Use of selected anthropogenic pesticides, nutrients, and biomarkers to spatially and temporally characterize eutrophication dynamics at a shallow lake (Lake Seeburg)

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Contents

Preface

This cumulative thesis consists of two published articles (Section 2 and 3) and a manuscript in preparation (Section 4). In the preceding introduction, the publications are embedded in a relevant context, conclusion and outlook complete the thesis.

The following papers form the main part of this thesis:

Warner, W.; Zeman-Kuhnert, S.; Heim, C.; Nachtigall, S.; Licha, T., 2021. Seasonal and spatial dynamics of selected pesticides and nutrients in a small lake catchment - Implications for agile monitoring strategies. Chemosphere 281, 130736. https://doi.org/10.1016/j.chemosphere.2021.130736. (Section 2)

Individual contributions: Sampling, chemical analysis, writing (review and editing).

Zeman-Kuhnert, S.; Thiel, V.; Heim, C., 2022. Effects of weather extremes on the nutrient dynamics of a shallow eutrophic lake as observed during a three-year monitoring study. Water 14, 2032. https://doi.org/10.3390/w14132032. (Section 3)

Individual contributions: Sampling, methodology, chemical analysis, data evaluation, writing (original draft), visualization.

Zeman-Kuhnert, S.; Heim, C.; Thiel, V., (manuscript in preparation). Qualitative reconstruction of eutrophication at a shallow eutrophic lake using sedimentary stenols and their degradation products. To be submitted to “Organic Geochemistry”. (Section 4)

Individual contributions: Sampling, chemical analysis, data evaluation, writing (original draft), visualization.

Abstract

Eutrophication of water bodies caused by high nutrient inputs, especially of phosphorus, is a global concern for a wide variety of ecosystems. To assess this problem, different monitoring approaches have been applied to a variety of water bodies worldwide. Its main focus is on the spatial monitoring of nutrient inputs, predominantly on allochthonous inputs. In contrast, the temporal monitoring of inputs is rarely considered. This includes possible variations of nutrient inputs within the seasons or due to extreme weather events. In addition, information on past eutrophication can be useful for retrospectively characterizing long-term changes in the organism composition of water bodies and reconstructing how the current eutrophic status arose. Lake systems can only be adequately understood when these factors are considered. The primary objective of this work is to develop different approaches for a better spatial and especially temporal characterization of eutrophication-relevant lake dynamics by using different substance classes. To this end, pesticides (using UPLC-MS/MS), bioavailable nutrients (using IC and photometry) and biomarkers (using GC-MS) were investigated in three different studies at the shallow (<4 m), eutrophic Lake Seeburg in southern Lower Saxony over a period of 1-3 years.

In the first study (Warner et al., 2021), pesticides with their metabolites and selected nutrients were analyzed monthly for one year, to suggest improvements in current monitoring strategies based on spatial and temporal input patterns. Two different groups of pesticides were tested. The first group consisted of pesticides that have been used in large quantities in recent decades but are no longer allowed to be used today (e.g., the beet herbicide chloridazon and its degradation products). The second group consisted of pesticides that are still widely used today (e.g., the selective pre-emergence herbicide metazachlor). The pesticides of the first group, along with nitrate, show a relatively constant input into adjacent waters throughout the year. The results indicate that they are stored in large quantities in the soil and, although no longer applied, are slowly leached out over years. The pesticides of the second group, as well as dissolved reactive phosphate (SRP), show a strong seasonality. Their maximum input into surrounding waters occurs shortly after application, which indicates rapid leaching by precipitation. The results of this study confirm the undesired input of pesticides into surrounding waters, especially after rain events. In addition, it has been demonstrated that more targeted sampling not only saves costs, but also allows for more successful remediation efforts due to better detection of spatial and temporal pollution hotspots.

The second study (Zeman-Kuhnert et al., 2022) focused on the effects of extreme weather events on the nutrient dynamics and cyanobacterial bloom composition in Lake Seeburg. Eutrophication-relevant parameters (water temperature, nitrate, ammonium, nitrite, and SRP) were studied monthly

in the lake for three years (2017-2019) and supported with monthly SRP measurements in the sediment pore water for one year (2018). Following a three-day heavy rain event in July 2017, anoxic waters with high SRP levels entered the lake from the upstream flooded wetland. This exceptionally high allochthonous nutrient input resulted in a relatively short (≈3 weeks) but very intense and monospecific cyanobacterial bloom. During the hot and dry summer of 2018, strong internal SRP redissolutions from the sediment resulted in the longest (≈3 month) observed cyanobacterial bloom. The results of this study reveal high internal and external nutrient inputs and a severe loss of microorganism diversity following weather extremes. Despite similar negative impacts, the causes of cyanobacterial blooms are fundamentally diverse and thus must be considered differently in remediation strategies.

In the third study (Zeman-Kuhnert et al., to be submitted), phytoplankton-related biomarkers, representative of allochthonous and autochthonous organism groups, were evaluated for their presence and conservation ability in the lake water and their transfer to the surface sediment. The primary objective was to study whether certain biomarkers can be used to reconstruct the eutrophication history of a lake. 26 biomarkers were clustered into 5 groups with similar characteristics using principal component analysis (PCA): (I) biomarkers discharged via the inflow, formed in the lake by (II) eukaryotes or (III) bacteria, (IV) compounds accumulating in the surface sediment, and (V) unsaturated C_{27} to C_{29} stenols with their saturated degradation products (C_{27} to C_{29} stanols) mainly present in lake water and sediment. The characteristics and seasonal distribution of the stenols showed potential to be used as a sedimentary eutrophication indicator. Therefore, they were additionally measured on two sediment cores to reconstruct the eutrophication history of the lake. The results show that autochthonously formed C_{27} and allochthonously formed C_{29} stenols, including their degradation products, contrast with sediment depth (highest C_{27} to C_{29} ratios at the surface, lowest with depth) and are thus considered as suitable biomarkers to qualitatively reconstruct the historical eutrophication trend.

In summary, the results of this thesis provide further insights with regard to a more precise characterization of the overall lake dynamics relevant to eutrophication. Potential spatial and temporal pollution hotspots (whether due to constant or short-term inputs) need to be identified. Information on how eutrophication has evolved in the past may also be useful for a better overall understanding of the process. Due to the consequences of climate change and the growing world population, it will become increasingly important in the future to identify potential impacts and changes on water bodies in order to better assess their consequences and to develop adapted measures.

Zusammenfassung

Eutrophierung von Gewässern verursacht durch hohe Nährstoffeinträge, insbesondere durch Phosphor, stellt ein globales Problem für verschiedenste Ökosysteme dar. Um dieses Problem zu erfassen, werden seit Jahrzehnten diverse Monitoringkonzepte an unterschiedlichsten Gewässern weltweit angewendet. Dabei steht die räumliche Erfassung von Nährstoffeinträgen, überwiegend von allochthonen Einträgen, im Vordergrund. Die zeitliche Erfassung von Einträgen wird allerdings nur selten berücksichtigt. Dazu zählen mögliche Schwankungen von Nährstoffeinträgen innerhalb der Jahreszeiten oder durch Extremwetterereignisse. Zusätzlich können eutrophierungsrelevante Informationen über die Vergangenheit nützlich sein, um rückwirkend langfristige Veränderungen der Organismenzusammensetzung in Gewässern zu charakterisieren und so zu rekonstruieren, wie der derzeitige eutrophe Zustand entstanden ist. Erst nach Berücksichtigung dieser Komponenten können Seesysteme hinreichend verstanden werden. Vorrangiges Ziel dieser Arbeit ist es, durch die Nutzung unterschiedlicher Substanzklassen verschiedene Ansätze zur besseren räumlichen und besonders zeitlichen Charakterisierung von eutrophierungsrelevanten Seedynamiken zu erarbeiten. Dazu wurden in drei verschiedenen Studien Pflanzenschutzmittel (mittels UPLC-MS/MS), bioverfügbare Nährstoffe (mittels IC und Photometrie) und Biomarker (mittels GC-MS) am flachen (<4 m), eutrophen Seeburger See in Südniedersachsen in einem Zeitraum von 1-3 Jahren untersucht.

