change pose a negative feedback to the efficacy of interventions. Thus, insight into the impact of interventions on GHG emissions is needed to reduce the reinforcing effect that eutrophication has on GHG emissions (Moss et al., 2011) and at the same time to provide an instrument for water managers to incorporate GHG emissions when selecting a treatment. Our dissolved GHG measurements indicated that LMB may not be a promising restoration measure in terms of mitigation of GHG emissions, given its overall higher GHG concentrations than other treatments (Figure 4-6). It was unexpected that the LMB treatments showed higher GHG values than the control treatments given that LMB applications should not target organic carbon. A potential cause for this may be that the newly formed LMB layer on the top of sediments hampers oxygen penetration creating a favorable anoxic environment for microbial gas production. Surprisingly, the dredged mesocosms did not show a significant reduction in GHG concentrations with treatments other than LMB. We speculate that the dredging exposed sediments did not differ substantially in organic C content relative to the non-dredged sediments. This research gives an indication of GHG emissions caused by promising interventions (Figure 4-6), though GHG flux of ebullition needs to be incorporated to provide an accurate estimation of the GHG emissions from sediments.

We propose a graphical model illustrating the underlying mechanisms for heatwave impacts on the efficacy of intervention measures (Figure 4-7). In general, the P cycle can be divided into two compartments, one representing a biological P loop that involves P fluxes between organic P and labile P via biological processes (i.e., decomposition and primary production), another representing a chemical P loop that involves P fluxes between chemical bound P (including Lanthanum bound P; redox-sensitive P: Fe/Mn-P; and pH-sensitive P: Al/Fe-P) and labile P via chemical sorption and desorption processes. Our results indicated that heatwave exposure increased the phosphorus pools stored in the biological loop, whereas the phosphorus pools in the chemical loop decreased.

The heatwave effect can play a role in phosphorus cycling through several mechanisms. Firstly, increasing temperature enhances decomposition of organic matter and release of detrital nutrients (Gudasz et al., 2010b). Furthermore, the decreased oxygen concentrations as a result of enhanced mineralization and respiration could lead to anoxic conditions at the sediment resulting in release of redox-sensitive phosphorus (Fe- and Mn-bound P; Cavalcante et al., 2018).

In addition, increasing DOC levels resulting from decomposition of organic matter has been found to interfere with the precipitations of La-P (Lürling et al., 2014; Spears et al., 2016) and Ca-P (Cao et al., 2007; Sindelar et al., 2015), thus, decreasing phosphorus immobilization via these pathways. Lei et al. (2018) suggests that high pH can overcome the negative DOC effects on Ca-P. The pH level is elevated owing to increased primary production and enhanced uptake of inorganic carbon. High pH would facilitate desorption of pH-sensitive P (Fe-/Al-P). Some laboratory experiments demonstrated negative impacts of high pH on the P removal efficacy of LMB (Kang et al., 2021), and attributed it to competition with hydroxyl ions for binding sites. However, the pH effects on Ca-/La- P precipitation are either established in short laboratory experiments or far from reaching a consensus. Thus, we decided not to include the pH effects on Ca-/La- P precipitation in our model.

With phosphorus pools locked in the biological loop, the chemical immobilization of labile P was inhibited. This maybe especially true for summer conditions, when temperatures are high and primary production is intensive, a high amount of P is stored in organisms, hampering the P-adsorption efficacy of chemical adsorbents, which underpins the importance of planning restoration activities during periods when most P is not already stored in biota. It is anticipated that inland waters may have prolonged growing seasons with a higher risk of long-lasting algal blooms under the effects of global warming, which is currently, however, rarely taken into consideration by lake managers when applying restoration measures (Jeppesen et al., 2007). In addition, warm lakes tend to be more productive than similar cold lakes, with everything else equal (Jeppesen et al., 2020). Our results on this temperate shallow urban water system could provide implications for eutrophication management of tropical lakes when selecting treatments, in which the restoration efforts are much limited compared to the lakes in the temperate zone (Thornton, 1987). Our results suggest that the intervention measures that only target SRP might take longer in inhibiting phytoplankton biomass in temperate systems when applied during warm periods with high rates of biological processes, whereas they might not be promising in tropical systems with no period where there is low organismal biomass (i.e., perennial growth).

Knowledge about the influence of temperature on chemical P binding capacity is lacking. Although it is hypothesized that warmer water can facilitate interactions between chemical compounds through increased kinetic energy, such positive temperature effects on P binding capacity are not conclusive for LMB and aluminum salts (Kang et al., 2021). We hypothesize that in highly productive systems temperature effects on biological processes are more important to nutrient cycling when compared with the direct temperature effects on the chemical nutrient de-/sorption, as most of the nutrients exist in organic forms. For these reasons, the temperature effects on chemical reactions are not included in our conceptual model.

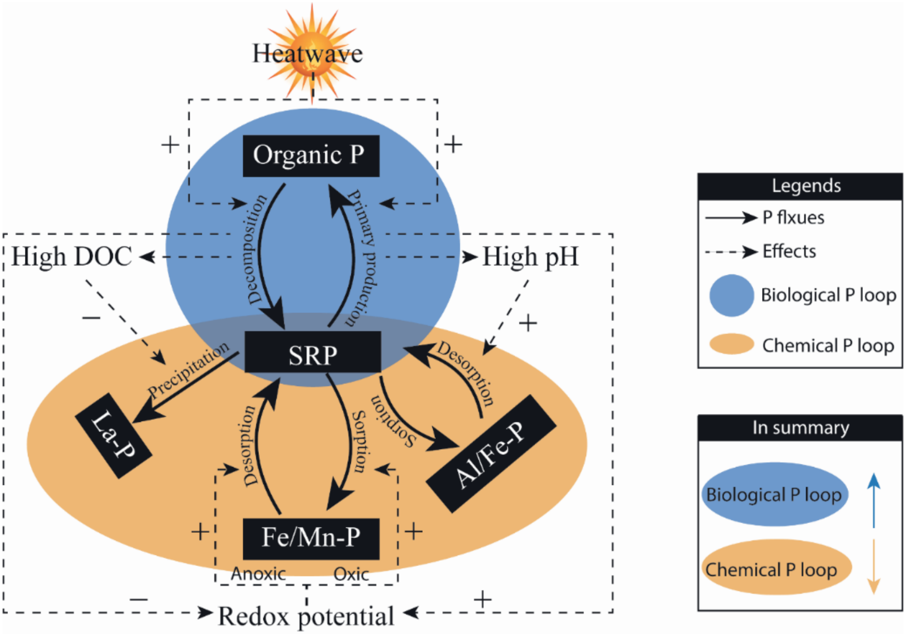

Figure 4-7. *Conceptual model illustrating the interaction between environmental conditions and internal phosphorus cycling. The solid lines represent the P fluxes between different P forms. The dashed lines with the "+" and "-" are the positive or negative effects on P fluxes during a heatwave event.*

4.5 Conclusions, caveats and recommendations

Using a replicated near-real world mesocosm study, we tested the efficacy of four restoration measures to control internal P-loading in a hypertrophic shallow urban system impacted by an extreme summer heatwave. Our sampling time interval was rather large for an event analysis, with high frequency measurements likely providing a more detailed insight on the water quality dynamics of the restored water.

Notwithstanding the limitations of our sampling regime, we were able to derive a conceptual model that explains the underlying pathways that determine the cycling of phosphorus between different forms, which can improve our understanding and prediction of the efficacy of restoration measures under future climate scenarios. Measurements of more variables such as dissolved organic carbon and the sediment redox potential are needed for validating the proposed conceptual model.

The take home messages of our study:

1. Dredging and Lanthanum modified bentonite are more effective than iron-lime sludge in decreasing phytoplankton biomass and improving water clarity.

2. Near-sediment aeration was not able to stimulate the iron trap in the sediment in shallow water systems.
3. The efficacy of the tested measures was hampered by a heatwave. We speculate that the heatwave, through its accelerating impacts on biogeochemical processes, locked P pools in the biological loop, i.e., the exchange between labile P and organic P. As a consequence, the efficacy of P adsorbents is hampered due to reduced P pools in the chemical loop.
4. As intervention measures that only target SRP may likely take longer in inhibiting phytoplankton biomass during warmer periods, we recommend an application strategy before the growing season (autumn or early spring in temperate systems) when the biological P loop is less prominent relative to the chemical P loop.

In conclusion, our results suggest that our current efforts on eutrophication control are very likely to be compromised under global warming, and more research on how to adapt our restoration measures to a warming world is needed.

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Supplementary information

CHAPTER V

Chapter V:

Process-based modeling for ecosystem service provisioning: Non-linear responses to restoration efforts in a quarry lake under climate change

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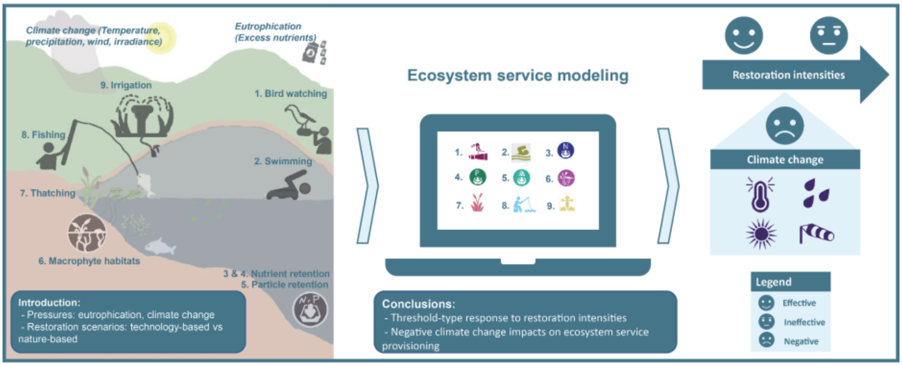

Abstract:

Healthy freshwater ecosystems can provide vital ecosystem services (ESs), and this capacity may be hampered due to water quality deterioration and climate change. In the currently available ES modeling tools, ecosystem processes are either absent or oversimplified, hindering the evaluation of impacts of restoration measures on ES provisioning. In this study, we propose an ES modeling tool that integrates lake physics, ecology and service provisioning into a holistic modeling framework. We applied this model to a Dutch quarry lake, to evaluate how nine ESs respond to technological-based (phosphorus (P) reduction) and nature-based measures (wetland restoration). As climate change might be affecting the future effectiveness of restoration efforts, we also studied the climate change impacts on the outcome of restoration measures and provisioning of ESs, using climate scenarios for the Netherlands in 2050. Our results indicate that both phosphorus reduction and wetland restoration mitigated eutrophication symptoms, resulting in increased oxygen concentrations and water transparency, and decreased phytoplankton biomass. Delivery of most ESs was improved, including swimming, P retention, and macrophyte habitat, whereas the ES provisioning that required a more productive system was impaired (sport fishing and bird watching). However, our modeling results suggested hampered effectiveness of restoration measures upon exposure to future climate conditions, which may require intensification of restoration efforts in the future to meet restoration targets. Importantly, ESs provisioning showed non-linear responses to increasing intensity of restoration measures, indicating that effectiveness of restoration measures does not necessarily increase proportionally. In conclusion, the ecosystem service modeling framework proposed in this study, provides a holistic evaluation of lake restoration measures on ecosystem services provisioning, and can contribute to development of climate-robust management strategies.

5.1 Introduction

We have entered a human-dominated geological epoch, coined the Anthropocene (Lewis and Maslin, 2015), characterized by an increasing impact and over-utilization of ecosystems by humans. In the Anthropocene, the demand for almost all ecosystem services is on the rise (Assessment, 2005). Ecosystem services (ESs) are defined as direct and indirect contributions of ecosystems to human well-being (Carpenter et al., 2009). In recent years, this concept of ecosystem service has guided ecosystem management and restoration efforts, aiming to integrate social, economic and ecological perspectives (Kull et al., 2015; Seppelt et al., 2011; Valencia Torres et al., 2021).

Quantifying ecosystem services can be instrumental in recognizing the benefits humans receive from ecosystems, providing stronger arguments for ecological restoration (Grizzetti et al., 2019; Guerry et al., 2015). Conveying restoration impacts in terms of the loss or gain of ESs can facilitate effective communication of restoration outcomes to policy-makers and river basin authorities responsible for implementing restoration measures (Wortley et al., 2013b). While modeling terrestrial ecosystem services often focuses on mapping ESs provisioning through spatial variations of catchment attributes (e.g., land use, topography, lithology) (Nelson and Daily, 2010), the dynamics of water quantity and quality necessitate a more explicit consideration in aquatic ecosystem service modeling (B. Grizzetti et al., 2016).

There is increasing evidence that freshwater ecosystem services provisioning is closely linked to the ecological quality (or ecological state) of different aquatic environments, including shallow lakes (Janssen et al., 2021), deep lakes (Seelen et al., 2021a), rivers and coastal waters (Grizzetti et al., 2019). Based on data reported under the European Water Framework Directive, Grizzetti et al. (2019) demonstrated that higher provisioning of ESs is mostly correlated with better ecological states, particularly for regulating services (e.g., water purification, erosion retention, flood protection) and cultural services (e.g., recreation). However, current modeling tools for water-related services primarily focus on water quantity (B. Grizzetti et al., 2016), with limited integration of services closely related to water quality (Keeler et al., 2012). Water quality dynamics are mediated by complex interactions among a myriad of ecosystem processes, which are often oversimplified in large-scale modeling frameworks. For instance, one widely-used ecosystem service model, InVEST, simplifies by using nutrient loading as a proxy for determining the availability of lake-related ESs (Nelson et al., 2009; Polasky et al., 2011), assuming simple linear responses of ecosystems to nutrient loading. This approach contradicts the resistance theory of ecosystems (Gómez-Baggethun et al., 2011; Ibelings et al., 2007), which supports threshold-type ecosystem responses to pressures. Consequently, the assessment of management actions often relies on variables collected at the landscape scale (e.g., Burkhard et al. 2012; Hernández-Romero et al. 2022), which may be inaccurate due to the aforementioned nonlinear responses or ill-fitting when assessing the impacts of in-lake restoration measures (Lürling and Mucci, 2020). Keeler et al. (2012) proposed a conceptual framework linking ecological-related services with corresponding water quality variables based on a review of existing ES models, emphasizing the importance of this link in assessing management actions. Nevertheless, an integrated ES modeling framework closely tied to water quality dynamics is still lacking.

Successful lake management efforts should also account for the effects of climate change in addition to eutrophication control (Salk et al., 2022). Previous studies have suggested nonlinear ecosystem responses to climate change pressures (Burkett et al., 2005). Climate change can influence lake physics and ecology, e.g., by changing stratification patterns and mineralization rates. This in turn may lead to water quality deterioration (Moss et al., 2011) and impair the effectiveness of restoration measures (Cabrerizo et al., 2020a; Zhan et al., 2022, 2021b), further affecting aquatic ES provisioning. It remains an urgent question for water managers to determine how robust their current measures for restoring ES provisioning are in light of future climate conditions. Addressing this question requires a model capable of simulating climate change impacts on lake physics (e.g., thermal regimes) and ecological processes.