In der ersten Studie (Warner et al., 2021) wurden Pflanzenschutzmittel mit ihren Metaboliten und ausgewählte Nährstoffe über ein Jahr monatlich untersucht, um anhand der räumlichen und zeitlichen Eintragsmuster Vorschläge für Verbesserungen in gängigen Gewässermonitoringstrategien geben zu können. Dafür wurden zwei verschiedene Gruppen von Pestiziden betrachtet. Zum einen Pestizide, die in den letzten Jahrzehnten in großen Mengen eingesetzt wurden, heute aber nicht mehr eingesetzt werden (z.B. das Rübenherbizid Chloridazon mit seinen Abbauprodukten), zum anderen solche, die heute noch weit verbreitet sind (z.B. das selektive Vorlaufherbizid Metazachlor). Die erstgenannte Pestizidgruppe zeigt, zusammen mit Nitrat, einen relativ konstanten Eintrag in die angrenzenden Gewässer über das gesamte Jahr. Die Ergebnisse legen nahe, dass sie in großer Menge im Boden gespeichert sind und, obwohl sie nicht mehr eingesetzt werden, langsam über Jahre hinweg ausgewaschen werden. Die Pestizide der zweiten Gruppe zeigen, zusammen mit gelöstem reaktivem Phosphat (SRP), eine starke Saisonalität. Ihr maximaler Eintrag in die umliegenden Gewässer ist bereits kurz nach dem Ausbringen sichtbar, was auf eine schnelle Auswaschung durch Niederschläge hindeutet. Die Ergebnisse dieser Studie bestätigen den unerwünschten Eintrag von Pestiziden in umliegende Gewässer, besonders nach Regenereignissen. Des Weiteren konnte gezeigt werden, dass gezieltere Probenahmen einerseits Ressourcen sparen, andererseits durch eine bessere

Erfassung räumlicher und zeitlicher Belastungshotspots erfolgreichere Sanierungseingriffe möglich sind.

Die zweite Studie (Zeman-Kuhnert et al., 2022) befasste sich mit dem Einfluss von Extremwetterereignissen auf die Nährstoffdynamiken und Cyanobakterienblütenzusammensetzung im Seeburger See. Dazu wurden eutrophierungsrelevante Parameter (Wassertemperatur, Nitrat, Ammonium, Nitrit und SRP) über drei Jahre (2017-2019) monatlich im Seewasser untersucht und mit monatlichen SRP-Messungen im Porenwasser des Sediments über ein Jahr (2018) ergänzt. Nach einem dreitägigen Starkregenereignis im Juli 2017 liefen anoxische Wässer mit hohen SRP-Gehalten vom flussaufwärts gelegenen, überschwemmten Feuchtgebiet in den See. Dieser außergewöhnlich hohe allochthone Nährstoffeintrag führte zwar zu einer relativ kurzen (≈3 Wochen) aber sehr intensiven und monospezifischen Cyanobakterienblüte. Im trockenen und heißen Sommer 2018 führten u.a. hohe Wassertemperaturen zu einer starken internen SRP-Rücklösung aus dem Sediment, welche die längste zu beobachtende Cyanobakterienblüte (≈3 Monaten) herbeiführte. Die Ergebnisse dieser Studie offenbaren die hohen internen bzw. externen Nährstoffeinträge und den starken Diversitätsverlust nach Wetterextremen. Trotz ihrer ähnlichen negativen Auswirkungen sind die Ursachen der Cyanobakterienblüten grundverschieden und müssen daher in Sanierungskonzepten unterschiedlich angegangen werden.

In der dritten Studie (Zeman-Kuhnert et al., liegt als Manuskript vor) wurden phytoplanktonbezogene Biomarker, die für allochthone und autochthone Organismengruppen repräsentativ sind, auf ihr Vorhandensein und ihre Erhaltungsfähigkeit im Seewasser sowie auf ihren Transfer in das Oberflächensediment untersucht. Übergeordnetes Ziel war es zu untersuchen, ob bestimmte Biomarker zur Rekonstruktion der Eutrophierungsgeschichte eines Sees verwendet werden können. Dazu wurden in einem ersten Schritt 26 Biomarker mittels Hauptkomponentenanalyse (PCA) in 5 Gruppen mit jeweils ähnlichen Eigenschaften zusammengefasst: (I) Biomarker, die über den Zufluss eingeleitet werden, (II) im See von Eukaryoten oder (III) Bakterien gebildet werden, (IV) sich im Oberflächensediment anreichern sowie (V) ungesättigte C_{27} bis C_{29} Stenole mit ihren gesättigten Abbauprodukten (C_{27} bis C_{29} Stanole), die hauptsächlich im Seewasser und im Sediment vorhanden sind. Das Verhalten und die saisonale Verteilung der letztgenannten Stenole zeigten Indizien für eine Nutzung als qualitativer Eutrophierungsanzeiger, weshalb sie zusätzlich an zwei Sedimentkernen gemessen wurden, um den Eutrophierungsverlauf des Sees zu rekonstruieren. Die Ergebnisse zeigen, dass sich die autochthon gebildeten C_{27} und die allochthon gebildeten C_{29} Stenole, einschließlich ihrer Abbauproduke, mit der Sedimenttiefe gegenläufig verhalten (höchste C_{27} zu C_{29} Verhältnisse an der Oberfläche, geringste in der Tiefe) und sich daher eignen, den historischen Eutrophierungstrend qualitativ zu rekonstruieren.

Alles in allem liefern die Ergebnisse dieser Doktorarbeit weiterführende Erkenntnisse in Bezug auf eine genauere Charakterisierung der gesamten eutrophierungsrelevanten Seedynamiken. Für ein besseres Verständnis müssen potentielle räumliche und zeitliche Belastungshotspots (sei es aufgrund konstanter aber auch kurzfristiger Einträge, z.B. nach Starkregenereignissen) ausfindig gemacht werden. Informationen darüber, wie sich die Eutrophierung in der Vergangenheit entwickelt hat, können ebenfalls für ein besseres Gesamtverständnis nützlich sein. Durch die Auswirkungen des Klimawandels (Temperaturanstieg, steigende Extremwetterereignisse etc.) und der wachsenden Weltbevölkerung, wird es in Zukunft immer notwendiger werden, die Auswirkungen und Veränderung auf Gewässer noch detaillierter zu erfassen, um deren Folgen besser abschätzen und angepasste Maßnahmen entwickeln zu können.

1. Introduction

1.1. Eutrophication at surface water bodies - problems and consequences

The steadily increasing eutrophication of surface waters poses a global threat to a wide variety of ecosystems (Kapsalis and Kalavrouziotis, 2021). Nutrient oversupply leads to changing organism compositions in water bodies resulting in, for instance, increased formation of cyanobacterial blooms (Qin et al., 2013). Cyanobacteria pose a threat to aquatic ecosystems due to their toxin production and formation of anoxic zones (Catherine et al., 2013; Diaz and Rosenberg, 2008; Quiblier et al., 2013). Negative consequences include a further decrease in biodiversity or (financial) challenges in the drinking water supply or tourism (Dodds et al., 2009; Smith, 2003). According to the latest report of the European Environment Agency on the condition of European waters, only around 40 % of the surface water bodies are in at least a good ecological status (European Environment Agency, 2018). While the situation in some European countries has slightly improved in recent years, the global situation is expected to worsen in the future, boosted by the expected increase in extreme weather events (European Environment Agency, 2018; Michalak et al., 2013; Sinha et al., 2017).

1.1.1. Spatial consideration of nutrient inputs

Anthropogenic nutrient inputs from point sources, such as obsolete wastewater treatment plants, or diffuse sources, such as surface runoff from agricultural areas, are the two main contributors to eutrophication (European Environment Agency, 2020). While point sources were the main nutrient supplier in the past, diffuse sources are currently the matter of concern in nearly all European countries (currently in Europe: diffuse sources 38%, point sources 18%) (European Environment Agency, 2018; Le Moal et al., 2019; van Drecht et al., 2009).

However, not only these allochthonous nutrient inputs lead to eutrophication; sedimentary nutrient resuspension can also have a significant impact (Søndergaard et al., 2013; Welch and Cooke, 2005). Nutrients that have entered a water body in the past, already promoted the formation of phytoplankton. After their demise, their organic material is deposited in the sediment together with nutrients bound therein. However, up to 85% of the deposited organic material is recycled within a few years and the former bound nutrients become available to the lake water again. Only about 4% remains in the sediment in the long term (Bloesch, 1995). These autochthonous sedimentary nutrient releases are a major reason for missing success after decades of external, allochthonous remediation

measures in various lakes (Jeppesen et al., 2005; Kiani et al., 2020; Pokorný and Hauser, 2002; Schindler, 2012).

As a result of these eutrophication issues, measures have been adopted nearly worldwide to counteract the degradation of water bodies. In Europe, the EU Water Framework Directive (European Comission, 2000) was adopted in 2000. It forms the framework legislation to standardize EU-wide water quality management with the major aim to reach "good" chemical and ecological water quality in all European waters by 2027 at the latest (Arle et al., 2016). Although the situation in Central Europe has improved slightly in recent years, the targets of the Water Framework Directive for an at least good ecological status are still not achieved in most water bodies.

1.1.2. Temporal consideration of nutrient inputs

The selective spatial assessment of allochthonous as well as autochthonous inputs, as described above, gives a first impression of the influencing factors, but is usually not sufficient for a complete characterization of the lake dynamics. Only with precise knowledge of the temporal aspects can the overall lake dynamics and thus the eutrophication level of a lake be determined in detail. However, current monitoring strategies have the limitation to capture only background inputs due to their rigid “grab/snapshot sampling method”, easily overlooking possible peak inputs after extreme weather events such as heavy rainfalls or snowmelts (Allan et al., 2006; Arle et al., 2016). Detailed knowledge of their impacts is needed, as they can cause the largest allochthonous inputs into the lake and are likely to increase in the future due to climate change (Jeppesen et al., 2021; Reichwaldt and Ghadouani, 2012).

A temporally accurate characterization should not only consider external inputs, but also the lake itself with its (surface) sediments. The above-mentioned sediment redistributions do not take place constantly within a year. Extreme sedimentary nutrient resuspensions can be noted in particular during late summer months, while little to no re-dissolution is observed in winter. In contrast, the sediment can even serve as a nutrient sink through the deposition of nutrients bound in dead organisms or fixed in particulate form (Orihel et al., 2017; Sondergaard et al., 2001). Only after consideration of both the spatial and temporal influencing factors, lake systems can be understood as a whole. This is particularly important because, on that basis, appropriate lake-specific measures can be applied in a further step to recreate polytrophic or, even better, oligotrophic conditions (Bormans et al., 2016; Ibelings et al., 2016; Steinman et al., 2009).

The aim of this thesis is to holistically study the factors that influence the ongoing anthropogenic eutrophication processes in lakes and to gain a better overall understanding of their dynamics. Three

different substance groups (pesticides, bioavailable nutrients and biomarkers) were tested on a shallow eutrophic lake, to assess to what extent they can be used for a spatial and especially temporal characterization. The results enabled the definition of better adapted monitoring strategies and a better understanding of the overall eutrophication dynamics.

1.2. Pesticide studies to improve current monitoring strategies

Within the last decades, pesticides have become a fundamental part of modern agriculture (Alexandratos and Bruinsma, 2012; Carvalho, 2017). In 2022, 452 different pesticides, so called active substances, were approved and in use across Europe. Of these, about 350,000 tons have been used each year since 2011 (European Comission, 2022; Eurostat, 2022). Despite their contribution to increasing food yields in the future, they are associated with negative aspects. Due to their partly good water solubility, pesticide can enter various water bodies by leaching or runoff, leading to increasing concentrations there with subsequent problems (Larson et al., 2018; Loos et al., 2010). However, not only the applied substances themselves, but often also their degradation products (metabolites) can be detected in waters in the ng/L to even µg/L range, partly with even higher persistence to degradation (Buttiglieri et al., 2009; Fenner et al., 2013; Reemtsma et al., 2013).

Aim of the study in Section 2 is to detect and quantify pesticides and their degradation products. However, it is not intended to replace nutrient studies. Rather, the study aims to suggest improvements of current standardized monitoring strategies. The advantage of pesticides over nutrients that directly contribute to eutrophication is their ability to provide information on their use over time. Not all pesticides have been and are used in the same way and moreover show different properties that can help to better understand input dynamics. In this context we distinguish:

I) Pesticides that have been widely used for decades and are regularly released into the environment, in some cases together with their metabolites; namely quinmerac, metazachlor, metolachlor and quinmerac (Fig. 1.1).

II) Pesticides that had been used for decades, have been banned for several years now, but are still detectable in water bodies, in some cases together with their metabolites; namely atrazine and chloridazon (Fig. 1.1).

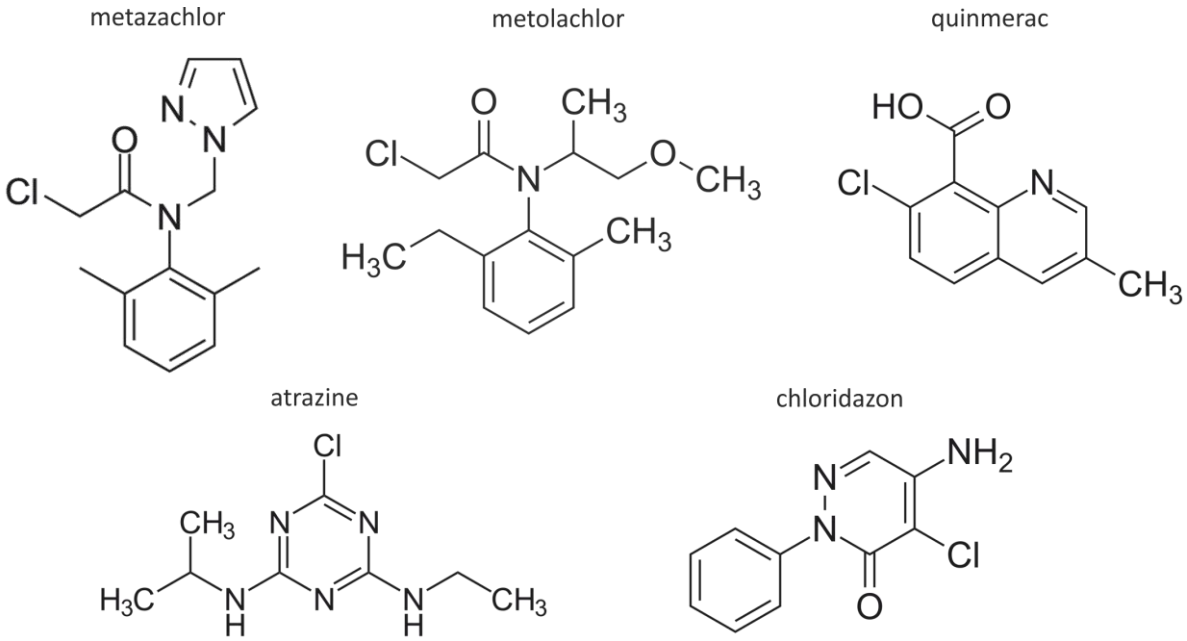

Fig. 1.1. Top: Molecules of metazachlor, metolachlor and quinmerac (group 1, pesticides still in use); bottom: molecules of atrazine and chloridazon (group 2, pesticides no longer in use). See text for further information.

Metazachlor, metolachlor and quinmerac each with their degradation products, are representatives of the pesticides still in use today. They are part of several post-emergence herbicides, applied few weeks after sowing in (spring or) autumn, depending on the field crops. Atrazine and chloridazon are representatives of the pesticides now banned in Europe. Early on, it was recognized that atrazine, a post-emergence herbicide used for weed control, degrades very slowly and therefore accumulates in more and more water bodies, including drinking waters (Graymore et al., 2001). In addition, it shows undesirable hormonal side effects in amphibians, especially frogs, even at very low concentrations (Hayes et al., 2002; Hayes et al., 2010). As a consequence, atrazine lost its approval in most European countries in the early 1990s before being banned throughout the EU in 2003. Nevertheless, it can still be detected in the aquatic environment along with its degradation products (Graymore et al., 2001). The beet herbicide chloridazon lost its approval only a few years ago (2019), but was used less and less in the years before the ban due to high requirements. The problem is not so much the herbicide itself, but mainly its degradation products, which are described as particularly resistant to further degradation, resulting in increasing accumulation in water bodies as well as drinking waters (Buttiglieri et al., 2009).

1.3. Nutrient studies to characterize the effects of eutrophication

An overabundance of nutrients is the primary cause of eutrophication with the formation of harmful algal blooms (Heisler et al., 2008). Therefore, their direct measurement is the most appropriate consequence. However, in recent decades it has been proven that not all nutrients are equally

responsible for negative eutrophication phenomena. Especially phosphorus turned out to be the major concern (Schindler et al., 2016). While phosphorus is the limiting factor in primary production in oligotrophic lakes, all other nutrients are generally present in sufficient amounts (Schindler, 2012). However, due to the use of phosphate-containing detergents starting in the 1950s and later due to the widespread use of artificial fertilizers in agriculture, phosphorus levels in water bodies increased dramatically (Reynolds and Davies, 2001).