To address the challenges posed by various pressures on lakes, such as eutrophication and climate change, different restoration strategies have been developed and can be divided into two groups: technological solutions and nature-based solutions. Technological restoration strategies focus on employing engineered solutions to mitigate stressors affecting lakes. One prominent technological approach involves the controlled removal or inactivation of excess phosphorus from water bodies and sediments using techniques like geoengineering, or dredging (Zhan et al., 2022). Phosphorus reduction strategies are amenable to implementation in diverse lake types and meet the increasing demands for spaces of different types of land-uses, as technological-based measures often require relatively less space and act at shorter time scales (Kim et al., 2021). In contrast, nature-based solutions (NbS), exemplified by wetland restoration, emphasize the use of natural features and processes to restore lakes. Importantly, NbS need to provide benefits for human well-being and biodiversity. Wetlands are a hotspot for biodiversity and act as natural filters that absorb excess nutrients, sediment, and contaminants from water bodies (Sollie et al., 2008). There is also a growing demand for nature-based solutions, as they are suggested to be potential adaptation strategies to climate change (Seddon et al., 2020b; van Leeuwen et al., 2021). Yet establishment of a dose-effect relationship is needed for the evidence-based implementation of these restoration measures (Seddon et al., 2020b). The main objective of this paper is to assess how effective our current lake restoration measures are in restoring ecosystem services provisioning, for which we followed this work flow: 1) Develop a model framework linking lake physics, ecology and ecosystem services provisioning. 2) Assess effectiveness of a nature-based restoration (wetland restoration) and a technological restoration measure (phosphorus reduction) in a eutrophic quarry lake. 3) Study the impacts of climate change on ES delivery, by running the model under two climate scenarios.

5.2 Methodology

5.2.1 An Integrative Ecosystem Service Modeling Framework

A freshwater one-dimensional lake physics model – FLake (Kirillin et al., 2011) – was used to predict the vertical temperature profile in the water column, based on weather data or climate scenarios. FLake uses climate data (air temperature, wind speed, solar radiance, humidity and cloud cover) as input. The output of FLake including mixing and water temperatures is subsequently imposed into a lake ecosystem model (PCLake+) as boundary conditions reflecting climate-related impacts (Fig. 1).

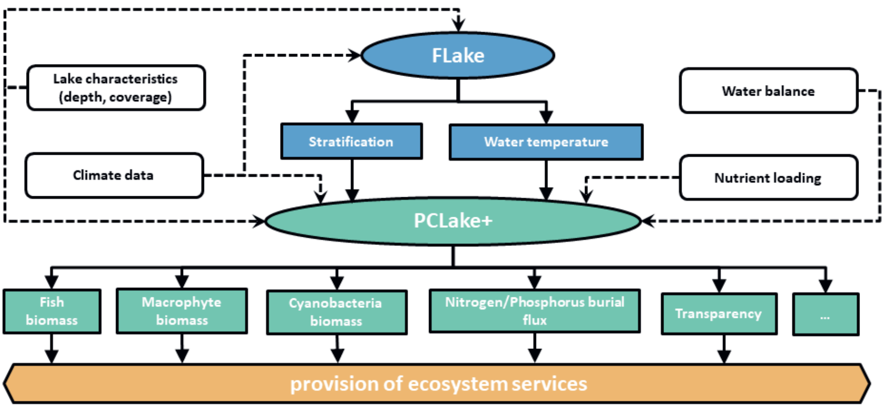

Figure 1. *Model chain for ecosystem service modeling. Rectangles denote state variables, ovals denote models, hexagon denotes ecosystem service module, rounded rectangles denote input data, solid arrows denote model input or output, dashed arrows denote data input. (Flake in blue, PCLake+ in green, input in white, output in orange).*

PCLake is a process-based ecological model that was developed to simulate water quality and assess the trophic state of lakes based on ecological interactions (Janse, 2005). It models nutrient cycling including nitrogen and phosphorus and a simple food web consisting of three functional groups of phytoplankton (cyanobacteria, green algae and diatoms), zooplankton, and fish. Moreover, it involves a wetland module that exhibits a purification function of the lake water, through biogeochemical processes explained in Janse et al. (2001). PCLake+ is an expanded version of PCLake that allows for water column stratification to take place, to model deep lakes (Janssen et al., 2019). After that, an extension was done by Chang et al. (2020) to include more realistic cyanobacterial traits, which modelled surface cyanobacterial biomass accumulation in addition to the epilimnion and hypolimnion biomass. In this study, we further expanded PCLake+ with a module for ecosystem services provisioning.

5.2.2 Modeling of ecosystem services provisioning

We built an ecosystem service module into PCLake+ to translate the water quality into a quantitative description of ecosystem services provisioning. We followed a framework for assessing ecosystem services proposed by Seelen et al. (2021a), which links ecosystem state indicators with ecosystem service provisioning through a threshold approach. The threshold values reflect the values that certain water quality parameter in a lake must attain to support the provision of a given service. The threshold values were based on published peer-reviewed literature, a field campaign covering 51 quarry lakes in the south of the Netherlands, and expert judgment (Table 1; see Seelen et al. 2021a for the supporting materials). Per ecosystem service, different aspects of the water quality requirements of the service are considered. For instance, the service of swimming is only suitable when the lake has sufficient transparency, the cyanobacterial biomass is at a safe level, and there is adequate vegetation-free water column. In the ES module, the suitability of delivering each ES was expressed by an indicator function ranging between 0-1, with “1” representing a fully suitable provisioning, “0” representing an unsuitable provisioning, and values in between representing a moderate suitability.

Table 1. *List of Ecosystem Services, their corresponding ecosystem state indicators and threshold values being included in the modeling framework. Ecosystem state indicators with a symbol (*) represent an adjustment from Seelen et al. (2022), with the decisions explained in SI section 2.*

Category	**Service**	**CICES Code**	**Ecosystem state indicators**	**Threshold values**
Provisioning	Professional fishing - fishponds	1.1.4.1	Steady state fish density (kg/ha)	>100 (suitable), 10-100 (moderate), < 10 (unsuitable)
	Common reed (Phragmites Australis) production for roof thatching	1.1.5.2	Helophytes shoot biomass (marsh zone, g DW/m^2)	>2500 (suitable)
	Irrigation	4.2.1.2	*Cyanobacterial chlorophyll-a (ug/L)	<12 (suitable), 12-75 (moderate), >75 (unsuitable)
Regulation and maintenance	Nutrient (P and N) burial in lake sediment	2.2.4.2	Reduction phosphorus/nitrogen load (%)	>50 (suitable), 20-50 (moderate), <20 (unsuitable)
	Maintenance of habitats for Water Framework Directive	2.2.4.2	*Surface coverage (%) with sufficient light (>4%)	>60 (suitable), 30-60 (moderate), <30 (unsuitable)
	Particle capture between macrophytes	2.1.1.2	Macrophyte biomass (gDW/m^2)	>200 (suitable), 20-200 (moderate), <20 (unsuitable)
Cultural	Swimming	6.1.1.1	Transparency (Secchi depth, m)	>1.5 (suitable)
			*Cyanobacterial chlorophyll-a (ug/L)	<12 (suitable), 12-75 (moderate), >75 (unsuitable)
			Plant nuisance: vegetation-free water column (m)	>0.5 (suitable)
	Bird watching	3.1.1.2	Fish density (kg/ha)	>67 (suitable)

	Helophyte density in littoral zone (g DW/m^2)	>73 (suitable)
	Transparency (Secchi depth, m)	>5 (suitable), 1.5-5 (moderate), < 1.5 (unsuitable)

In total, nine ESs are modelled with their water quality requirements summarized in Table 1. We followed the Common International Classification of Ecosystem Services (CICES; Haines-Young and Potschin, 2012), in which the ESs are divided into four different groups: *provisioning* (water, materials, energy and others), *regulation and maintenance* (remediation and regulation of the biophysical environment, flow regulation, regulation of the physic-chemical and biotic environment), *cultural* (physical or experiential use of ecosystems, intellectual representations of ecosystems), and *abiotic* (abiotic materials, energy, and space) *services*. We selected the ecosystem services that can be provided by quarry lakes following Seelen et al. (2022). Our final selection was constrained by the capacity of PCLake+ to compute quantitative ecological state indicators. Some adjustments have been made to the ecosystem model that are described in detail in SI section 1. A brief summary of the main modifications: 1). Hypoxia inhibition effect on fish growth is included into PCLake+; 2). We ran our model using hourly meteorological input data to capture the diurnal variations in light, temperature, evaporation, and rainfall, as drivers of water quality dynamics.

5.2.3 Model application and validation

Our developed ES modeling framework was applied to a quarry lake located in the south of Netherlands – "Put aan de Omloop" (51°79'22.8"N, 4°95'15.2"E). "Put aan de Omloop" or Lake de Omloop is a typical quarry lake that was created as a result of sand mining activities, showing up on topographic maps since 1969 (see https://www.topotijdreis.nl/). After creation, the lake has undergone a land-use induced eutrophication process, resulting in an increasing frequency of algae blooms. The lake is characterized by a relatively small surface area (59,370 m^2) with an average water depth of 7.7 m (see Figure SI-1 for lake bathymetry). The lake sediment is identified as sand-type soil, covered with a fluffy layer of organic matter resulting from an accumulation of detritus originating from primary production. The water and nutrient budgets are summarized in Table SI-1, with the detailed methodology on estimation of each source described in SI section 4. In short, this lake is isolated from any surface flows and fed by both groundwater and precipitation (respectively 47.8%

and 52.2%), resulting in a long residence time of ca. 1724 days. The background eutrophic level is high attributed to fertilizer application in the surrounding agriculture area, with especially high nitrogen loading (≈ 0.018 g N/m^2/day), and phosphorus loading (≈ 0.45 mg P/m^2/day). Given the fact that this lake is mainly regulated by the ground water state which is relatively stable over time within a time window of a year, for simplification, we assumed static water inflows and external nutrient loading as the forcing data for PCLake+. Wind fetch was calculated based on the measured wind speed and direction using an approach introduced in Janssen et al. (2017). We reduced the wind speed by half to account for the windbreak effects by the forests surrounding the study site (Jeong and Lee, 2020).

The ecosystem model PCLake+ used in this study was calibrated based on a generic lake dataset of primarily Dutch lakes (Janse et al., 2010). PCLake+ has a large set of parameters (>250), making overfitting the model a risk when subjecting it to site-specific calibration when data is not abundantly present. Hence, we rely on the generic calibration for our study and only adjust boundary conditions of the lake (i.e., depth, hydraulic and nutrient loads, climate forcing, wind fetch, etc., see Table SI-1).

We collected meteorological input data from the closest weather station of the Royal Netherlands Meteorological Institute (Herwijnen, https://www.knmidata.nl/) from 2011 as a reference year. FLake simulation suggests that the lake is a dimictic lake undergoing thermal summer stratification (i.e., mixing depth ≠ lake depth), which is confirmed by the measured depth profiles of water quality variables in the summer of 2014 (see Fig. SI-2), and occasional winter inverse stratification (Figure 2-a). Under a climate change scenario, the summer stratification was prolonged by more than two weeks, with an earlier on-set in spring and a postponed termination in autumn. Winter stratification however becomes much rarer with warmer temperature. A detailed description of the current ecosystem states can be found in SI section 2.

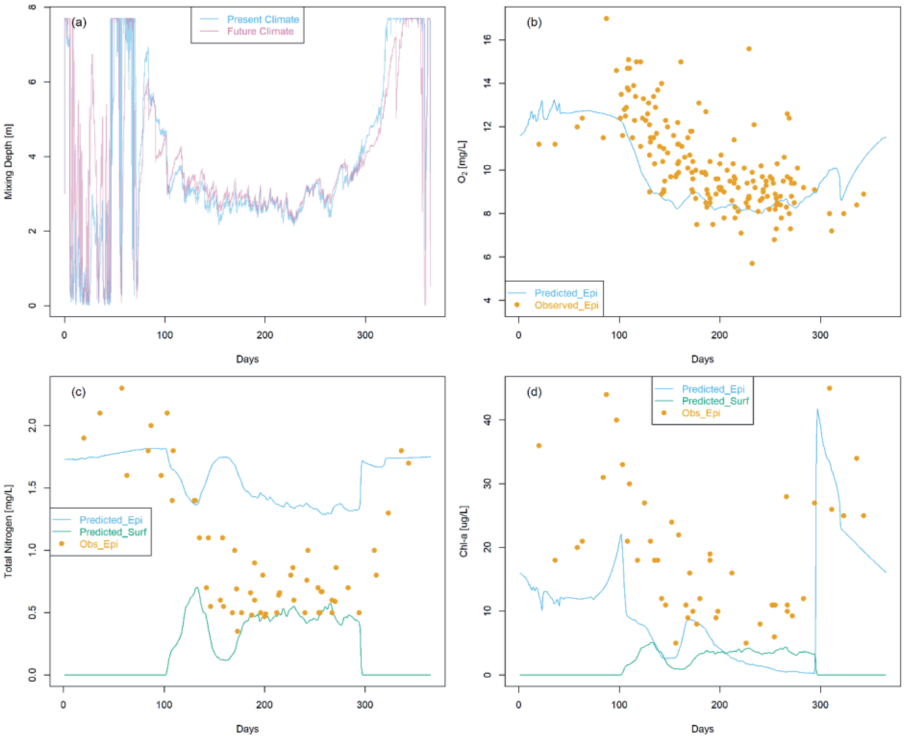

__Figure 2.__ Model results validation. Panel a: predicted mixing depth dynamics by FLake under present climate and future climate. Panels (c-d): Comparison between observed and predicted water quality variables under current climate conditions. The predicted oxygen concentrations are plotted for both the epilimnion (_Epi), while a surface layer (_Surf) is plotted in the total nitrogen and Chlorophyll-a which models surface cyanobacterial accumulation.

We combined the field measurements from the period from 2003-2016 (see appendix B for dataset, combinedly shown in Figure 2 c-d & Figure SI-3), to valid the PCLake+ performance. A suite of water quality data was measured intermittently with water samples taken in the epilimnion, at ~50 cm below the water surface. We ran PCLake+ for a period of 30 years to reach equilibrium states which are no longer dependent on the initial states. The simulation results of the last year was used for validating if the model is able to capture the generic dynamics of the lake ecosystem. Without any calibration of the default model parameters, PCLake+ showed an overall adequate performance in capturing the generic water quality dynamics in the study lake, especially regarding timing of the onset and offset of summer peaks (see Figure 2, panels c-d). The statistical agreements between the simulation and observation data were evaluated on the coefficient of determination (R^2) and Root Mean Square

Deviation (RMSE). To exemplify, O_2: $R^2 = 0.36$, Root Mean RMSE = 2.04 mg/L; TN: $R^2 = 0.40$, RMSE = 0.71 mg/L; Tot-Chla: $R^2 = 0.44$, RMSE = 13.3 μg/L.

5.2.4 Scenario analysis

(1) Restoration scenarios: After validation of the model performances, we simulated different restoration scenarios that can potentially tackle the water quality deterioration in Lake De Omloop. Note that no real restoration has taken place in the lake to date. We evaluated two different types of restoration scenarios with respect to their impacts on the lake ecosystem states and subsequently ecosystem service provisioning. The restoration scenarios include a technology-based measure – phosphorus reduction, and a nature-based measure – wetland restoration. We undertook a bifurcation analysis of the validated model for the studied quarry lake, to study how the lake ecosystem responds to different levels of restoration intensities. For each level of restoration, the model output variables during summer period (day 150 to day 210) were averaged to represent the response of ecosystem states as well as ecosystem service provisioning.