In spring and summer, an oversupply of nutrients can still be used by various organisms. Despite the occasional massive occurrence of e.g. diatoms or green algae, negative consequences in water bodies can only be observed in extreme cases (Jansson, 1990; Jeppesen et al., 2007). However, the situation changes in late summer when water temperatures are highest. If nutrients, especially phosphorus, are still present in the waters, cyanobacteria enjoy ideal conditions. They can outcompete almost all other microorganisms and spread massively (Paerl and Huisman, 2008; Paerl and Otten, 2013). A major reason for their dominance is the ability of heterocystous cyanobacteria to fix atmospheric nitrogen and thus depend only on bioavailable phosphorus (Herrero et al., 2001; Stewart and Lex, 1970). However, not only bioavailable nutrients from the water column can be used by cyanobacteria, indirectly also those of the sediment. During cyanobacterial blooms, physical and biological conditions in the lake and consequently also in the surface sediment change (Smolders et al., 2006). Favored by low oxygen, rising pH levels and high water temperatures in late summer, the altered conditions in the surface sediment lead to the release of mineral-bound phosphates. They diffuse into the water column where they are bioavailable for further microbial growth, resulting in an internal amplification effect (Randall et al., 2019).

Aim of the study in Section 3 is to assess both the spatial and current temporal nutrient dynamics of the lake system. Measurements of allochthonous inputs at the inflow were conducted monthly over a period of 3 years. To assess the autochthonous inputs, we performed in-lake water analyses monthly for three years and sedimentary pore water analyses monthly for one year. We evaluated the effects of extreme weather events (a strong rain event and a dry period) on the allochthonous and autochthonous nutrient inputs and the associated varying microorganism composition.

1.4. Biomarker studies to reconstruct the eutrophication history

To understand the overall lake dynamics and to categorize the current level of eutrophication, additional information on certain environmental processes in the recent past is useful. However, nutrient measurements in the lake and sediments do not provide information on whether and how the organism composition in the lake has changed over time. Due to the rapid decay of microbial organisms it is not possible to use DNA-reconstructions for exact species determination. Biomarker

analyses of microbial membrane lipids, which can be preserved in sediments for millions of years, are widely used for the reconstruction of specific organism groups (Cranwell, 1984; Parrish et al., 2000). The advantage of this additional information is to characterize the effects of past eutrophication more precisely and to be able to make more accurate statements about the historic trend (Cranwell et al., 1987; Volkman et al., 1998).

Various biomarkers for the reconstruction of organisms and the characterization of eutrophication are described in the literature. For example, long-chain saturated n-fatty acids (≥ C_{20}) (Harvey, 1994), n-alkanes (≥ *n*-C_{27}) (Eglinton and Hamilton, 1967) or unsaturated sterols of C_{29} (Huang and Meinschein, 1979) are attributed to terrestrial inputs. Indications of an autochthonous, aquatic origin are for instance 3- to 8-methylheptadecane and some unsaturated C_{18} fatty acids (formed by cyanobacteria) (Coates et al., 2014; Los and Mironov, 2015), unsaturated C_{20} fatty acids (mainly from diatoms plus certain algae) (Fujibayashi et al., 2016; Volkman et al., 1989) or unsaturated C_{27}, C_{28} sterols (eukaryotic phyto- and zooplankton, micro- and macroalgae) (Huang and Meinschein, 1979; Volkman, 2003). Oligotrophic lakes tend to be dominated by allochthonous, terrestrial organic sources, while eutrophic lakes tend to be dominated by aquatic sources. Thus, assuming that the current trophic state is preserved in individual sediment layers, a change from biomarkers of terrestrial origin to aquatic biomarkers with decreasing sediment depth could indicate increasing eutrophication (Huang and Meinschein, 1979). However, in order to reliably use biomarkers to reconstruct past eutrophication, potential differences in the deposition and degradation of organic molecules must be understood. In the literature, this is often only incompletely the case. Therefore, it needs to be clarified whether the biomarkers used are equally stable, or whether some are already degraded in the water column before being deposited in the sedimentary record which would lead to preservation bias (Meyers and Ishiwatari, 1993).

In Section 4, comprehensive biomarker studies were conducted in the inflow, lake and surface sediments of Lake Seeburg. The objective was to study the preservation of phytoplankton related biomarkers and to test which are suitable to characterize the eutrophication history. In a further step, appropriate biomarkers for the reconstruction of the eutrophication history were tested at Lake Seeburg.

1.5. Study site - Lake Seeburg

The studies on which this thesis is based were performed at Lake Seeburg (for image see Fig. 1.2) between January 2017 and June 2020. It is located about 15 km E of the city of Göttingen (51°33’52’’ N, 10°09’52’’ E) in southern Lower Saxony, covers 0.89 km^2, has a water volume of 2 million m^3, a mean water depth of 2 m and a maximum water depth of 4 m (Streif, 1970). The lake

is a water-filled sinkhole and was formed by subsurface leaching of Permian evaporites about 10.000 years ago (Streif, 1970). A large part of the catchment area is used as agricultural area. Increasing eutrophication of the lake has been observed in recent decades, resulting in regular cyanobacterial blooms since 2005. Further lake characteristics relevant to the respective studies are described in the corresponding methods sections.

Major reasons for selecting this lake were a good data base from preliminary studies, its high eutrophication, good accessibility and small size. Shallow waters are particularly susceptible to sediment re-dissolution due to their low depth (Bormans et al., 2016). Main factors for their susceptibility are a missing thermocline with the accompanying physicochemical barrier, a large ratio of sediments surface area to water volume, and a strong turbulence of the water body up to the sediment layer, which can lead to stirring up of organic and inorganic material (Lorenz et al., 2017).

Fig. 1.2. Image of Lake Seeburg facing east-southeast during a cyanobacteria bloom in August 2016. The bloom is clearly visible at the lower right edge of the image (west side of the lake). Source: https://www.hna.de/lokales/goettingen/blaualgen-sofort-striktes-badeverbot-seeburger-6675369. html.

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2. Seasonal and spatial dynamics of selected pesticides and nutrients in a small lake catchment - Implications for agile monitoring strategies

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Intensive anthropogenic pressure such as high inputs of nutrients and pesticides severely threaten most European water bodies. Small catchments ≤10 km^2 are not monitored under the Water Framework Directive but play an important role in freshwater ecosystems. The high complexity in seasonal and spatial dynamics require more than a one-size-fits-all approach in water quality monitoring. Often located in rural areas with a high agricultural activity, small catchments often carry high amounts of nutrients, pesticides and their transformation products affecting drinking water resources. With a low-cost approach of a monthly sampling campaign over the course of one year combined with meaningful indicators for potential pollution sources within the catchment this study could elucidate catchment dynamics and two hotspots for pesticides and nutrients. Two different groups of pesticides were observed (I) pesticides on long-term use which were applied in high amounts over the last decades (e.g., chloridazon and its transformation products) and (II) pesticides on short-term use, newly introduced into the market. Especially transformation products of pesticides from group (I) together with nitrate showed a steady release from two fields into the receiving water bodies over the year, probably being stored in the soil layers over the years of application slowly leaching out. Pesticides from group (II) showed a strong seasonality, released from another hotspot area probably due to run-off shortly after application. Streamlining this knowledge into targeted measures and an agile monitoring strategy for the respective catchments may allow a sustainable improvement of water quality and a better ecosystem protection.

2.1. Introduction

Nowadays, most waters bodies are under intensive anthropogenic pressure (Carpenter et al., 1998; Garnier et al., 2010; Herrero-Hernández et al., 2013; Lawniczak et al., 2016; Loos et al., 2010; Moschet et al., 2014; Vonberg et al., 2014). High inputs of nutrients such as phosphate (P) and nitrate (N) were identified as principal cause of eutrophication in freshwater bodies often resulting in a decrease or change in biodiversity (Mainstone and Parr, 2002; Watson et al., 2016; Weijters et al., 2009). In the 1980/1990s high fluxes of nutrients into surface waters were mostly associated to point-sources from population and wastewater (Cole et al., 1993). Technical solutions such as P and N elimination in wastewater treatment, restoration of leaking sewage pipelines and the replacement of sodium tripolyphosphate with zeolites in washing detergents lead to a significant decrease of nutrient input of N and P since the mid-1990s (Robertson et al., 2016; Snider et al., 2017; Van Drecht et al., 2009). Today, as most point-sources are well understood and regulated (Carter, 2000), diffusive sources such as agricultural fertilizers and manure entering the aquatic environment via field run-off and/or atmospheric deposition are under critical concern (Cole et al., 1993; Le Moal et al., 2019). Despite several years of environmental research many slowly flowing water bodies suffer from severe and recurring eutrophication events.

Beside elevated nutrient concentrations, constantly rising concentrations of pesticides in water bodies become problematic especially for drinking water production (Casado et al., 2019; Tröger et al., 2018). Once released into the environment, pesticides often undergo biotic or abiotic degradation leading to transformation products (TPs), often also referred to as metabolites (Fenner et al., 2013). These TPs are often highly persistent to degradation even during water treatment and can have a higher mobility in the aquatic environment leading to a high risk to accumulate in the water cycle (Buttiglieri et al., 2009; Jekel et al., 2015a,b; Rodríguez-González et al., 2017). Due to their high mobility they can potentially leach through the soil and reach the groundwater (Neukum and Meyer, 2019). Pesticides have by design potent structures regarding (eco-)toxcity (Fenner et al., 2013) and endocrine disrupting properties (Masiá et al., 2013), which is often threatening to non-target biota (Liess and Von Der Ohe, 2005). Nowadays, TPs can be found ubiquitously in surface and ground water bodies in the range of ng/L to µg/L (Fenner et al., 2013; Neukum and Meyer, 2019; Reemtsma et al., 2013; Reh et al., 2013). Although pesticides are mostly associated with pest control, another significant source is wash-off from facades as some are used as biocides in anti-microbial paintings (Wittmer et al., 2010, 2011).

In agricultural areas pesticides often show seasonal variations in surface waters with peak concentration shortly after application due to spray drift or run-off after rain events (Buttiglieri et al.,

2009; Byer et al., 2011; Jensen and Olesen, 2014; Lupi et al., 2019; Sandin et al., 2018; Ulrich et al., 2018). Pesticides which lost their approval and are no longer applied can still pose a risk as they are potentially released into the environment over long time (Farlin et al., 2013; Silva et al., 2019). In most European countries atrazine lost its approval in the early 1990s, followed by a complete prohibition in the EU in 2004 (European Commission, 2004). Despite its ban it can still be found in European waterbodies (Hillebrand et al., 2014; Vonberg et al., 2014) and similar trends are observable with the metabolites of the ubiquitous used beet root herbicide chloridazon which was recently banned from use (Neukum and Meyer, 2019).

As nutrients and pesticides are a burden for European water bodies, water quality is not only regulated nation-wide but on a European level. To achieve a "good water quality" for surface and groundwater and to make data comparable throughout the member states with a standardization of monitoring criteria, water quality is regulated under the Water Framework Directive (WFD) throughout all European countries (Directive, 2000/60/EC). Differentiating between ecological and chemical status, the WFD defines Environmental Quality Standards (EQS) for water quality to be monitored throughout a defined period depending on the current water status. Elevated concentrations of nutrients in surface and groundwater are the main cause for failing a good water quality status (Arle et al., 2016). Nevertheless, only 38% of surface waters are according to the WFD regulation at least in good chemical condition and only about 40% are at least in good ecological status across Europe (European Environment Agency, 2018). Only 6.7% of all German rivers and 26.1% of all lakes are in good or very good ecological condition (European Environment Agency, 2018). Current monitoring strategies have a limited temporal resolution, a limited number of target compounds (Allan et al., 2006) and a limited seasonal coverage as the current grab sampling method is likely to oversee peak concentrations of pollutants e.g., due to dilution effects after heavy rainfall and snowmelt events (Hillebrand et al., 2014; Holvoet et al., 2007; Spycher et al., 2018). The current strategy only allows 'snapshots' of water quality (Arle et al., 2016). Improving water quality on a long-term perspective by implementing cost-effective measures based on a profound understanding of underlying processes and dynamics are a key factor (Koski et al., 2020). A further obstacle is the underrepresentation of small water bodies as only larger water bodies with a catchment area ≥10 km^2 are included into routine monitoring. More than 90% of all water bodies in Germany belong to small water systems and thus their protection and management is not regulated under the WFD (German Environment Agency, 2017). Only 12% of all small catchments are included in the national monitoring program of Germany (Brinke et al., 2015). Small water systems are particularly exposed to inputs and are more vulnerable due to their low water volumes and their close connection to adjacent agricultural fields (Lorenz et al., 2017). The retention of pesticides and other pollutants by sorption, sedimentation, plant uptake or microbial degradation is usually low in small water bodies

(Das Gupta et al., 2016; Ma et al., 2016). Nevertheless, small catchments play an important role in freshwater ecosystems as they support higher proportions of biodiversity than larger water bodies (Biggs et al., 2007; Szöcs et al., 2017). Small catchments are highly complex due to dynamic concentration profiles, a large number of active compounds differing seasonally, and major knowledge gaps on their dynamics (Spycher et al., 2018). A holistic approach for small catchments is strongly needed, allowing site specific measures for an overall and sustainable improvement of water quality (Brils et al., 2010).

In this study a small lake catchment regarding its seasonal dynamics of nutrients and pesticides including their metabolites was investigated, to suggest monitoring implications and to fill major knowledge gaps by a combined survey of pesticide and nutrient dynamics. We decided for a small lake system in Central Germany which is routinely monitored by a national monitoring program and according to WFD standards the lake and its tributary River Aue would receive a bad chemical and ecological status. Lake Seeburg has a catchment of 31.5 km^2 suffering from silting-up and significant eutrophication problems for decades, potentially due to intense agricultural activity in the catchment. Eutrophication leads to strong recurring algae blooms of cyanobacteria (anabaena) between August and September. As the catchment functions as nature and wildlife conservation area for birds a reliable water quality monitoring approach to ensure safe water quality is needed.

To understand the different dynamics between pesticides of long-term use vs. recently approved pesticides a major differentiation was made between two groups of pesticides and their TPs:

I. Pesticides which are no longer approved such as chloridazon (with its TPs desphenyl chloridazon and methyl desphenyl chloridazon) and atrazine (with its TPs desisopropyl atrazine and desethyl atrazine).

II. Pesticides which are in use like quinmerac (with its TPs methyl quinmerac, BH 518-2 and BH 518-5) and, metazachlor (with its TPs BH 479-4, BH 479-8 and BH 479-12), and metolachlor (with its TPs metolachlor oxanilic acid and metolachlor sulfonic acid).

Both quinmerac and metazachlor are part of various herbicide mixtures applied as post-emergence herbicides few weeks after sowing (in spring or autumn) depending on the field crops. Understanding the temporal and spatial distribution of pesticides will allow to answer the following key questions of the study:

1) Are the concentration patterns of nutrients correlated to the concentration patterns of pesticides and do they have the same source and dynamics?

2) Can we observe different dynamics for pesticides which are actively applied and which are no longer in use?

3) Can we develop a risk-based approach within the monitoring strategy applicable for small lake catchments with a high agricultural pressure to protect these in a more sustainable way?

2.2. Material and methods

2.2.1. Sampling

The sampling campaign was carried out for one year between September 2017 and August 2018 at Lake Seeburg catchment in monthly intervals at the first working day of every month. Lake Seeburg is located in Central Germany (51°33′ 52′′ N, 10°09′ 52′′ E) and covers 0.89 km^2. Its maximum depth is 4 m with a water volume of 2×10^6 m^3 and has an average water residence of 0.33 years (Nixdorf et al., 2004). When selecting the sampling points (SP), attention was paid to cover critical points within the catchment, such as the intersections of streams, wetlands and run-off from the federal road nearby (a map with all sampling points can be found in Fig. 2.1) Sampling points 1 to 5 represent the course of the River Aue, with a share of 98% of the main inflow to Lake Seeburg. Sampling point 3 is located in an adjacent wetland that is being flooded regularly during rain events and drains into the River Aue. Four smaller streams draining agricultural areas and contributing to the River Aue were sampled (a to d) to quantify the impact of smaller tributaries. At the lake itself sampling was carried out near the inflow (SP 6) and the outflow (SP 7) of the lake, to identify a possible gradient of pollutant concentrations in the lake. Samples were collected in glass bottles to ensure the stability of the analytes, samples were stored cool and dark at 4 °C after collection to ensure stability of all analytes (Gawlik et al., 2012; Hillebrand et al., 2013). All samples were analyzed within 24 h after collection.

2.2.2. Chemicals and analysis

Ammonium fluorite, formic acid and methanol were purchased from VWR Chemicals (all analytical grades). The internal standard consisted of respectively 20 µg/L atenolol D_6, melamine ^{13}C, atrazine D_5, theobromine D_6 and chloridazon D_5 in methanol. Nitric acid (65% p.a.) was purchased from Merck, Na_2CO_3 and $NaHCO_3$ from Roth (all analytical grades). Ultrapure water was obtained using a combined water purification system consisting of an Elix 5 and Milli-Q Gradient A10, both from Millipore. The standards consisted of NO_3^-, Cl^-, SO_4^{2-}, F^-, PO_4^{3-}, Br^- and Ca^{2+}, Mg^{2+}, Na^+, K^+, Li^+, Sr^{2+}, Ba^{2+} purchased from Merck Analytical.

Temperature (T), electrical conductivity (EC), pH and oxygen were recorded using a multi-parameter portable meter (Multiline 3630 IDS, WTW GmbH, Germany) directly at the water sampling positions.