Technology-based restoration scenarios exhibit variable effectiveness in P reduction (Zhan et al., 2022). We simulated the full spectrum of P reduction effectiveness ranging between 0% and 100% (with 7% increments), to investigate the impact of varying levels of effectiveness on ecological states and subsequently ES provisioning. A P reduction of 0% represents the initial condition without restoration treatment, while a P reduction of 100% represents that the lake is devoid of phosphorus loading. A complete removal of phosphorus loading is not common in practice but theoretically can be achieved by technological approaches, for instance, through using a filtration system with P-binder pumping water thoroughly and repeatedly. Note that we assume technology-based measures solely reduce P without affecting nitrogen (N). This assumption is based on the fact that P is often the primary target element for most chemical adsorbents, though some engineering measures, such as dredging, target both P and N (Zhan et al., 2022).

In addition, we investigate the effectiveness of nature-based restoration scenarios in the form of purifying wetland creation. This was carried out via expansion of the wetland fraction in the model, a parameter representing the size of the wetland area relative to that of the lake area ranging between 0 and 100%. Several ecological processes are present in the wetland module: transport and settling of suspended solids, denitrification, nutrient uptake by marsh vegetation (increasing nutrient retention), and improvement of habitat conditions for predatory fish. The substances and process descriptions (mineralization, settling, P adsorption, nitrification and denitrification) are analogous to those in the lake model, except that the water depth is much lower (default 0.5 m), settling velocities are higher due to the absence of wind action and resuspension is assumed to be zero. Phytoplankton is assumed not to grow in the shadow of the reed vegetation. Mixing between the water columns of the lake and the wetland is described by an exchange coefficient (representing both dispersive transport and transport due to water level changes) multiplied by the concentration difference. We explored the impacts of an increased coverage of wetland area ranging from 10% to 100% (relative to water surface area, with 5% increments). Theoretically, however, this value can go beyond 100%., representing a larger wetland area relative to that of the lake.

To assess the magnitude of restoration effects, we applied linear regression models to the scenario results. For ecosystem state indicators, we calculated a slope-to-intercept ratio (=slope/intercept, in %) as a standardized indicator metric for the magnitude of change in the ecosystem state variables in relation to their initial levels. For instance, a slope-to-intercept ratio of 100% or -100% indicates that, with 100% increments in restoration intensity, the response variable is increased or decreased by 100%, respectively, compared to their initial states without restoration. As for ecosystem services provisioning that are scaled and ranging between 0-1, we convert the slope into percentage as an indicator of the magnitude of the response. We reported the adjusted R-square of the regression model that corrects for the sample size effect (Thompson, 2007). An adjusted R-square value of 1 represented a linear relationship, whereas a value smaller than 1 indicates a non-linear relationship, validated by a visual inspection. All statistical analyses were performed in R language (Team, 2019b).

(2) Climate change: To evaluate the impacts of climate change on ecosystem states and subsequent service delivery, we followed the predictions of future climates scenarios for the Netherlands by KNMI (Royal Netherlands Meteorological Institute Ministry of Infrastructure and the Environment; Attema et al. 2014). We implemented the climate scenario changes for the prediction of climate around 2050 under global warming and high changes in air circulation patterns, representing the "most extreme" scenario at that time. This scenario shows an increase in air temperature by 2.3 °C, an increase in precipitation by 5%, and an increase in solar radiation by 1.2%. These future climate conditions were first implemented in FLake for simulation of lake physics under climate change, from which the outputted mixing depth and water temperature vertical profile were used to force PCLake+ for prediction of lake ecology. To assess the magnitude of difference in ecosystem responses between two climate scenarios, we calculated an effect size metric using Hedges's g_s (Lakens, 2013). Effect size is regarded as a standardized metric which can be understood

regardless of the scale of measured variables. For interpretation of effect sizes we followed adopted Hedges's g_s thresholds: no evidence ($|g_s| < 0.2$); weak ($|g_s| < 0.5$); moderate ($|g_s| <0.8$) and strong ($|g_s| >= 0.8$) (Munthali et al., 2022; Thompson, 2007). We used *R* package *effsize* for the effect size calculations (Torchiano, 2016). For visualization of our results, we used a color-blind-friendly color palette following (Wong, 2011).

5.3 Results

5.3.1 The impacts of restoration scenarios on ecosystem state indicators

The responses of ecosystem state indicators and ecosystem service provisioning upon exposure to increasing restoration intensity are depicted in Figure 3 and 4, with statistics of regression analyses summarized in Table SI - 2 and 3, respectively. Overall, both P reduction and wetland restoration scenarios showed positive eutrophication control effects, with increased epilimnion oxygen concentrations (For P reduction: slope/intercept= 5%, adjusted $R^2 = 0.98$; For wetland restoration: slope/intercept = 2%, adjusted $R^2 = 0.99$), increased Secchi disc depths (For P reduction: slope/intercept = 64%, adjusted $R^2 = 0.83$; For wetland restoration: slope/intercept = 90%, adjusted $R^2 = 0.98$), and decreased cyanobacteria concentrations in upper layer (For P reduction: slope/intercept = -47%, adjusted $R^2 = 1.00$; For wetland restoration: slope/intercept = -43%, adjusted $R^2 = 0.93$). In addition, light conditions for macrophyte growth were improved, indicated by greatly increased critical depths (For P reduction: slope/intercept = 113%, adjusted $R^2 = 0.98$; For wetland restoration: slope/intercept = 129%, adjusted $R^2 = 0.99$).

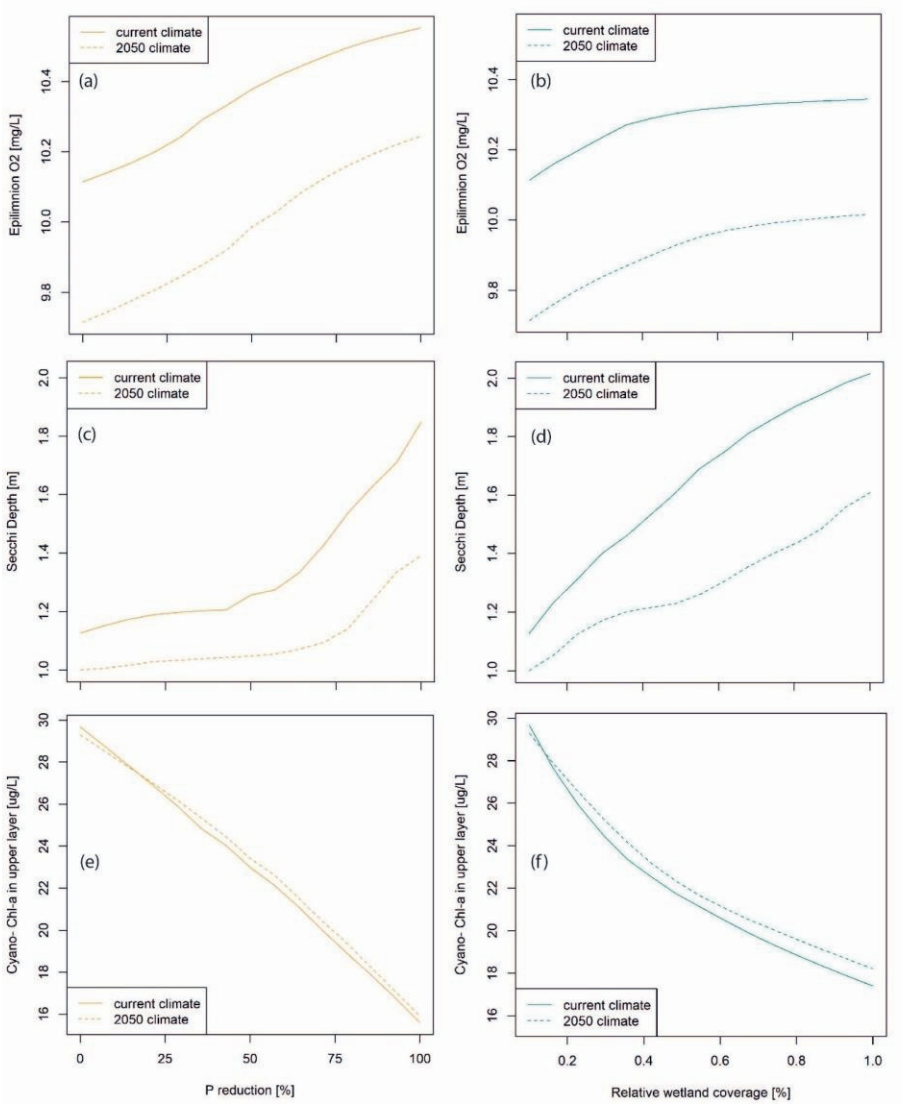

Figure 3. *The response of ecosystem state indicators to increasing intensity of a technical restoration (dark yellow) or a nature-based solution (green). The solid lines represent the current climate, while the dashed lines represent the future 2050 climate scenario.*

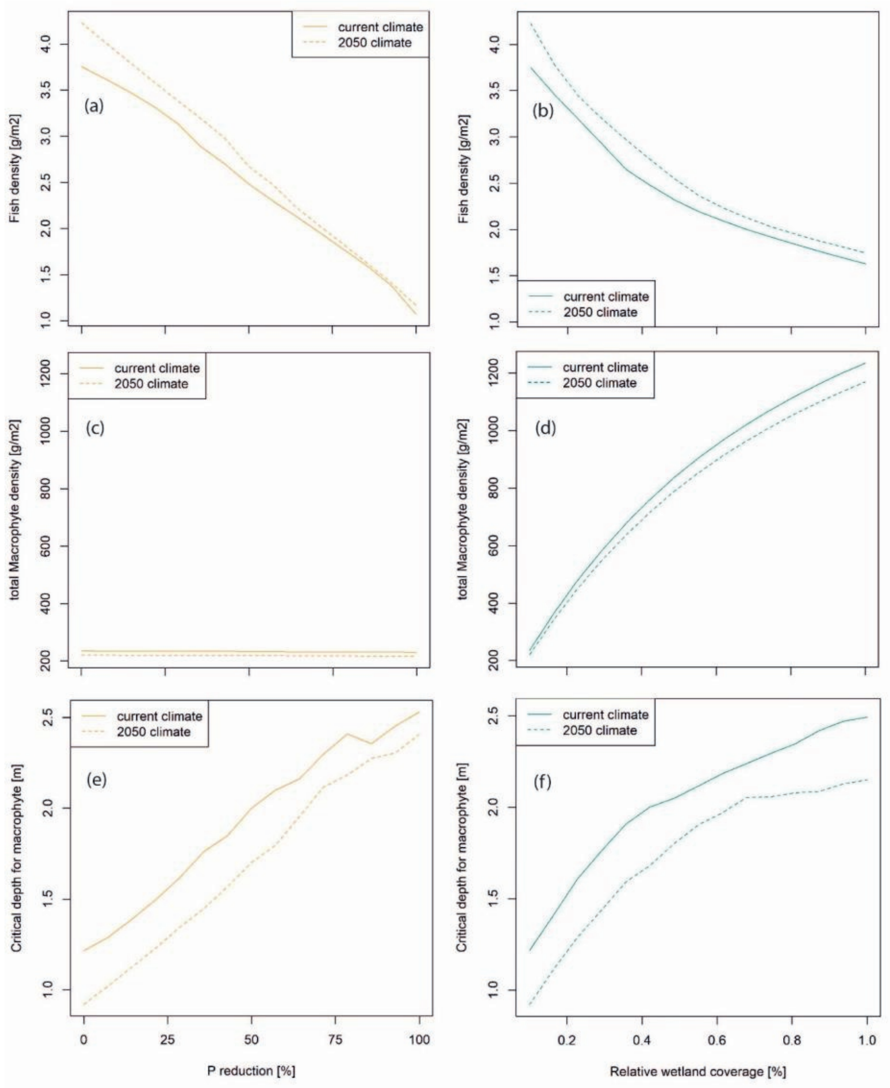

Figure 4. *The response of ecosystem state indicators to increasing intensity of a technical restoration (dark yellow) or a nature-based solution (green). The solid lines represent the current climate, while the dashed lines represent the future 2050 climate scenario.*

However, improved light conditions by P reduction did not lead to increase in the total macrophyte density (helophyte in wetland zone + vegetation in lakes in g/m^2: slope/intercept = -2%, adjusted R^2 = 1). In contrast, wetland restoration led to largely increased total macrophyte density (slope/intercept = 435%, adjusted R^2 = 0.96). Helophyte densities in wetland zone that are not light-limited showed a slight decline in response to both measures (For P reduction: slope/intercept = -2%, adjusted R^2 = 1.00; For wetland restoration: slope/intercept = -5%, adjusted R^2 = 0.92). The total fish biomass was decreased upon exposure to both restoration scenarios (For P reduction: slope/intercept = -70%, adjusted R^2 = 1.00; For wetland restoration: slope/intercept = -62%, adjusted R^2 = 0.92).

5.3.2 The changes of ecosystem service delivery in response to restorations

In general, the restoration scenarios led to an increase in most ESs provisioning including macrophyte habitats (For P reduction: slope = 30%, adjusted R^2 = 0.92; For wetland restoration: slope= 57%, adjusted R^2 = 0.92), phosphorus sequestration (For P reduction: slope= 44%, adjusted R^2 = 0.87; For wetland restoration: slope = 60%, adjusted R^2 = 0.76), irrigation (For P reduction: slope = 21%, adjusted R^2 = 1; For wetland restoration: slope = 19%, adjusted R^2 = 0.99), and swimming (For P reduction: slope = 14%, adjusted R^2 = 0.92; For wetland restoration: slope = 16%, adjusted R^2 = 0.96).

However, two services decreased in response to restorations, namely bird watching (For P reduction: slope = -7%, adjusted R^2 = 0.88; For wetland restoration: slope = -2%, adjusted R^2 = 0.36) and fishing (For P reduction: slope = -30%, adjusted R^2 = 1.00; For wetland restoration: slope = -25%, adjusted R^2 = 0.92). These two measures are closely dependent on fish biomass, which are reduced by both restoration scenarios. While the P reduction measure showed no effect on nitrogen retention, the wetland restoration measure improved both phosphorus and nitrogen retention capabilities (For wetland restoration: slope coefficient = 0.25, intercept coefficient = 0.03, R^2 = 1.00, $p < 0.001$). For ESs that are dependent on macrophyte biomass, P reduction showed weak effects (For thatching: slope = -1%, adjusted R^2 = 1; For particle capture: slope = -1%, adjusted R^2 = 1), whereas wetland restoration showed positive effects (For thatching: slope = 9%, adjusted R^2 = 0.17; For particle capture: slope = 5%, adjusted R^2 = 0.12).