The ortho-phosphate or soluble reactive phosphate concentrations (SRP) were analyzed via photometry according to EN ISO 6878 using an UviLine 9400 photometer by SI-Analytics. Nitrate was analyzed via ion chromatography (IC) using a chromatograph 883 Basic IC plus by Metrohm. Prior to measurement, water samples were filtrated with 0.2 µm nylon filters by Carl Roth GmbH. For separation a Metrosep A. Supp 5, 250 × 4.0 mm column was used. The separation was performed at 25 °C, the injection volume was set to 20 µL at a flow rate of 0.7 mL/min. The used eluents were 3.2 mmol/L Na_2CO_3 and 1.0 mmol/L $NaHCO_3$. Ammonium was analyzed via IC using a 820 IC separation unit, a 818 IC pump unit, a 837 IC degasser unit and a 819 IC detector by Metrohm. Before measurement, samples were filtered (mesh 0.22 µm), acidified (0.1% HNO_3), and diluted 1:2 with 3.0 mmol/L HNO_3. For separation a Metrosep C3, 250 × 4.0 mm was used. The column oven performed at 40 °C, the injection volume was set to 20 µL at a flow rate of 1.0 ml/min. The eluent was 4.5 mmol HNO_3. For full QA data see Tab. A1.

For analysis of trace organics including pesticides 1 mL of each sample was spiked with 20 µL of the internal standard mix and centrifuged for 15 min at 5000 rpm. The separation and quantitation of the analytes was done on an ultrahigh-performance liquid chromatographic separation with tandem mass spectrometric detection (UPLC/MS-MS). The UPLC system (NEXERA X2, SHIMADZU) consists of a high-pressure gradient system with two pumps (LC-30AD) and a degasser (DGU-20A). For chromatographic separation a Phenomenex Luna® Omega 1.6 µm Polar C18 100 Å, 100 × 2.1 mm column, with a pre column and a 0.2 µm particle filter was used. The column oven (CTO-20AC) performed the separation at 50 °C and the injection volume was set to 50 µL at a flow rate of 0.55 ml/min. Eluent A was 2 mmol/L NH_4F with 0.01% formic acid in ultrapure water, eluent B was methanol. The elution gradient started at 10% methanol within the first 0.5 min followed by a linear increase to 95% methanol within 6.5 min. It was held there for 1.5 min, continued by a decrease back to 10% methanol within 0.05 min and was kept at this value for 0.2 min. A mass spectrometer Sciex Qtrap 6500+ was used for detection and quantification. It was operated in low mass mode with Electrospray Interface (+ESI set to 500 °C). Ion source gas 1 was set to 70 psi, source gas 2 to 50 psi, ionspray voltage (IS) to 5500 V for positive ionization mode and to -4500 V for negative ionization mode. Detection was performed in Multiple Reaction Monitoring (MRM) and two transitions per analyte were monitored. Detection limits (DL) varied from 0.3 ng/L (chloridazon) to 11 ng/L (desethyl atrazine), which is suitable for the analysis of water samples in the framework of an indicator concept. For full QA data see Tab. A2.

2.3. Results and discussion

The lowest water temperatures appeared at all sampling points in February (2.0 °C and 5.0 °C) and highest at all sampling points in August and June (13.5 °C and 26.7 °C). The oxygen-levels in River Aue and its tributaries were relatively constant throughout the year. A decrease of electrical conductivity (EC, for full EC Data please see Tab. A3 and Fig. A5) downstream the River Aue towards the lake might indicate dilution by groundwater discharge. Highest EC values can be found from autumn to winter (from October to December with 440 µS/cm up to 962 µS/cm) and lake (measured at the inlet and outlet) during spring-time (in March and April with 737 µS/cm).

With a preliminary catchment appraisal three potential sources for nutrients were determined: domestic wastewater, manure or artificial fertilizer and urban run-off. The method of choice in differentiating potential sources and therefore assigning the nutrients to them is an indicator set based on source-specific micropollutants (Jekel et al., 2015a,b; Warner et al., 2019). For indicating wastewater influence the artificial sweetener acesulfame (Buerge et al., 2009), caffeine including its human metabolite paraxanthine (Hillebrand et al., 2012), the topical pain reliever benzocaine and valsartan acid (Nödler et al., 2016), a human metabolite from the widely prescribed blood pressure regulator valsartan, were chosen. For indicating urban run-off nicotine was used, which is usually detected in urban areas originated by leaching out of tossed cigarette butts (Roder et al., 2014). Sulfadimidine, a veterinary antibiotic, was designated as an indicator for manure (Christian et al., 2003; Martínez-Carballo et al., 2007). The absence of caffeine, paraxanthine, benzocaine proves that no untreated waste water enters the catchment and nutrients can be solely allocated to agriculture. Sulfadimidine, a veterinary antibiotic, was found in traces throughout the monitoring period probably indicating the use of manure as fertilizer as there is no livestock production in the catchment.

Despite its prohibition in 1992, atrazine is found equally distributed over the catchment in 117 of 154 samples (76%) in low (2-12 ng/L) concentrations compared to other catchments (Loos et al., 2013). Atrazine's TP desisopropyl atrazine was not detected in any sample, probably due to the overall low concentration of atrazine which is in accordance with previous studies where concentrations varied from not detected to many hundred ng/L (Carafa et al., 2007; Kundu et al., 2019; Nödler et al., 2013; Reh et al., 2015). Metolachlor was not detected in any sample either, but its TPs metolachlor oxanilic acid (detected in 8 samples) and metolachlor sulfonic acid (detected in 2 samples), were found at several SPs in winter (September to February). It is likely that metolachlor was used in the past within this catchment and is no longer detectable due to its fast metabolism of 5-30 days (Hvézdová et al., 2018; Lewis et al., 2016). Chloridazon's TPs desphenyl chloridazon anddesphenyl methyl chloridazon

were detected in all samples (100%), even if chloridazon is not applied anymore. With a mean flow rate of 300 L/min (NLWKN, 2010), approximately 3442 g desphenyl chloridazon, 76 g desphenyl methyl chloridazon, 244 g quinmerac, 1934 g of metazchlor's TPs metazachlor acid BH 479-4 and 5233 g metazachlor sulfonic acid (BH 479-8) enter the lake within a year. Pesticide losses often originate from relatively small fractions of agricultural landscape (Doppler et al., 2014; Freitas et al., 2008). Different transport dynamics and their release into the aquatic environment is primarily driven by compound properties such as pKa and log P (Schaffer and Licha, 2014, 2015). Sorption is one of the key processes in the environmental fate of pesticides in soil. It determines their distribution in the soil/water environment and is controlled by soil and compound properties (Kah and Brown, 2007). As all pesticides are ionizable the prevalent pH value plays a crucial role regarding sorption behavior, log D would have been a more accurate approach then log P (Kah and Brown, 2008; Schaffer and Licha, 2015). As soil pH was not a focus of this study, interpretation will be simplified to log P and as Meylan et al. (1996) simplifies log P as an indicator for the likelihood for a compound to remain in the soil phase rather than accumulating in the water phase. The log P values of all pesticides vary between -0.195 ± 0.546 (metolachlor sulfonic acid) and 2.636 ± 0.205 (atrazine)[1] indicating a low sorption tendency to soil. Nevertheless, the amount applied in the catchment region seem to be more important than the respective log P (Tesfamichael and Kaluarachchi, 2006).

2.3.1. Seasonal dynamics

Most studies report elevated pesticide concentrations in surface water during spring and early summer (Szöcs et al., 2017) while others report no seasonal dynamics at all (Moschet et al., 2014) indicating a strong dependency on individual catchment characteristics.

Quinmerac, metazachlor and ammonium show the concentration patterns over the monitoring period with a maximum in October 2017 (Fig. 2.1). In this case probably heavy rain events (e.g., 05.10.2017, 19.4 mm)[2] shortly after the application of the combined pesticides mixture of quinmerac and metazachlor for winter rapeseed (e.g., ADAMA Fuego®TOP) with flooding causing a high and rapid input of quinmerac and metazachlor into River Aue and its tributaries. This is in agreement with Matamoros et al. (2012) who also observed highest pesticide concentrations during heavy rainfall resulting from run-off. The first detection of quinmerac in the lake is one month after its first occurrence in the tributaries resulting in a one month approximate travel time from field to lake.

[1]All compound properties are obtained from https://scifinder.cas.org (accessed 10.03.2020).
[2]All precipitation data is for city of Göttingen, close to Lake Seeburg obtained from the US National Oceanographic and Atmospheric Administration (NOAA) data base (https://www.noaa.gov).