Most ESs responded non-linearly to the intensity of the restoration measures (see Figure 5), with the effects on ES being overall more pronounced at intensified interventions. For macrophyte habitat, the restoration effects were marginal until P reduction reached 50% or wetland coverage was larger than 30%. For nitrogen retention, a response was only found after the wetland coverage reaches ca. 30%. For phosphorus retention, P reduction showed increased effect with intensified interventions, whereas the wetland restoration effect declined with increased wetland coverage. Similar response patterns were found for swimming service under P reduction, where a positive response emerged only after P reduction of ca. 50-70%.

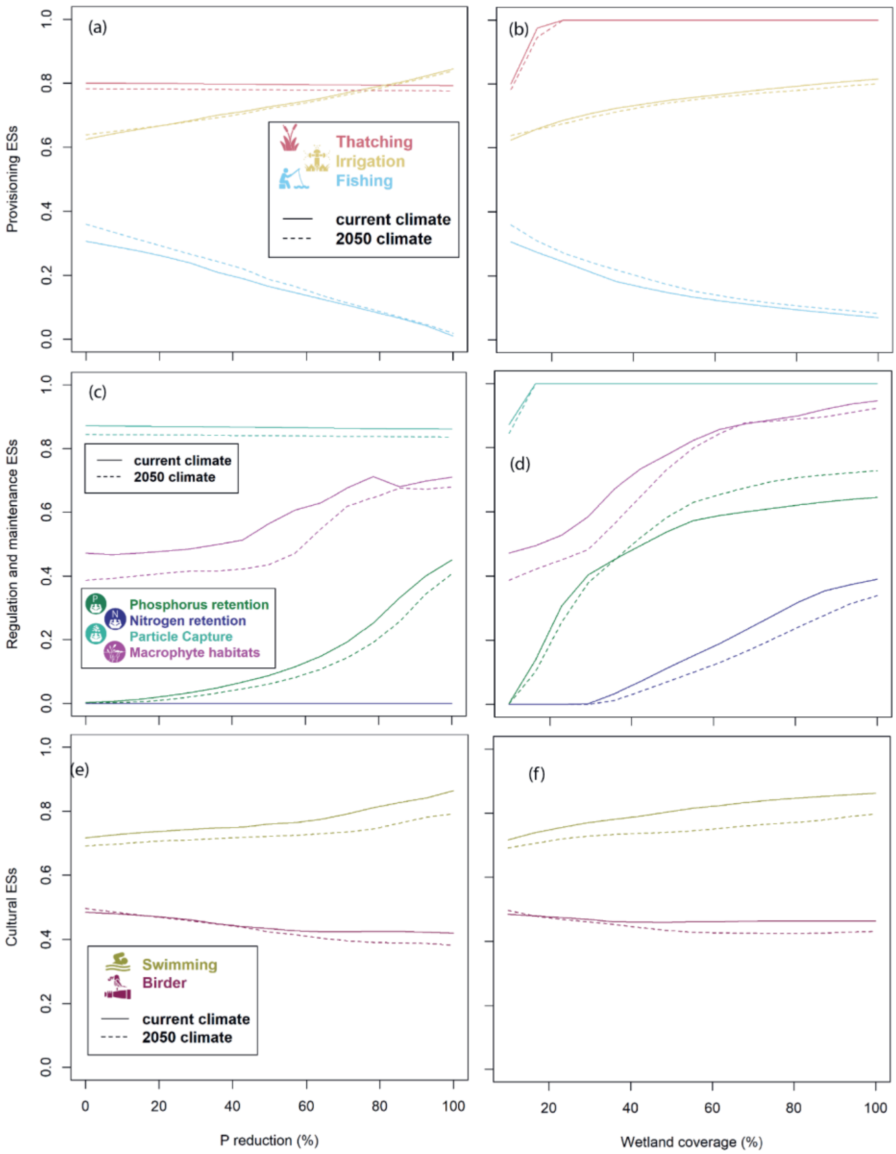

Figure 5. *The responses of ecosystem service provisioning to P reduction (left panels) or wetland restoration (right panels). The solid lines represent the current climate, while the dashed lines represent the future 2050 climate conditions. Icons are in the same colors as the corresponding services for illustrative purpose.*

5.3.3 Climate change impacts on ecosystem state indicators and ecosystem services provisioning

Under the 2050 Dutch climate change scenario (see dashed lines in Figure 3-4 for bifurcation analyses, and Figure 6 for the statistics of Hedges's g_s effect size test), eutrophication symptoms were reinforced with declined oxygen concentrations in both epilimnion (For P reduction: strong Hedges's g_s; For wetland restoration: strong Hedges's g_s) and hypolimnion (For P reduction: strong Hedges's g_s; For wetland restoration: strong Hedges's g_s), decreased Secchi disc depth (For P reduction: strong Hedges's g_s; For wetland restoration: strong Hedges's g_s). Though the cyanobacteria chlorophyll-a in the upper layer (surface + epilimnion) showed negligible increase under future climate conditions (For P reduction: no evidence Hedges's g_s; For wetland restoration: no evidence Hedges's g_s), the surface bloom showed a strong response (For P reduction: moderate Hedges's g_s; For wetland restoration: strong Hedges's g_s). Climate change showed a negative effect on macrophyte growth under P reduction scenarios (For P reduction: strong Hedges's g_s), whereas negligible effect was detected upon exposure to wetland restoration (no evidence Hedges's g_s).

Ecosystem state indicators

	DO (mg/L)	Secchi depth (m)	Cyano- Chla (μg/L)	Fish density (g/m2)	Total macrophyte density (g/m2)	Critical depth for macrophyte (m)
Phosphorus Reduction	-2.15	-1.32	0.06	0.21	-9.56	-0.48
Wetland Restoration	-4.14	-1.42	0.16	0.29	-0.15	-0.27

Ecosystem services provisioning

	Macrophyte habitat	Phosphorus retention	Nitrogen retention	Irrigation	Swimming	Thatching	Bird watching	Fishing	Particle capture
Phosphorus Reduction	-0.63	-0.21		-0.04	-1.11	-6.9	-0.4	0.21	-8.16
Wetland Restoration	-0.24	0.17	-0.29	-0.16	-1.45	-0.06	-1.29	0.29	-0.05

Effect of climate change		Hedges' g
Decreasing	Strong evidence	g < -0.8
	Moderate evidence	-0.8 < g < -0.5
	Weak evidence	-0.5 < g < -0.2
No effect	No evidence	-0.2 < g < 0.2
Increasing	Weak evidence	0.2 < g < 0.5
	Moderate evidence	0.5 < g < 0.8
	Strong evidence	g > 0.8

Figure 6. *Summary of effect size values using Hedges's g_s. DO = dissolved oxygen, Cyano- Chla = cyanobacterial chlorophyll-a. Strength of evidence takes the form of no, small, medium and large, with positive Hedges's g_s indicating an increase under future climate conditions and negative Hedges's g_s indicating a decrease. Note that DO here stands for epilimnion DO concentration, and cyano- Chla stands for cyanobacterial chlorophyll-a in the upper layer (surface + epilimnion). Statistics for hypolimnion DO and cyanobacterial chlorophyll-a in the surface layer can be found in Table SI-2.*

The provisioning of almost all ESs was hampered under future climate conditions (see dashed lines in Figure 5 for bifurcation analyses), with the effect sizes varying among ESs and upon restoration scenarios (Figure 6). The service 'swimming' was vulnerable to climate change (For P reduction: strong Hedges's g_s;

For wetland restoration: weak Hedges's g_s). In contrast, the service 'fishing' showed limited improvement in suitability under 2050 Dutch climate conditions (For P reduction: weak Hedges's g_s; For wetland restoration: weak Hedges's g_s). Relative to P reduction, wetland restoration was able to mitigate climate change impacts on macrophyte-related ESs, which includes macrophyte habitat (For P reduction: moderate Hedges's g_s; For wetland restoration: weak Hedges's g_s), the availability of macrophytes for thatching (For P reduction: strong Hedges's g_s; For wetland restoration: no evidence Hedges's g_s), and particle capture (For P reduction: strong Hedges's g_s; For wetland restoration: no evidence Hedges's g_s).

5.4 Discussion

Our modeling framework enabled us to evaluate how the provision of nine ecosystem services in a quarry lake was impacted by a technology-based (phosphorus reduction) and a nature-based (wetland restoration) restoration scenario, under current and future climate scenarios. To this end, we provided an ecosystem service modeling approach that comprehensively incorporates complex ecosystem processes, filling what had been, to the best of our knowledge, a previously existing gap. Our results indicated that both types of restoration scenarios could mitigate eutrophication symptoms. However, the effectiveness of both restoration measures did not linearly increase with the restoration intensity. The ESs that require good water quality were improved, including swimming, irrigation and macrophyte habitat, whereas services requiring more productive systems were hampered (sport fishing and bird watching). Overall, climate change showed negative impacts on the provisioning of ESs.

5.4.1 The effectiveness of restoration scenarios on ES provisioning

The technology-based solution simulated in this study focused solely on phosphorus reduction, as phosphorus is the commonly targeted element in geo-engineering approaches (e.g., through the application of lanthanum-modified bentonite). Solutions that also target N are available, such as dredging or some chemical amendments (Gibbs et al., 2011). In contrast, the nature-based solution, i.e., wetland restoration, in our simulation targeted both nitrogen and phosphorus simultaneously. Furthermore, it can also contribute to removal of organic materials, which not only consists of organic carbon, but also contains organic nutrients (Reinl et al., 2022).

The technology-based solution simulated was more effective at high degrees of intensity, suggesting a lagged system response to the reduction of phosphorus loading. Such delayed system response could be attributed to the relatively high background nutrient loading and eutrophic state of this lake, suggested by the high internal loading measured from the lake sediments (1.35 mg P/m^2/day, see SI section 2). In lakes that are degraded for years, most of nutrients are locked in biological forms, which are less available for nutrient binding (Zhan et al., 2022). Moreover, the nutrients released from sediments will be brought into the upper water layer during wind mixing, which constantly charges the primary production (Schindler, 2006).

In contrast, wetland restoration showed an opposite relationship, i.e., decreased effectivity with larger wetland coverage. This is in contrast to previous studies on eutrophication control by wetland restoration suggesting that only a large percentage of wetland area led to a significant restoration effect (Janse et al., 2001; Sollie et al., 2008). However, these studies were carried out on shallow lakes. Deep lakes are inherently different due to their pronounced seasonal stratification and water column mixing (Wetzel, 2001). Deep lakes showed higher water column stability due to stratification (Crisman et al., 2005). A potential explanation of our contrasting results could be that deep systems tend to become less stable with increased wetland restoration, impairing the wetland restoration effectiveness.

Overall, our results revealed non-linear impacts by restoration scenarios on the ecosystem state indicators as well as on the provisioning of ecosystem services. These results hint at the existence of a threshold relationship between restoration efforts and societal benefits in the form of ecosystem services (Iwasa et al., 2007). In other words, incremental increases in restoration efforts do not translate into proportionate enhancements in the water quality or the provisioning of ecosystem services. Our modeling outcomes underscore the presence of an optimum level of restoration efforts, that produces the desired outcomes. Hence, river basin authorities and policy makers should be aware of such non-linear responses in their ecosystems and their services, and make use of tools such as the one presented here to better understand the optimal effort needed to reach desired outcomes.

5.4.2 Climate change impacts on ES delivery

We used FLake to provide a more explicit description of mixing regime and vertical water temperature, which was then used to force PCLake+ for predicting lake ecosystem dynamics under future climate conditions. The model performance was validated by comparing with observed water quality data under current climate condition. Note that we took a simplified approach to climate change in this study, focusing on direct impacts to the lake ecosystem itself. However, over the time span of restoration, compounding changes may also take place that are not considered in the model, from climatic impacts on the wider catchment, e.g., increased droughts, land use change, increasing runoff, to changing nutrient loads and load ratios. The predicted impacts of climate change on eutrophication symptoms, including higher surface cyanobacteria biomass and lower water transparency, align with findings from earlier studies on climate change effects on freshwater ecology (Jeppesen et al., 2020; Nielsen et al., 2014). FLake predicted a prolonged summer stratification in 2050 climate scenario compared to the current climate conditions, which is in line with previous modeling studies (Feldbauer et al., 2022).

Our results indicate that climate change, overall, may have negative impacts on eutrophication control and ES provisioning, with the effects being more pronounced on the direct ecosystem state indicators than the ES provisioning. This supports the conclusion from previous studies (Zhan et al., 2022, 2021b) that an intensification of nutrient intervention measures could overcome the negative impacts by climate change. In other words, to acquire the same magnitude of eutrophication control or ES provisioning, higher intensities of restoration measures (both technical-based and nature-based solutions) will be required under future climate conditions. Moreover, the Hedges's *g* effect size tests on climate change impacts showed that wetland restoration had overall lower effect size values, which indicates that nature-based solutions as restoration approach may offer greater potential for climate-adaption and resilience of wetland ecosystems.

5.4.3 Strengths and future development possibilities of the ES modeling framework

By building an ecosystem service module into a modeling framework that incorporates complex physical and ecological processes, our approach was able to study the linkages between ecosystem states and ecosystem services in a more quantitative way, as a follow-up of the recommendations by previous studies (Janssen et al., 2021; Seelen et al., 2021a). Using our approach, managers can make more quantitative estimations of ES provisioning under different restoration scenarios, their effectiveness, and how they might evolve in the future.

Our results suggest a conflict between good water quality (low primary production and biomass) and high fishery production, as claimed in previous studies (Matsuzaki et al., 2018; Seelen et al., 2021a). By integrating multiple ESs into one framework, we were able to illustrate the contrasting requirements of ecosystem states by different services, thus studying possible trade-offs between ESs (Janssen et al., 2021).

Our ES modeling framework can pave the way for comprehensive cost-benefit assessment between restoration scenarios. The monetary cost of wetland restoration was demonstrated by field applications to be higher over an order of magnitude than in-lake measures (Huser et al., 2016). In addition, nature-based solutions such as wetland restoration have higher demands of space and time, which are usually limited in intensively populated urban areas (Cooke et al., 2018). Which measure to select requires a comprehensive evaluation of its effectiveness as well as economical cost. In this study, we studied the scenarios of two restoration measures individually in order to derive mechanistic understanding of their individual impacts. However, our modeling framework is capable of evaluating a mix of the two restoration measures to study their combined effects.

It is important to recognize that our modeling outcomes represent a knowledge-based estimation of how ecosystems might respond to the two restoration scenarios tested, built upon a set of assumptions such as an extended timeline for restoration to take effect. In practice, restoration effectiveness will depend on a combination of political, societal, economic and ecological factors. Our model offers managers and policy makers an evidence-based, first-order impact assessment from an ecological standpoint, highlighting potential benefits gained or lost in terms of ecosystem service provisioning due to an envisioned restoration scenario. Importantly, our model provides working hypotheses on restoration strategies that need to be validated by experimental approaches and/or observational data.

Our analysis is not exhaustive of all ecosystem services provided by freshwater lakes. It is limited by the ability to quantify ESs as well as the capabilities of PCLake+ of modeling the required ecosystem state indicators, being limited to water-based ecosystem services. In addition, the assessment of ES suitability often relies on people's perceptions and can vary across cultures (Pereira et al., 2020). For instance, people's perception of aquatic plants as nuisance is found to be dependent on their relation to the area, with visitors being less likely than residents to perceive macrophytes as a nuisance (Hussner et al., 2017). Seelen et al. (2019) survey data shows Europeans greatly underestimate their personal water use. To achieve a wider range of ecosystem services in our modeling framework, we envision expansions and improvements to the current model, such as making greenhouse gas fluxes explicit (Santos et al., 2022a) and utilizing our model across lake networks (Sven Teurlincx et al., 2019; van Wijk et al., 2022). Our modeling framework is designed to facilitate the incorporation of new and adjusted ecosystem services and is easy to modify. Importantly, making it open source allows for the synthesis of multidisciplinary knowledge required for ecosystem service assessment.

5.5 Conclusion

Incorporating an ecosystem service module into a modeling framework that considers complex physical and ecological processes has allowed us to explore the linkages between ecosystem states and ecosystem services in a quantitative manner.

Our study employed this framework to a quarry lake, and evaluated the impacts of two restoration scenarios on ecosystem state indicators and provisioning of ecosystem services (ESs) under current and 2050 climate scenarios, leading to several take-home messages:

1. Our scenario analyses revealed non-linear relationships between the level of restoration intensity and the resulting outcomes of ecosystem service provisioning. Phosphorus reduction scenarios demonstrated increasing effectiveness with higher intensities, while the intensive wetland construction tended to exhibit decreasing effectiveness in the studied deep lake.
2. Both measures showed positive effects on ESs that requires good water quality, such as swimming, irrigation, and macrophyte habitat. However, they had negative effects on ESs that require more productive systems, such as fishing and bird watching.
3. Climate change had adverse impacts on the effectiveness of restoration measures regarding ecosystem state indicators and ESs provisioning. To achieve the same level of eutrophication control and ES provisioning, greater intensities of restoration measures (both technology-based and nature-based solutions) will be necessary under future climate conditions. Notably, our results indicate that nature-based restoration may display greater resilience to climate change, as evidenced by their overall weaker climate change effects.

Our ecosystem service modeling framework equips managers with the instruments to quantitatively estimate ES provisioning under various restoration scenarios, assess their effectiveness, and anticipate how the restoration impacts may evolve in the future. In conclusion, this framework is a valuable resource for decision-makers seeking optimal restoration strategies while considering the challenges posed by climate change.

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Supplementary information:

Process-based modeling for ecosystem service provisioning: Non-linear responses to restoration efforts in a quarry lake under climate change

CHAPTER VI

Chapter VI- General Discussion

6.1 Recap of the main objectives and outline of the general synthesis

We have entered the Anthropocene, an era characterized by unprecedented human impacts on ecosystems, and these impacts are projected to escalate due to the growth of the world's population which is expected to peak in the mid-2080s (Lewis and Maslin, 2015; Steffen et al., 2011). Consequently, there is an increasing demand for ecosystem services across almost all types of ecosystems (Carpenter et al., 2009), leading to the degradation of various habitats, including freshwater ecosystems (Dodds et al., 2013). Another significant driver of ecosystem degradation is the ongoing climate warming since the 1950s, which is primarily attributed to human activities (likelihood > 95%) (Change, 2022). Climate change has been well-documented as a critical factor contributing to water quality deterioration in aquatic ecosystems (Moss et al., 2011).

In response to these challenges, several aquatic ecosystem restoration measures have been developed and implemented (Waajen, 2017). However, uncertainties persist regarding the robustness of these measures in the face of climate change. In addressing this crucial question, I have followed a framework proposed in Chapter I, which integrates four key components of aquatic ecosystem restoration (Figure 6-1): environment pressures, ecosystem functions, ecosystem services, and restoration measures.

In Chapter II, we conducted a microcosm experiment to investigate the impacts of two climatic stressors on primary production and nutrient dynamics. Moving on to Chapter III, our focus was to evaluate the effectiveness of a widely used nutrient intervention measure, Lanthanum-modified Bentonite (LMB), when subjected to a heatwave. The experiment excluded primary producers, allowing me to focus on abiotic nutrient fluxes and greenhouse gas emissions at the water-sediment interface.

In Chapter IV, we evaluated four restoration measures, including LMB, to assess their efficacy in controlling eutrophication under the disturbance of a heatwave. For this experiment, the complete species assemblage is included, allowing me to investigate changes in ecosystem function within a more complex environmental setting.

In Chapter V, we developed an ecosystem service (ES) modeling framework to establish a semi-quantitative link between ecosystem functions and the provisioning of ecosystem services. Using this framework, I evaluated gradients of intensities for two restoration measures under both current and future climatic conditions.

Finally, in this chapter I synthesize the results from Chapter II, III, IV and V to address five themes essential for climate-robust aquatic ecosystem restoration:

1) The interactions of multiple environmental stressors on ecosystem functions: Synergistic vs. antagonistic effects;
2) The short-term and long-lasting impacts of extreme climatic events on ecosystems;
3) The effectiveness of restoration measures under the disturbance of extreme climatic events
4) Gaining insights into the mechanisms to make steps towards climate-robust water quality management;
5) Evaluating lake restoration success based on ecosystem service delivery.

Overall, my thesis aims to shed light on critical aspects of aquatic ecosystem restoration to better inform future management strategies in the face of the challenges of the Anthropocene.

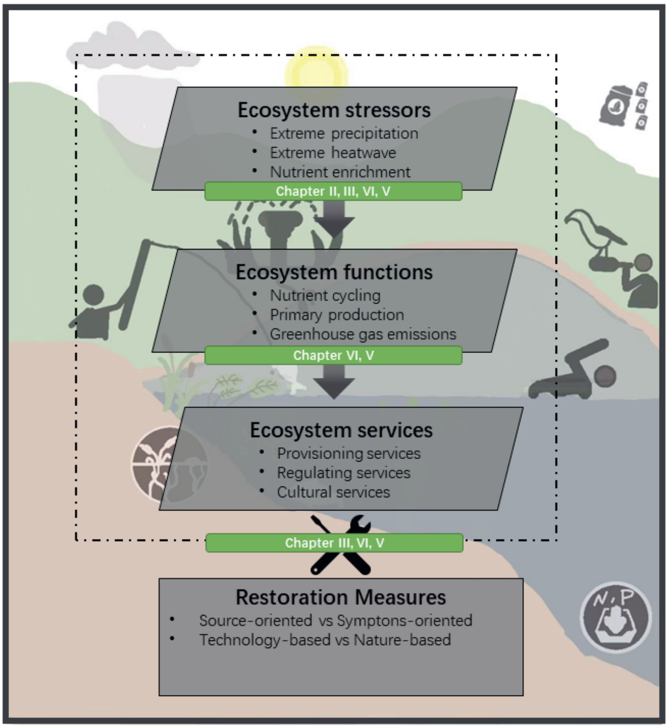

Figure 6-1. *Connections of Chapters to corresponding components in the framework (adapted from Figure 1-6 to align with the results of chapters).*

6.1.1 The interactions of multiple environmental stressors on ecosystem functions: Synergistic vs. Antagonistic effects

In the Anthropocene, our freshwater ecosystems face the impact of multiple stressors, and their interactions play a critical role in determining the ultimate responses of these ecosystems (Christensen et al., 2006). Here, stressors refer to any natural or anthropogenic pressure that leads to measurable changes, be they positive or negative, in biological response. Piggott et al. (2015) categorized potential interactions among multiple stressors into four types: 1) two single stressor effects oppose each other, 2) act in the same direction, 3) when both stressors have no effect individually, and 4) when one single stressor has a significant effect and the other stressor does not have a significant effect. Côté et al. (2016) further refined the conceptualization of the interactions among ecosystem stressors (see Figure 6-2).

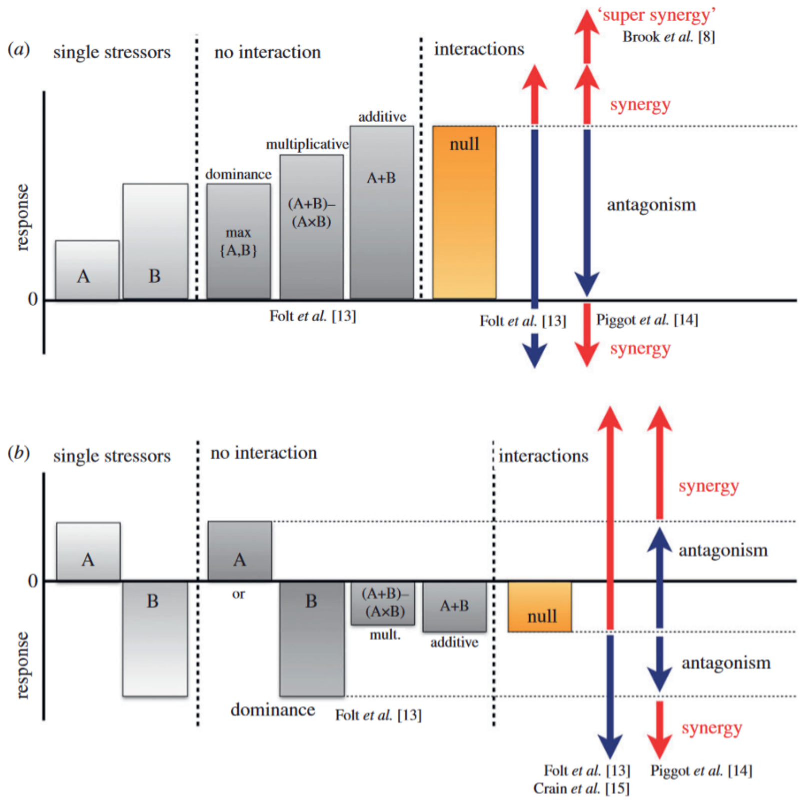

Figure 6-2. *Conceptual model for illustration of interactions among multiple stressors from Côté et al. (2016). (a) Two stressors (A and B) impact a biological response in the same direction when acting separately. (b) Two stressors have opposing effects on a biological response.*

In this thesis, I explored three types of climatic stressors: prolonged warming (Chapters II and V), extreme heatwaves (Chapters III and IV), and extreme precipitation (Chapter II). By applying nutrient intervention measures, we studied the re-oligotrophication process (Chapters III, IV and V). Our findings provide support for the notion that phytoplankton blooms thrive in warmer conditions (Paerl and Huisman, 2008), as evidenced by increased phytoplankton proliferations under both "press" conditions (prolonged warmer temperature in Chapters II and V) and "pulse" perturbations (heatwave exposures in Chapters II and IV). Additionally, the results of Chapter II indicate that warmer temperatures favor cyanobacteria, consistent with some studies (S. Kosten et al., 2012; Lurling et al., 2018). However, in the mesocosm experiment conducted in an urban canal (Chapter IV), we did not observe a higher response in cyanobacteria biomass during the heatwave period in comparison to green algae and diatoms. Other studies have reported contrasting patterns where warming may lead to lower cyanobacteria abundance (Lürling et al., 2017b). S. Kosten et al. (2012) & Lurling et al. (2018) tested this hypothesis across 39 mesotrophic to hypertrophic lakes and found that 36% of the cases showed lower cyanobacteria with elevated temperature. Overall, the relationship between warmer conditions and cyanobacteria dominance is not conclusive and may be species-dependent (Lurling et al., 2018), likely influenced by other factors such as seasonal temperature variations or food web structure (Urrutia-Cordero et al., 2020).

The impacts of extreme precipitation event are inconclusive, influenced by various interconnected factors. On one hand, extreme precipitation can have a negative effect on primary production: runoff pulses may result in a hydrological diluting effect on phytoplankton biomass (Wood et al., 2017), and runoff water with high suspended solids can increase turbidity, limiting light availability for phytoplankton growth (Feuchtmayr et al., 2019; Kasprzak et al., 2017; Morabito et al., 2018). Conversely, nutrient pulses introduced by runoff events may also stimulate primary productivity and lead to increased phytoplankton biomass (De Senerpont Domis et al., 2013; Zwart et al., 2017). Our findings from Chapter II suggest that under eutrophic conditions, the hydrological diluting effects resulting from the extreme precipitation event outweigh the positive effects induced by nutrient addition.

In Chapter II, the treatments exposed to an extreme precipitation event and warming revealed an antagonistic interaction, although this effect seemed to be transient, likely due to the short-term impact of extreme precipitation. In the modeling study of Chapter V, the effects of climate change on ecosystem states varied across nutrient pollution levels for some biological parameters, leading to both antagonistic and synergistic outcomes. For instance, the modeling results demonstrated a synergistic interaction between nutrient pollution and climate change on fish biomass, while an antagonistic interaction was observed on water transparency (as indicated by Secchi depth). Previous research has highlighted a mixture of antagonistic and synergistic interactions between climatic stressors, with phytoplankton communities showing diverse responses to various climate scenarios (Bergkemper et al., 2018; A. D. Richardson et al., 2019). A meta-analysis of multiple stressor studies on freshwater ecosystems by Jackson et al. (2016) revealed that antagonistic impacts were predominant (48%), followed by synergistic (28%), and additive interaction (16%). Given the high variability in the interaction effects of multiple stressors, I think it is crucial for future studies examining multiple stressors to consider geographical differences. Geographical variations can influence the nature, frequency, and severity of stressors (Donat et al., 2016). Incorporating regional projections will guide the selection of appropriate climate stressors to assess the likely pressures and responses of aquatic ecosystems, as demonstrated in Chapter II. Accordingly, the composition of run-off treatment in Chapter II was simulated based on real world conditions in lake De Omloop, which served as a case study for validating our model expansion in Chapter V. For the same reason, in the climate change scenario of Chapter V, we applied the Dutch climate change scenarios conducted by KNMI (Royal Netherlands Meteorological Institute) to capture relevant regional impacts.

6.1.2 The short-term and long-lasting impacts of extreme climatic events on ecosystems

One of the prominent aspects of climate change is the increased intensification, frequency, and duration of extreme climatic events (ECEs) (Stott, 2016). Regional projections for the EU suggest more frequent and intense heatwave events (McGregor et al., 2005; Woolway et al., 2021), with higher temperature tracking an increase in higher intensity of precipitation events during summer (Klein Tank and Lenderink, 2009). Consequently, research on extreme climatic events has significantly increased (Easterling et al., 2000), accounting for one fifth of published papers on climate change research in 2006. ECEs studied in this thesis, i.e., extreme heatwaves (Chapters III and IV) and extreme precipitation events (Chapter II), are known for their sudden and short-term nature, raising questions about whether their impacts on ecosystems are also transient. (Van de Pol et al., 2017) identified three types of ecosystem responses to short-term pulse perturbations (see Figure 6-3): 1) short recovery, 2) long recovery (hysteresis), and 3) state change or regime shift. The findings from our experiments in Chapter II, III and IV can provide valuable insights into this question.