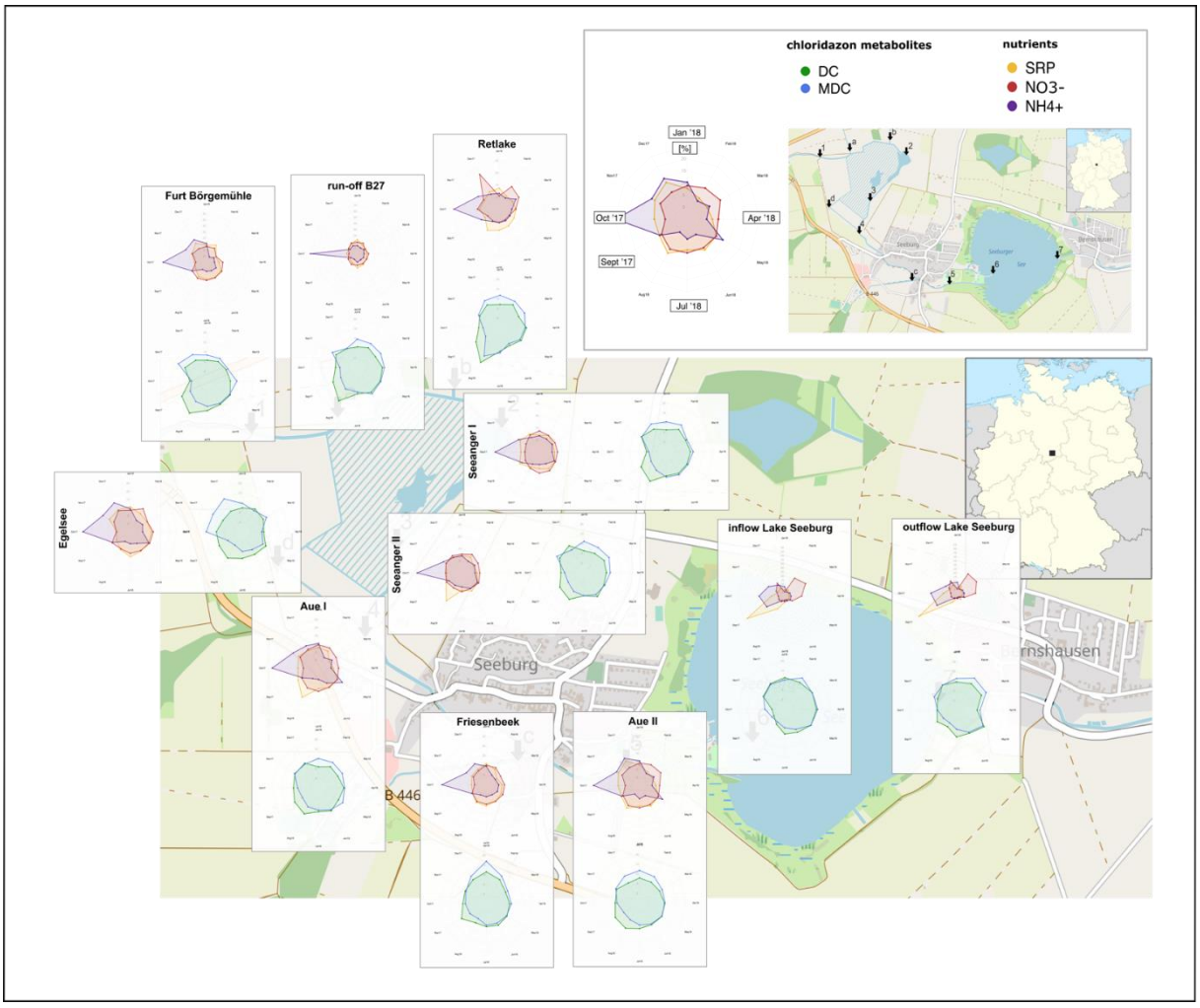

Fig. 2.1. Seasonal dynamics of the chloridazon metabolites desphenyl chloridazon (DC), methyl desphenyl chloridazon (MDC), soluble reactive phosphorus (SRP), nitrate (NO^{3-}) and ammonium (NH_4^+). While NH_4^+ shows a seasonal variation throughout the catchment, NO^{3-} is equally released throughout the year with seasonal maxima during late summer and fall in the in- and outflow of Lake Seeburg. For a better comparability, the data were converted to percent related to the compound's maximum concentration. Complete concentration data can be found in the Supplementary Data Figs. A1-A4. For a detailed view, please refer to the high resolution figure provided digitally.

2.3.1.1. Metazachlor and its TPs

In Lake Seeburg the highest concentrations of both metabolites appear around the same time, in the eastern part of the lake (SP 7), however, one month later, followed by a decrease until July/August, similar to the seasonal behavior of quinmerac (Fig. 2.2). The half-life of metazachlor in the environment is reported to vary between 11.6 and 77.0 days (Walker and Brown, 1985), 10.92-12.68 days (Mantzos et al., 2016) or 11.9 days (Mamy et al., 2008). Nevertheless,

Metazachlor's TPs reach their concentration peaks in the lake one to three months later as a combination of travel time and transformation.

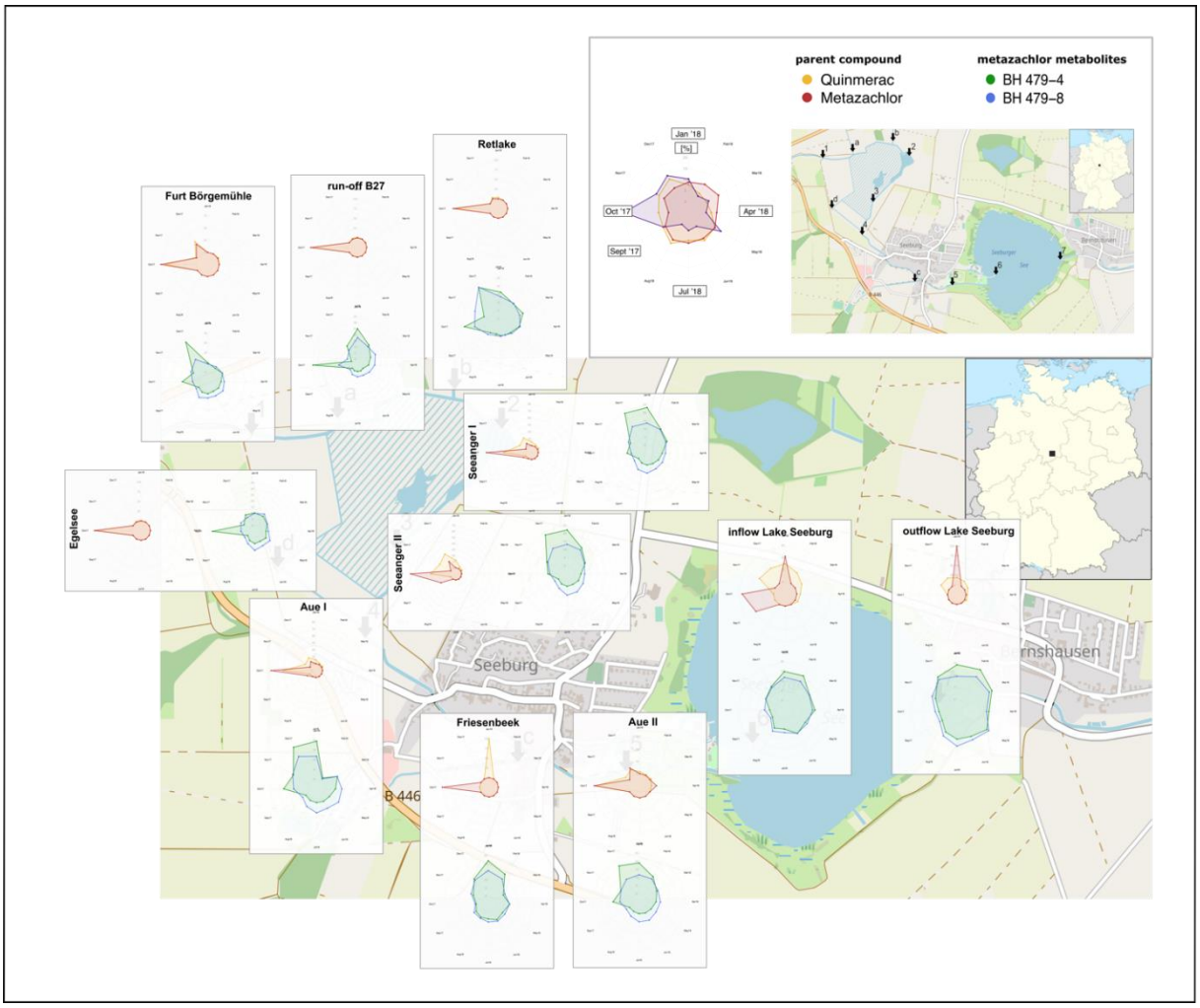

Fig. 2.2. Seasonal dynamics of quinmerac, metazachlor and its metabolites BH 479-4 and BH 479-8. A sharp seasonal maximum for quinmerac during fall is observable. Seasonal maxima for the metabolites are predomenantly observable for certain sampling points (e.g., Egelsee) adjacent to agricultural fields, while they get diluted throughout the catchment. For a better comparability, the data were converted to percent related to the compound's maximum concentration. Complete concentration data can be found in the Supplementary Data Figs. A1-A4. For a detailed view, please refer to the high resolution figure provided digitally.