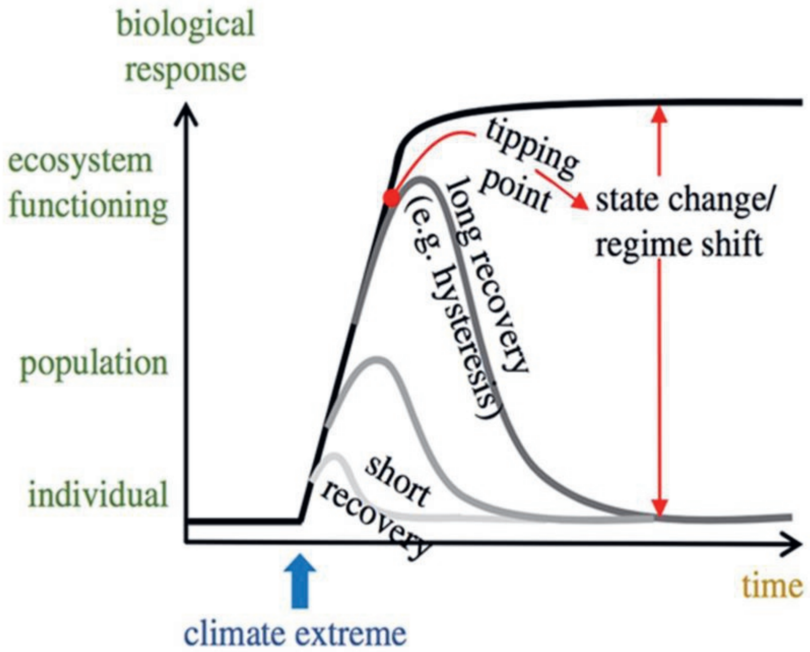

Figure 6-3. *Scenarios of biological response upon exposure to a climate extreme (Modified from Van de Pol et al. (2017).*

The results of our experiment in Chapter II indicate that the extreme precipitation event had minimal and short-lived effects on the microcosm assemblage. The phytoplankton biomass showed a temporary change (see Figure 2-1 b in Chapter II), recovering before the end of the experiment. The increase in suspended solids following the runoff application was also short-lived. The increased nutrient availability due to runoff did not result in long-lasting effects, although redox-sensitive and organic P fractions, which account for a large proportion of the runoff sediment P pools, might take longer to mobilize than the duration of our three-week experiment (Reinl et al., 2022).

In Chapter III, the before and after heatwave experimental design (BACI; Smith et al., 1993) allowed us to investigate the post-disturbance recovery of biogeochemical processes, as opposed to with continuous warming effects studied in Chapters II and V. The heatwave-induced P releases persisted until the end of the three-week experiment. Additionally, long-lasting effects of the heatwave were evident in the measurements of dissolved greenhouse gasses throughout the experiment in Chapter III (Figure 6-4), with an increase in CO2-equivalent concentrations upon heatwave exposure, followed by partial recovery, but ultimately settling at a higher GHG equilibrium compared to pre-heatwave levels and control groups. This indicated a regime shift according to Van de Pol et al. (2017).

In the two-month experiment conducted in a eutrophic urban canal with a more complex and real-world environmental setting (Chapter IV), the heatwave negatively impacted the effectiveness of all tested measures. This led to increased nutrient releases, elevated phytoplankton biomass, and reduced water clarity compared to the pre-heatwave phase. Notably, the system did not fully recover from the heatwave impacts, further supporting the notion that the effects of heatwave may be long-lived rather than transient.

In conclusion, our results suggest that the impact of extreme precipitation on a eutrophic system is likely to be transient, as the effect of nutrient addition through runoff might be offset by the dilution effect of runoff (Chapter II). Conversely, the impacts of heatwaves on a eutrophic system appear to be more persistent, lasting for weeks or even months (Chapters III and VI). It is important to realize the potential role that the trophic state of the study system plays in how extreme climatic events unfold. For oligotrophic systems, runoff events may likely lead to increased phytoplankton productivity (Reinl et al., 2021). To gain a deeper understanding, further research should validate these mechanisms in more diverse environmental settings, utilizing approaches such as mesocosm infrastructure that allows greater control over physical conditions (e.g., project Aquacosm: https://www.aquacosm.eu/), and employing higher temporal resolution of measurements (e.g., automatic monitoring techniques; Marcé et al. 2016).

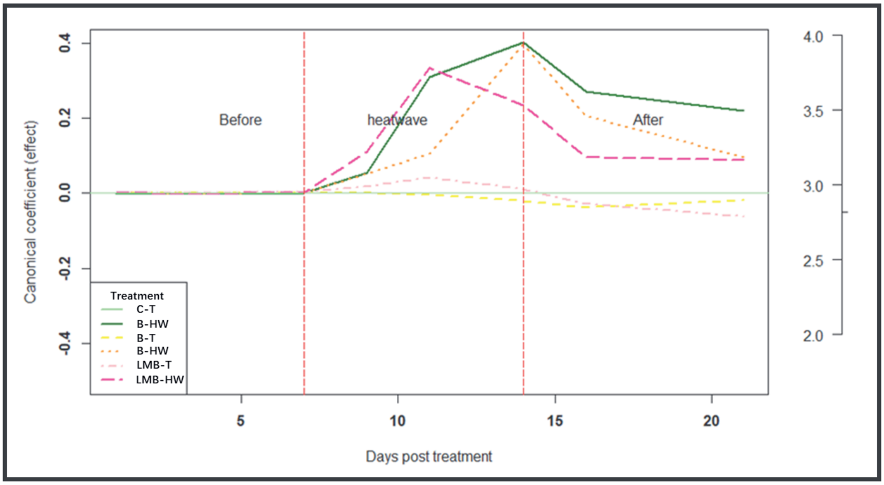

Figure 6-4. Principal response curve analysis (PRC; Paul J. Van den Brink and Braak, 1999) of the dynamics of CO2-equivalent over the course of the experiment in Chapter III. C-T in light green color: no nutrient intervention treatment + no heatwave treatment; C-HW in dark green color: no nutrient intervention + heatwave treatment; B-T in yellow color: Bentonite treatment + no heatwave treatment; B-HW in orange: Bentonite treatment + heatwave treatment; LMB-T in light purple: LMB treatment + no heatwave treatment; LMB-HW in dark purple: LMB treatment + heatwave treatment. The calculation of CO2-equivalent followed the equation:

$$CO2eq = 1/(1+21+310) * CO2 + 21/(1+21+310) * CH4 + 310/(1+21+310) * N2O$$

6.1.3 The effectiveness of restoration measures under the disturbance of extreme climatic events

The concept of ecosystem degradation leading to reduced resilience to environmental pressures has been a topic of discussion for some time (Holling, 1973; Scheffer et al., 2001). Scheffer et al. (2001) proposed the ball-in-valley model as a conceptual framework for ecosystem resilience (see Figure 6-5), wherein a desired ecosystem state is represented by a ball in a wider and deeper valley, signifying higher resilience to disturbances without transitioning to alternative states in neighboring valleys. A logical deduction of this theory would be that restoration of the degraded ecosystems can enhance their resilience to extreme climatic events disturbances (Standish et al., 2014).

Supporting evidence for this hypothesis includes studies such as Sheehan et al. (2021), which showed that rewilding of Protected Areas in Lyme Bay, United Kingdom, led to the enhanced recovery of reef assemblages after extreme storm disturbances, and Derolez et al. (2020), which showed increased resilience to anoxia crises after restoration in Thau lagoon upon heatwaves. Similarly, investigations into the oligotrophication of freshwater ecosystems suggest increased resilience to climate change, characterized by reduced phytoplankton biomass (Cabrerizo et al., 2020a) and lower greenhouse gas emissions (Aben et al., 2017; Davidson et al., 2015a; Marotta et al., 2014; Peacock et al., 2019). However, disagreements also exist, such as a controlled experiment by Stelzer et al. (2022), which did not observe differences in the response of the chlorophyll-a levels between different eutrophication levels to pulse perturbation of the oxidant hydrogen peroxide. In this thesis, we explored whether restored ecosystems exhibit higher resilience to climatic stressors, specifically assessing whether restoration measures can mitigate the impacts of ECE perturbations. Drawing from a 55-year dataset of reservoir water quality and quantity variables, Munthali et al. (2022) suggested improved resilience of water quality related variables to ECEs following significant nutrient reduction.

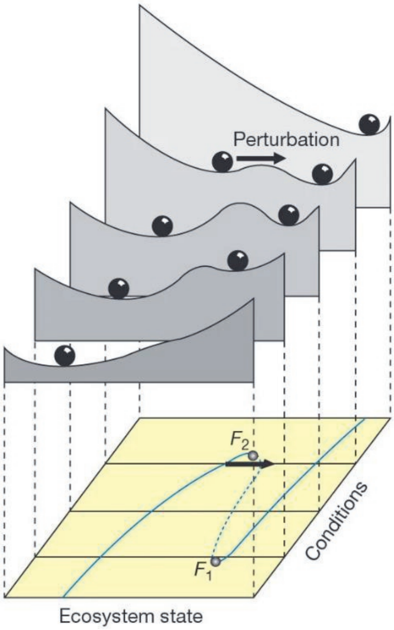

Figure 6-5. *Ball-in-valley conceptual model for illustration of the relationship between ecosystem conditions and ecosystem resilience (Figure from Scheffer et al. 2001, p. 200). The stability landscapes depict the equilibria and their basins of attraction at five different conditions. Stable equilibria correspond to valleys; the unstable middle section of the folded equilibrium curve corresponds to a hill. If the size of the attraction basin is small, resilience is small and even a moderate perturbation may bring the system into the alternative basin of attraction.*

Our experimental findings in Chapters III and IV demonstrated that our restoration measures, which involved intervening nutrient releases, effectively alleviated eutrophication symptoms. These measures led to decreased phosphorus (P) releases, reduced primary producer biomass, increased oxygen levels, and improved transparency, consistent with previous studies (Janse, 2005; D. W. Schindler, 1974; Waajen, 2017). However, when examining the response of the restored systems to heatwave events, our initial hypothesis that restoration measures can mitigate the impacts of ECE perturbations did not seem to be supported. In Chapter III, the heatwave treatment resulted in a significant 11% increase in P concentration. In the eutrophic microcosms of Chapter III, no significant heatwave impacts were observed, likely due to the dramatic nutrient releases overshadowing the heatwave effects. Furthermore, in Chapter IV, we observed increases in N and P concentrations during the heatwave period, and our linear-mixed effect models did not show significant differences between restoration and control treatments.

Additionally, the measurements of dissolved greenhouse gas (GHG) concentrations and nitrogen also did not suggest an increased resilience of the system to heatwaves. This was evidenced by a similar increase in the GHG concentrations between the restoration and control groups upon heatwave exposure in Chapter III and non-significant differences in GHG levels by the end of the two-month experiment in Chapter IV. A study by Nijman et al. (2022) in an 18-month experiment yielded contrasting results, showing that LMB and dredging can reduce methane emissions over a longer timeframe, as they only observed significant effects in the second year from the start of the experiment. This discrepancy might be explained by the kinetics of P inactivation by LMB, which requires a certain time for all binding sites to be occupied (Dithmer et al., 2016a), especially in the presence of high DOC (Lurling et al., 2014), as was the case in our systems. However, the different results could also be attributed to difference in the foodweb structure between our experiments (Chapter III: exclusion of primary production, Chapter IV: presence of phytoplankton) and their study (Nijman et al., 2022). Therefore, their contrasting results do not dismiss our speculation that microbial activities for GHG emission are less likely to be limited by reducing C, N and P availability (Redfield, 1958). Moreover, the nitrogen measurements in Chapter III suggested a stimulated nitrification by the heatwave with increased ammonium loss and the accumulation of dissolved oxidized nitrogen species, regardless of the restoration measures. These nitrogen and GHG concentration dynamics further indicate that microbial processes like mineralization, nitrification and denitrification are more temperature-sensitive (de Klein et al., 2017; Veraart et al., 2011) and less likely to be nutrient-limited, at least over the course of months.

On the other hand, the opposite hypothesis could also be supported: heavily impacted systems may be more resistant to a change upon perturbation. For instance, a shallow lake mesocosm experiment by J. Richardson et al. (2019) revealed that eutrophication treatments led to lower responses to heating compared to control groups. However, our experimental results in Chapters III and IV did not show any significant differences between restoration measures and control groups in their responses to the heatwaves. One potential explanation could be the under-dosing of our restoration measures, as discussed by Nijman et al. (2022). This speculation finds support in the modeling results of Chapter V, where we simulated a gradient of restoration intensities under current and future climate scenarios. We observed that negative climate change impacts on water quality became more pronounced relative to the current climate scenario along restoration intensities (evidenced by Secchi depth, Chl-a concentrations, fish biomass, and macrophyte). These results indicate that eutrophic systems might be less responsive to changes in climate conditions given their already advanced water quality deterioration, whereas oligotrophic aquatic ecosystems may be more sensitive to biogeochemical changes under climate change (Reinl et al., 2021). Nevertheless, our conclusions remain that the effectiveness of our restoration measures may be compromised under climate change, and an intensified restoration approach seems to be inevitable.

6.1.4 Evaluating lake restoration success based on ecosystem service delivery

In Chapter IV, our experimental results demonstrated the positive impacts of nutrient interventions on ecosystem functions, such as primary production and nutrient release. However, the implications of these changes in water quality parameters for human well-being may not be readily apparent to water managers and stakeholders, which hinders the effective evaluation of restoration measures (Seppelt et al., 2011). The concept of ecosystem service was adopted in Chapter V to address this limitation (Boyd and Banzhaf, 2007; Haines-Young and Potschin, 2012). In this chapter, we developed an ecosystem service modeling framework for lake ecosystems, following a threshold approach proposed by Seelen et al. (2021a). We expanded the ecosystem model - PCLake+ with an ecosystem service module, and we coupled it with a lake physics model - FLake to incorporate climate impacts. Our ES modeling tool contributes to addressing the poorly integrated water quality-related ecosystem services in the current ecosystem service modeling tools (Keeler et al., 2012).

While the mesocosm experiment in Chapter IV assessed the effects of one single dose of different types of nutrient interventions on eutrophication symptoms, our ES modeling framework in Chapter V allowed us to simulate a gradient of restoration intensities and evaluated their impacts on ecosystem service provisioning. Our ES framework demonstrated its capacity to study how stressors and system structure affect ecosystem services, providing valuable insights where knowledge is scarce (Hering et al., 2010). The results revealed non-linear impacts of restoration measures on the ecosystem state indicators as well as on the ecosystem service provisioning, suggesting a threshold relationship between restoration efforts and societal benefits in the form of ecosystem services. As restoration intensity increased, most ecosystem services, such as swimming, P retention, and macrophyte habitat, showed improvement, while those requiring a more productive system, like sport fishing and bird watching, were impaired. The framework also showed its capacity to assess the contrasting water quality requirements of different ecosystem services, as suggested by Seelen et al. (2021a). However, there are limitations that need to be addressed in follow-up studies. Firstly, the analysis is not exhaustive of all ecosystem services provided by freshwater lakes. It is limited by the quantifiability of ESs as well as the capabilities of PCLake+ on modeling the required ecosystem state indicators, being limited to water-based ecosystem services. Secondly, the evaluation of ES suitability is often influenced by people's perception, which can vary culturally (Pereira et al., 2020). For instance, people's perception of aquatic plants as a nuisance is found to be dependent on their relation to the area, with visitors being less likely than residents to perceive macrophytes as a nuisance (Hussner et al., 2017). Seelen et al. (2019) showed that perception of water threats can differ between scientists and nonscientists, with climate change impacts often being perceived as "abstract" threats, or less tangible relative to threats like industrial pollution, sewage overflow etc. Different approaches may be needed to collect and model impacts of such perception differences. For example, Thiemer et al. (2023) used a Bayesian Belief Network to integrate people's perception of macrophytes as nuisance or not into decision-making on use of restoration measures. Their survey data suggested that residents are more likely to perceive macrophytes as nuisance in comparison to visitors.

Last but not least, the concept of ecosystem service has been criticized for its anthropocentric nature (Silvertown, 2015), tending to neglect other values of ecosystems. Inclusion of diverse ecosystem value perspectives in decision-making is crucial for adaptive management under climate change (Pereira et al., 2020). To address this, frameworks like the Nature Future Framework (NFF) have been proposed, recognizing three value perspectives: Nature for Society (Nature's benefits to people, e.g., ecosystem services), Nature as Culture (Living in harmony people one with nature) and Nature for Nature (Intrinsic value of nature, space allocated for nature). Kramer et al. (2023a) demonstrated that currently aquatic ecosystem models have a strong focus on Nature for Nature and to some extent Nature for Society perspectives, but do not capture Nature as Culture.

Notwithstanding these limitations, our ES modeling framework provides a more comprehensive understanding of the potential benefits and trade-offs of restoration efforts, bridging the gap between ecological changes and their relevance for human well-being and decision-making processes. Additionally, it can contribute to improving the representation of freshwater ecosystems in global environmental assessment models (Environment, 2019; Potts et al., 2016). By describing restoration outcomes in the form of ecosystem services, water managers can better advocate for restoration efforts and work towards achieving the Water Framework Directive's aim of achieving 'good status' for all water bodies (with 47% of EU water bodies failing to meet the aim; Commission, 2012). To further promote the widespread use of our ES modeling framework, I envision expanding and improving the current model. This includes explicit modeling of greenhouse gas fluxes (Santos et al., 2022b), application of the model across lake networks (Kramer et al., 2023b; van Wijk et al., 2022), and incorporating the Dynamic Energy Budget principle for a more realistic representation of physiological processes (Troost et al., 2010). Importantly, our modeling framework is easily modifiable and open-source, allowing for the integration of multidisciplinary knowledge required for ecosystem service provisioning in diverse contexts.

6.2 Lake ecosystem modeling

Models are simplified representations of a lake ecosystem, with a series of mathematical equations describing the interrelations between water quality variables. They often carry a great deal of uncertainty, resulting from 1) model structure, where multiple equally valid representations of the system can exist; 2) uncertain parameter values that influence the model's behavior and outcomes; 3) uncertain initial states, which can impact the model's accuracy in predicting future states; and 4) observation errors, used for forcing, calibrating and validating the models against real-world data. There is a common question for every single model: "how truthful it is". For these kinds of questions, I often answer with a common aphorism by the statistician George Box: "all models are wrong, but some are useful" (Curchoe, 2020). I think there are two aspects of the "True or not", for one, models are only approximations of real-world, based on assumptions (whether implied or clearly stated). As a result, the truthfulness of a model cannot be unambiguously stated. On the other hand, it is debatable, from a philosophical point of view, whether a system is an entity that really exists, or whether it is a construct of the human mind to represent our mental conception (Descheemaeker et al., 2021). I would rather take away the "But" part, that "some models are useful". In this aspect, ecosystem modeling is a pragmatic approach that can help us to address real-world problems and increase our understanding of the functioning of the ecosystem. Thus, in Chapter V of this thesis, I focused more on the questions "Is the model good enough for this particular application?" Lake models are intensively used in water management as they enable us to evaluate variable scenarios on our lake ecosystem states at whole lake scale, as it was used in Chapter V. Afterall, experiments at the whole-lake scale are only possible in a few cases (Pace et al., 2019), but not applicable in most of the cases.

6.3 Gaining insights into the mechanisms to make steps towards climate-robust water quality management

In Chapters III and IV, we investigated four commonly used restoration measures. Chapter III focused on a geoengineering technique called Lanthanum-modified Bentonite (LMB), designed to immobilize phosphorus in sediments. Our results confirmed that the LMB's effect was a result of P inactivation (Haghseresht et al., 2009), showing no impact on nitrogen species. Bentonite-only treatment had no influence on P dynamics, underpinning that LMB's effect was not caused by a thin clay layer deposition on the sediment. This contrasts with the findings of Zamparas et al. (2012), who observed such a bentonite treatment effect in a shorter experiment (3h) with heavy mixing of the slurry with solution.

In Chapter IV, we extended our investigation to real-world conditions and examined three additional commonly-used nutrient intervention measures: sediment-dredging, iron-lime sludge (an iron-containing geoengineering compound) and aeration (artificial oxygenation). Among these measures, dredging and lanthanum modified bentonite exhibited the highest efficacy in controlling eutrophication. Interestingly, Lürling and Faassen (2012) suggest that combining these two measures could be more effective than using them individually. On the other hand, iron-lime sludge appeared less effective, likely due to reducing sediments hindering its iron-based P-binding capacity, consistent with findings from previous studies (Gächter and Müller, 2003). We also found that aeration, despite its widespread use, did not effectively control eutrophication in our shallow system (ca. 3m deep), likely due to air pumping enhancing sediment resuspension and nutrient release. Our results align with previous findings (Visser et al., 2016), supporting that aeration is only effective in deeper water systems. Our investigations in Chapter V, where we modelled the effects of wetland in controlling eutrophication, also revealed different responses between shallow and deep lakes. We observed decreased wetland purification effects with increased wetland coverage in our studied deep lake (7.7m), contrary to the findings of a previous modeling study on shallow lake (2m; Janse et al. 2001).

To summarize the interactions of these nutrient intervention measures with heatwaves (Chapters III and IV), we proposed a conceptual model (Figure 4-7 in Chapter IV). The model suggests that heatwaves lock nutrients in the biological P loop, involving the exchange between labile P and organic P, while the P fraction in the chemical P loop decreases. As a consequence, the efficacy of chemical agents targeting P-reduction through chemical binding is hindered during heatwaves. This phenomenon of bloom-induced internal nutrient release was also observed in a case study in Lake Taihu, China (Kang et al., 2023). To counteract the negative impacts by climate change, we recommend two strategies: 1) Implement restoration measures outside of the high primary production season, and 2) consider harvesting phytoplankton biomass to break the biological nutrient cycles. To enhance the efficacy of mechanical harvesting, robotic techniques may be used, e.g., Seacleaner project uses robotics for harvesting coastal litters (https://seaclear-project.eu/).

Summary:

Our climate is getting more and more extreme, with increasing frequency as well as the intensity of extreme climatic events (ECEs). It remains a question if our current restoration efforts are still effective under climate change and other increasing anthropogenic pressures. In Chapters II, III and VI, I used controlled experiments to evaluate two ECEs, including heatwave and extreme precipitation events on the ecosystem functions (primary productivity), and their impacts on the effectiveness of different eutrophication control measures. In Chapter V, I used a modeling approach to investigate how the sustainable ecosystem service provisioning is impacted by alternative restoration and climate scenarios. During my PhD research, I have carried out various types of methodologies including controlled experiments and modeling approaches.

In Chapter II, my co-authors and I addressed the concerns regarding the combined effects of multiple, coinciding stressors on phytoplankton. Our results further support that higher water temperatures under eutrophic conditions will support larger phytoplankton biomasses, especially cyanobacteria. However, the extreme precipitation event had minimal and short-lived effects on the microcosm assemblage. Overall, the combined effect of the two climate stressors resulted in an interaction lesser than that of the individual stressors, i.e., the precipitation runoff event was not amplified by temperature.

In Chapters III and VI, my co-authors and I tested the heatwave impacts on the effectiveness of different restoration measures by the laboratory microcosm experiment and in situ mesocosm experiment, respectively. Our results suggested that the efficacy of the four tested measures was hampered by a heatwave. We speculate that the heatwave, through its accelerating impacts on biogeochemical processes, locked P pools in the biological loop, i.e., the exchange between labile P and organic P. As a consequence, the efficacy of P adsorbents is hampered due to reduced P pools in the chemical loop. Dredging and Lanthanum modified bentonite are more effective than iron-lime sludge in decreasing phytoplankton biomass and improving water clarity. Near-sediment aeration was not able to stimulate the iron trap in the sediment in shallow water systems. As intervention measures that only target SRP may likely take longer in inhibiting phytoplankton biomass during warmer periods, we recommend an application strategy before the growing season (autumn or early spring in temperate systems) when the biological P loop is less prominent relative to the chemical P loop. In addition, the experiments gave an indication of eutrophication control measures on GHG; we did not test reduction of GHG concentrations upon interventions.

In Chapter V, I developed an ecosystem service modeling framework, in which I coupled a lake physic model with a lake ecosystem model, and the ecosystem model with an ecosystem service module. This is, to the best of our knowledge, for the first time that ecosystem service provisioning in lakes is quantitatively modelled based on the dynamics of water quality. This tool enables water managers to simulate alternative scenarios of eutrophication control measures and climate change impacts. Our scenario analyses indicate that: 1) The restoration measures showed non-linear impacts on the ecosystem state indicators as well as on the ecosystem services (ESs) provisioning. Phosphorus (P) reduction is more effective at high intensity, whereas wetland restoration showed a decreased effectiveness over intensity; 2) Both measures showed positive effects on ESs that requires good water quality, such as swimming, irrigation, and macrophyte habitat, but negative effects on ESs that require more productive systems (e.g., fishing and bird watches); 3) Climate change posed negative impacts to the effectiveness of restoration measures on ecosystem state indicators and ESs provisioning, an intensification of restoration measures will be needed under climate change.

List of publications

(Update: October 2023):

2023

- Michael F. Meyer*, Merritt E. Harlan*, Robert T. Hensley*, **Qing Zhan***, Nahit S. Börekçi, Tuba Bucak, Alli N. Cramer, Johannes Feldbauer, Robert Ladwig, Jorrit P. Mesman, Isabella A. Oleksy, Rachel M. Pilla, Jacob A. Zwart, Elisa Calamita, Nicholas J. Gubbins, Mary E. Lofton, Daniel A. Maciel, Nicholas S. Marzolf, Freya Olsson, Audrey N. Thellman, R. Quinn Thomas, Michael J. Vlah (2023). Hacking Limnology Workshops and DSOS23: Growing a Workforce for the Nexus of Data Science, Open *Science, and the Aquatic Sciences. Limnology and Oceanography Bulletin, https://doi.org/10.1002/lob.10607*

- **Qing Zhan***, Lisette N. de Senerpont Domis, Miquel Lürling, Rafael Marcé, Tom Heuts, Sven Teurlincx (2023). Process-based modeling for ecosystem service provisioning: Non-linear responses to restoration efforts in a quarry lake under climate change. *Journal of Environmental Management, Volume 348, 119163 https://doi.org/10.1016/j.jenvman.2023.119163*

- Margaret Armstrong*, **Qing Zhan**, Elias Munthali, Hui Jin, Sven Teurlincx, Piet Peters, Miquel Lürling, Lisette N. de Senerpont Domis* (2023). Stressors in a bottle: a microcosm study on phytoplankton assemblage response to extreme precipitation event under climate warming. *Freshwater Biology, Volume 68, Issue 8, https://doi.org/10.1111/fwb.14109*

2022

- Margaret Armstrong*, Hazal Aksu Bahçeci, Ellen van Donk, Asmita Dubey, Thijs Frenken, Berte M Gebreyohanes Belay, Alena S Gsell, Tom S Heuts, Lilith Kramer, Miquel Lürling, Maarten Ouboter, Laura MS Seelen, Sven Teurlincx, Nandini Vasantha Raman, **Qing Zhan**, Lisette N de Senerpont Domis (2022). Making waves: Lessons learned from the COVID-19 anthropause in the Netherlands on urban aquatic ecosystem services provisioning and management. *Water Research*, 118934, https://doi.org/10.1016/j.watres.2022.118934
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- **Zhan, Q.***, Teurlincx, S., van Herpen, F., Raman, N. V., Lürling, M., Waajen, G., & de Senerpont Domis, L. N. (2022). Towards climate-robust water quality management: Testing the efficacy of different eutrophication control measures during a heatwave in an urban canal. *Science of the Total Environment*, *828*, [154421]. https://doi.org/10.1016/j.scitotenv.2022.154421

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- **Zhan, Q.***, Kong, X., & Rinke, K. (2021). High-frequency monitoring enables operational opportunities to reduce the dissolved organic carbon (DOC) load in Germany's largest drinking water reservoir. *Inland Waters*, *12*(2), 245-260. https://doi.org/10.1080/20442041.2021.1987796
- Reinl, K. L.*, Brookes, J. D., Carey, C. C., Harris, T. D., Ibelings, B., Morales-Williams, A. M., de Senerpont Domis, L., Atkins, K. S., Isles, P. D. F., Mesman, J. P., North, R. L., Rudstam, L. G., Stelzer, J. A. A., Venkiteswaran, J. J., Yokota, K., & **Zhan, Q.** (2021). Cyanobacterial blooms in oligotrophic lakes: Shifting the high-nutrient paradigm. *Freshwater Biology*, *66*(9), 1846-1859. https://doi.org/10.1111/fwb.13791
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About the author （关于作者）:

我不得不承认，以下中文主要依赖谷歌翻译。我本想改善一下，结果发现，我的中文不一定比它的好，于是作罢。。。回想一下，在中国以外生活已经有 7 年多了，就让我原谅自己的语言吧。。。我不得不先澄清我下面的一些故事片段带有一些灰色幽默（最起码是我的初衷），如有冒犯，请记住你们是我生命中不可分割的一部分，本人充满感激之情！

我于 1994 年 11 月 27 日出生于中国湖北省黄石市。黄石市人口超过 200 万，我很惊讶它比阿姆斯特丹还大。虽然在中国以外，甚至在湖北省以外，它不为人知。我童年的大部分时间都是在黄石度过的，直到高中，虽然由于父母的生意，我多次在包括武汉及其周边地区在内的各个城市之间辗转。我记得我的一位小学（花湖小学）班主任曾诙谐地抱怨过："我们学校不是菜市场，不能随意出入"。嗯，这是我至今仍记得来自老师为数不多的教导之一。我的童年记忆充满了与我的伙伴和我的狗狗（"飞虎"）一起在大自然中的冒险。飞虎在自然探险方面做得非常出色，提醒我们注意蛇等危险动物。然而，他不太适应城市环境，导致了他的故事的悲伤结局……我希望我能更好地懂得如何训练他。

2016年，德国世界杯那一年，我的初一（黄石十八中），我找到了一个新伙伴——足球！无论我走到哪里，它都跟着我，直到现在。为了让我专心上课，班主任和妈妈配合得很好，采取了“胡萝卜加大棒”的策略。我的老师告诉我，如果我表现好并进入更好的高中，我会有更好的体育基础设施。我彼时太年轻太天真居然相信他们。虽然高中有足球场，但你没有时间去踢球。更重要的是妈妈的决心，有一次我离家抗议，结果难以忍受饥饿放弃了……最终我向他们妥协，放弃了上体校的念头，参加了初中学业考试。

我高中就读于黄石市实验中学，在我们“小”城市也算是市重点高中。高中时期是比较无聊甚至苦恼的，三年的时间都在准备一场考试——高考。但有些片段难以忘记，比如：1）我的一位同班同学对班主任的评价：“也许你在拯救我们的未来，但你却毁了我们的青春！”我忍不住为他的勇于直言鼓掌。2) 我必须在全班同学面前对课间踢足球进行自我批评。同时作为一名足球迷和一名中国学生，我意识到我拿到了一个悲剧的剧本。3）另一个难忘的经历是，我被班头的鼓励（“挑衅”）激发斗志，她说她要把我踢出“最快班”。两个月之内，我就从稳定的倒数10名跃升至学校前10名。我仍然记得我的老师们令人惊讶的面部表情，以及当你满足他们的期望时，他们的态度会发生多么戏剧性的变化。突然，我的班头像对待她的儿子一样对待我，邀请我去她的办公室吃午饭……最终在高考中，我至少为自己取得了令人满意的成绩（前 5%），但对我妈妈来说却不是。我妈妈希望我重新学习并重新参加高考，以取得和我姐姐一样好的成绩（前 0.3%）。我回复她：“妈妈，每个人都说自己表现不好（甚至是我姐姐……），但你知道吗，我可以向你保证，如果我重考，我只会表现更差，因为我不想重新经历地狱折磨！”显然，我的决心阻止了她的想法，就像她对我的足球梦所做的那样。我的另一个梦想（众多梦想中的一个）在高中时被打破，但这一次不是因为我亲爱的妈妈。我梦想成为一名飞行员，像《壮志凌云》中的汤姆·克鲁斯一样酷。不幸的是，我因为戴眼镜而没被选上。更让我觉得遗憾的是，它离我太近了：我的同桌被选上了，并嘲笑我：“这就是为什么我晚自习过后不跟你们一起去网吧”。那是我第一次真心地后悔迷恋电脑游戏。

选择大学我听从了喜欢历史的姐姐的建议，去了南京这座有着悠久历史的城市。虽然我对历史一点兴趣都没有，但由于南京的足球氛围在中国比较好，我在南京度过了美好的四年 -- 终于没有人能阻止我踢足球了。哦不对，我是去那里上本科的……我在南京农业大学获得了学士学位。我选择“环境科学”作为我的学士课程，因为它包含两个都吸引了我兴趣的术语。环境：

我在学校里听各种环境问题和污染耳朵已经听出茧了。与中国许多其他城市一样，黄石是一个快速发展的城市，我亲眼目睹了我家前面的湖泊和植被区域如何消失并被高楼大厦所取代。这些经历为我最大的抱负之一奠定了基础：解决环境问题。科学：我相信科学产生的知识是解决每个问题的最终解决方案。至于最后我对本科专业的印象，也许如一位同专业学长总结到："当我们选择环境科学这个专业时，我们想的是拯救世界；读完过后，发现需要被拯救的是我们自己。"客观来说这个专业太广泛了，涵盖了从空气到土壤、到水的一切，以至于最后你不知道自己到底能做什么。我的大多数本科同学都转行了，完全放弃了环境科学，也许收入才是王道。回想我四年的本科生涯，没有什么比为资源环境学院赢得第一个学院杯更令人难忘的了，尤其是在上个赛季我担任队长时被大学队友做局之后。一个毕业学长教训道：永远不要让你的命运掌握在别人手中。还有一件值得吹牛的事就是我跟随这个学长组建的 TBS（江湖人称"特别帅"）球队叱咤南京业余足球界。当你足够强的时候，别人就做不了局了。。。

当我不知道本科毕业后该做什么时，我跟随我的朋友去了一个关于在德国攻读硕士学位的研讨会。我朋友是德国队的球迷。我很觉得出国看看是什么样子并不是一个坏主意。我妈妈再次不同意，因为她认为我想出去踢足球而不是学习。她说的没错，但这一次她无法阻止我，因为我的父亲经济上支持我。我父亲年轻时就游历过中国，显然他把我出国旅行视为一种顺理成章的升级。经过两年的德语准备和一些考试，我跟随 JJ 来到一个我没听说过的德国城市马格德堡攻读硕士学位。相对于本科，在我的硕士学习期间，我决定深专一个地球系统而不是啥都学。我发现土壤很重要，但太静态（无意冒犯陆地科学家），流体系统的动态性质对我更有吸引力。空中和海洋系统虽然令人着迷，但过于庞大且超出人类控制范围（同样是那个愚昧无知的我的个人观点）。在我看来，淡水生态系统是最理想的研究系统，具有足够的活力，而且规模也不是太大，我们仍然可以对此做点什么。在我的硕士论文中，我在 Dr Karsten Rinke 的指导下，研究了亥姆霍兹环境研究中心湖泊研究部饮用水水库的水质动态。在那里作为论文学生和助理工作的一年多的时间里，我加深了对科学的兴趣，并决定在完成硕士学位后攻读博士学位。除了学习之外，我确实花了很多时间在足球上，我加入了当地的足球俱乐部 SV Arminia，并参加了 Landesklasse 联赛。当我在一个不到千人的小村庄遇到一些"硬骨头"时，我意识到中国国家队只进过一次世界杯是有原因的。总的

来说，我在马格德堡度过了美好的三年，感谢 JJ、我的朋友们、同事们和队友们。

攻读博士学位的雄心使我来到了位于瓦赫宁根的荷兰生态研究所。瓦赫宁根对我来说并不完全陌生，因为我之前有机会拜访了那里的一位朋友。这座小城市引起了我的兴趣，由于其高度的国际化，在一些人中赢得了“欧洲纽约”的绰号。当谈到我的博士学位时，我真的没有什么可抱怨的，我非常幸运能够拥有最好的日常导师 – Prof. Dr Lisette de Senerpont Domis，她在专业和个人方面为我提供了卓越的指导和支持。就我个人而言，2012 年至 2016 年这四年可不是在公园里散步的四年。和很多人一样，我需要经历不同层面的多重危机，这些危机深刻地影响了我的生活，也重塑了我对世界的看法。但生活就像过山车，永远不会完美。和在其他地方一样，我遇到了朋友，也度过了美好/糟糕的时刻。我想总结一下我读博期间的美好的事情：比如遇见 SQ，和 Five、QQ 一起度过了难忘的两年多；获得博士学位，成为我大家族的第一位博士生（可用来吹牛…）；我不会有困难地介绍我来自哪里（武汉附近…）；但在我心中真正会留下的是与很多人在一起的无数美好回忆，它们可能也会给你带来微笑，就像我现在所做的那样。当我反思这段旅程时，我的心情复杂，尚未消化，但需要承认我生命的这一章已经结束（流泪是可以原谅的）。

About the author in English:

I was born on November 27th, 1994 in Huangshi City, Hubei Province, China. Huangshi has a population of over 2 million, I am surprised it is even larger than Amsterdam. It is fairly unknown outside of China, and even beyond Hubei province. I spent most of my childhood in Huangshi until high school, though I temporarily moved among various cities including Wuhan and its surrounding, following my parents' business. I recall a humorous complaint from one of my Elementary school (Huahu Elementary school) head teachers: “Our school is not a vegetable market, you can't come and go just as you please”. Well, that makes one of the few lessons from my teachers I can still remember until now. My childhood memories are filled with adventures in nature alongside my buddies and my dog, Feihu (meaning “flying tiger”). Feihu did an excellent job in nature adventure alerting us from dangerous animals like snakes. However, he struggled to adapt to the urban environment, leading to a sad end to his story…I wish I knew better how to train him.

In the first year of my middle school (Huangshi No.18 Middle School) in 2016, the year of the Germany World Cup, I found a new buddy - soccer! It follows me everywhere I go, even until now. In order to let me concentrate on class, my headteacher collaborated quite well with my mom using a “carrot and stick” strategy. My teacher told me that I would have better infrastructure for sports if I perform well and go to a better high school. I was too young and too naive to believe him. Although you have a soccer playground in the high school, you won’t have time to play. More importantly is my mom’s determination. I failed in the leaving-home protest after one day because of hunger…I surrendered to them and quitted the idea of going to sports school, and prepared for the Academic Test for the Junior High School Students.

I went to the Huangshi Experimental Senior School for high school. It is not as good as the provincial key high school, but still a municipal key high school. The high school period was relatively boring and even distressing, the entire three years dedicated to preparing for one exam - The National College Entrance Examination (“gaokao”). I remember a few highlights: 1) A comment from one of my classmates to the headteacher: “Maybe you are saving our future, but you have ruined our youth!” I couldn’t stop applauding for his bravery. 2) I had to make a self-criticism in front of all the classmates for playing soccer during the break. It is a tragedy of being a soccer fan and a Chinese student at the same time. 3) Another unforgettable experience is that I was triggered by my headteacher's encouragement (“provocation”), who stated she would kick me out of the “rocket” classroom, where students with the best performances were gathered. Within two months, I made a leap from the stable bottom 10 to the top 10 in the school. I still remember my teachers’ surprising facial expressions and how dramatic their attitudes can change when you meet their expectations. Suddenly, my headteacher treated me like her son, inviting me to her office for lunch… Eventually in the gaokao, I achieved a satisfying performance for myself at least (top 5%), but not for my mom. My mom wanted me to restudy and retake the gaokao, to perform as good as my older sister (top 0.3%). I replied to her: “Mom, everyone says they didn’t perform well (even my older sister…), but you know what, I can guarantee you I will only perform worse if I retake it because I do not want to re-go through hell!” Apparently, my determination stopped her from dreaming, just like what she did to my soccer dream. Another dream of mine (out of many) was broken during high school, but this time not because of my dear mom. I dreamed of being a pilot, as cool as Tom Cruise in “Top Gun”. Unfortunately, I was deselected because of wearing glasses. More unfortunate is that it is so close to me: my classmate sitting next to me made it, and teased me: “That’s why I didn’t join you guys to the Internet Cafe after the Night self-learning”. That was the first time I sincerely regretted playing too many computer games.

For my Bachelor, following my older sister's advice, who is a fan of history, I went to Nanjing City, a city with a lot of history. Although I am not interested in history at all, I had a wonderful four years in Nanjing because of its relatively good soccer atmosphere in China, and finally no one could stop me from playing soccer anymore. Actually, I went there to study…I did my Bachelor's in Nanjing Agricultural University. I chose "environmental science" as my bachelor programme because it consists of two terms that both attracted my interest. Environment: I have been overwhelmingly introduced to all kinds of environmental problems, pollutions throughout my schools. Huangshi is a fast-growing city like many other Chinese cities and I witnessed how the lake and vegetation area in front of my home disappeared and was replaced by high rise buildings. These experiences formed the basis for one of my strongest ambitions: to tackle the environmental problems. Science: it was just my belief that knowledge produced by science is the ultimate solution to every single problem. What I do remember about my Bachelor programm, maybe a comment from one of my college classmates: "When we chose this major in environmental science, we envisioned ourselves as saviors of the world. However, upon completing this program, we came to realize that we are the ones in need of saving." The program was too broad for me, covering everything from air to soil, to water, so that you don't know what you can do exactly. Most of my college classmates changed their career trajectories, moving away from environmental science entirely, probably it is clearer to follow money. Reflecting on my 4-year Bachelor's life, nothing is more memorable than winning the first College cup for our Resource and Environmental College, especially after being cheated by my university teammates in the previous season when I was captain. One lesson learned as told by a senior: never let your fate be in the hands of others. Another thing worth bragging about is that I joined the TBS (known as "super cool" in Jinaghu) team formed by this senior, and we dominated the Nanjing amateur football world. When you are strong enough, no one can stop you anymore…

When I did not know what to do after Bachelor, I followed my friend and went to a workshop about pursuing a Master's in Germany. My friend is a fan of the German soccer team. I found it is not a bad idea to go abroad and see what it looks like. My mom disagreed again as she thought I wanted to go out to play soccer rather than study. She is partly true, but she could not stop me this time, because my father supported me. My father traveled across China when he was young, apparently, he regarded my traveling abroad as a logical upscaling. After two-year of preparation for German and some exams, I followed JJ and ended up doing my masters in Magdeburg, a random city in Germany to me. During my master's studies, I wanted to focus on one of the Earth Systems to expand my efforts further. I found soil is important but too static (no offense to terrestrial scientists), the dynamic nature of fluid systems is more appealing to me. Air and marine systems, while fascinating, are too vast and beyond human control (again personal opinion at that age). Freshwater ecosystems appeared to me to be the most ideal study system, dynamic enough, and not too big that we can still do something about it. In my Master thesis, I worked on the water quality dynamics in a drinking water reservoir at Helmholtz-Centre for Environmental Research, in the Lake Research department, under supervision by Dr. Karsten Rinke. During the stay there for more than one year as a thesis student and working as an assistant, I deepened my interest in science and decided to pursue a PhD after completion of my master's degree. Besides the study, I indeed spent a lot of time on soccer, I joined a local soccer club, SV Arminia and played the Landesklasse liga. When I met some "hard bones" in a small village with a population less than thousand, I realized that there is a reason why the CN national team only qualified World Cup for one time. Overall, it was a nice three years for me living in Magdeburg, thanks to JJ, my friends, my colleagues, and my teammates.

The ambition of pursuing a PhD brought me to the Netherlands Institute of Ecology in Wageningen. Wageningen was not entirely unfamiliar to me, as I had the chance to visit a friend there before seeking my PhD. The small city piqued my interest, earning the nickname "EU New York" among some people due to its high international component. When it comes to my Ph.D. program, I truly have very little to complain about, I am incredibly fortunate to have had the best daily supervisor - Prof. dr. Lisette de Senerpont Domis, who provided me exceptional guidance and support both professionally and personally. On a personal level, these 4 years from 2012 to 2016 were no walk in the park. Just like many others, I needed to go through multiple crises at different levels, which deeply impacted my life and reshaped my perspective on the world. But life is a rollercoaster, and it is never perfect. As in any other place, I met friends and had good/bad moments. I want to summarize good things during my PhD trajectory: like meeting SQ, having a memorable two years together with Five and QQ; Receiving my PhD degree, being the first doctor in my family (hopefully…); I won't have a challenge of introducing where I am from (nearby Wuhan); But what I really hope to leave out are the countless wonderful memories with you, which may bring a smile to your faces just like they do for me right now. As I reflect on this journey, it is with a mix of emotions that I have not digested yet but need to acknowledge this chapter of my life has come to an end (tears are fine).

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Oral Presentations

- *Effectiveness of phosphorus control under extreme heatwaves: implications for sediment nutrient release and greenhouse gasses emission.* MANTEL Symposium, 14-15 April 2020, Online
- *Effectiveness of different eutrophication control measures: implication for water quality dynamics and resistance to heatwave disturbance.* ASLO summer meeting, 22-27 June 2021, Online
- *Towards climate-robust water quality management: Testing the efficacy of different eutrophication control measures during a heatwave in an urban canal*. JASM2022, 19 May 2022, Grant Rapids, USA
- *Modelling the response of aquatic ecosystem services to restoration measures under different climate scenarios*. ALSO ECRs Making Waves in Aquatic Sciences: Amplifying voices, 23 February 2023, Online

SENSE coordinator PhD education

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Colophon

The research presented in this thesis was conducted at the department of Aquatic Ecology at the Netherlands Institute of Ecology (NIOO-KNAW), Wageningen, the Netherlands.

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