2.3.1.2. Phosphorus

A major aim of our study was to understand nutrient dynamics, especially of SRP which is immediately accessible to plants and algae and induces advanced eutrophication processes in the lake. Not only the elevated concentrations from the inflows, but also internal SRP cycling seemed a major problem for the lake. In the River Aue and its tributaries (SPs 1, 2, 5 and a-d) the concentrations vary from 0.06 mg/L in March 2018 to 0.343 mg/L in December 2017. SRP does not

show a strong seasonal variation in the River Aue and its tributaries and is constantly low at SP 1 (average value 0.12 mg/L) but concentrations nearly double along the flow path towards SP 5 (average value 0.22 mg/L) almost throughout the year (Fig. 2.1). Increased concentrations from inflows c and d (average values of 0.27 and 0.28 mg/L) which drain agricultural areas were identified as constant point sources (approximately 0.35 mg/L November–December; July–September). P-loss associated with fertilizers are usually found shortly after application (Udeigwe et al., 2010) by run-off or interflow (Finlayson and Silburn, 1996) and has a seasonal maximum in late autumn and spring due to an elevated precipitation (McDowell and Trudgill, 2000). Seasonal maxima in the lake in autumn can be explained by increased mixing processes in the lake water and release of SRP from the lake sediment (Schindler et al., 2016). This is supported by our study. With highest temperatures and low oxygen values in August, the wetland (SP 3) released peak concentrations of P (0.66 mg/L) into the river. If the application of P-containing fertilizers was in excess of the amount required by the plants, P can built up in deeper soil layers where it can be re-mobilized long after its application by subsurface flow, contributing to eutrophication (McDowell and Sharpley, 2001a,b). This can especially be observed for the wetland which had been in intensive agricultural use until the 1990s. Due to a permanent release of SRP from this area and fowling conditions in summer, even more SRP can be mobilized from deeper soil layers. Such steady release of P could function as long-term reservoirs resulting in extensive fertilization during the last decades, slowly releasing P into the surface waters and transporting it to the lake which is in accordance to the study by Sandin et al. (2018).

2.3.1.3. Ammonium

At all sampling points the highest ammonium concentrations were detected in October 2017, with maximum values up to 2.65 mg/L in the tributaries and up to 0.485 mg/L in the lake, probably due to the application of fertilizers and following run-off (Fig. 2.1). During the remaining months ammonium concentrations remain low and relatively constant. After heavy rainfalls (13.07.2017, 19.6 mm) reported in July 2017, the wetland at SP 2, and the fields around tributary B were flooded and the fowling processes in this area in the following months released high concentrations of ammonia. The drainage of this area took several months, which is recordable by higher ammonium values in the tributary until January 2018. In the lake, not only the high ammonium inflow from the tributary, but also the decline of a cyanobacterial bloom in September 2017, followed by the biodegradation of the organic matter, resulted in higher concentrations of ammonium from October 2017 to January 2018. A clear concentration peak of both ammonium and metazachlor (with the exception for the lake) can be seen at all sampling points in October 2017.

2.3.2. Spatial variations

Finding solutions for monitoring implications, the knowledge on pollutant sources and dynamics is a pivotal point to obtain the right measures for improving water quality on catchment scale.

2.3.2.1. Choridazon, its TPs and nitrate

The main input of nitrate and the TPs of chloridazon can be allocated to small streams draining agricultural fields. Chloridazon metabolites have highest concentrations at SP b (Retlake) and SP a (run-off B27), while nitrate shows highest concentration at SP c (Friesenbeek) and SP d (Egelsee) (Fig. 2.3). Chloridazon lost its approval in Germany and needed to be used up by mid-2020. It was applied excessively with low regulation over the last decades and especially its TPs can be already found in drinking water.

Chloridazon was still detected in 37 of 154 samples (24%), but the observed concentrations were generally low (<10 ng/L). However, due its expiring approval in 2018 and the stricter regulations for this herbicide the application of chloridazon was very scarce over the last 5 years in the studied area (personal communication with 'Landwirtschaftskammer Niedersachsen'). The concentrations of the TPs are significantly higher as desphenyl chloridazon and methyl desphenyl chloridazon concentrations show high concentrations up to mg/L-range at all sampling points. The constant appearance of desphenyl chloridazon and methyl desphenyl chloridazon without any seasonal variation indicates the use of chloridazon in the catchment area of Lake Seeburg in the past and strongly indicate that the soil could function as reservoir for long-term leachate of chloridazon's TPs.

Under laboratory conditions chloridazon is completely metabolized to desphenyl chloridazon within the experimental time of 98 days but was resistant to further degradation according to Buttiglieri et al. (2009). However, the transformation kinetics may seem to be significantly different for environmental conditions. Model calculations for aquifers show that the metabolites of chloridazon, especially desphenyl chloridazon, will still be detectable in water bodies in the coming decades (Neukum and Meyer, 2019).

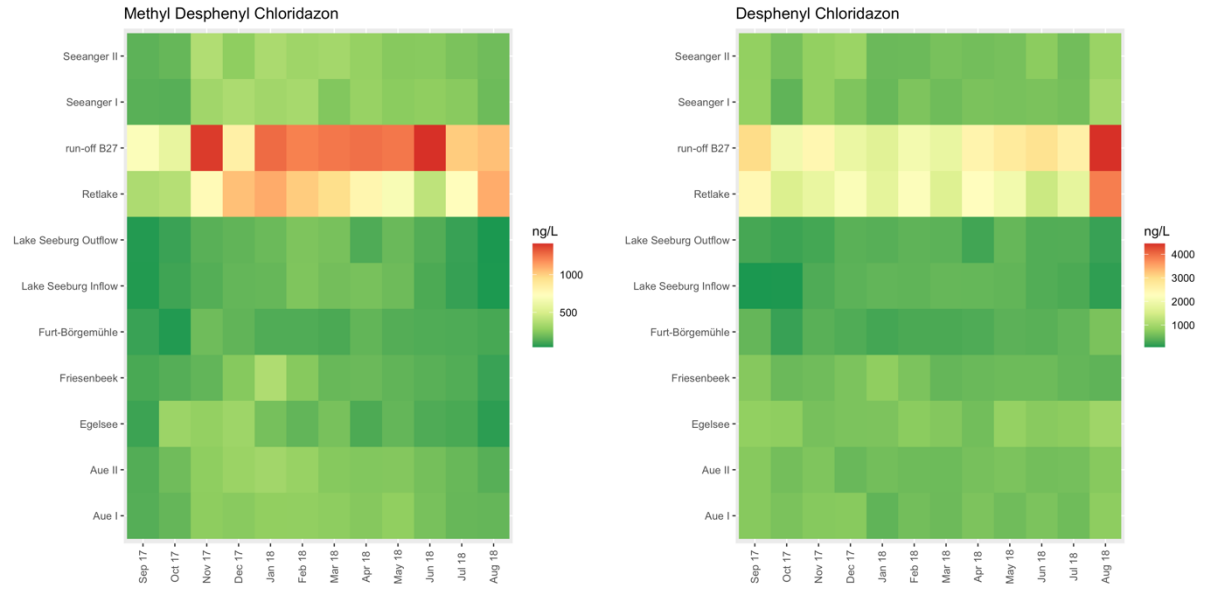

Fig. 2.3. Spatial distribution of desphenyl chloridazon and desphenyl methyl chloridazon in ng/L. Instead of being evenly distributed over the catchment, clear hotspots are observable.

2.3.2.2. Metazachlor TPs BH 479-4 and BH 479-8 and nitrate

Beside their seasonal occurrence during late fall/winter the input of metazachlor's metabolites can be allocated to two hotspots, SP d (Egelsee) and SP c (Friesenbeek), as discussed probably released by run-off from the adjacent agricultural fields after application (Fig. 2.4). While nitrate concentrations in the lake itself are low, probably due to consumption during growth season of aquaphytes, high concentrations of nitrate can be found in SP d (Egelsee) and SP c (Friesenbeek) probably originating from fertilizer applications on adjacent fields and its discharge during discussed run-off-events after application.

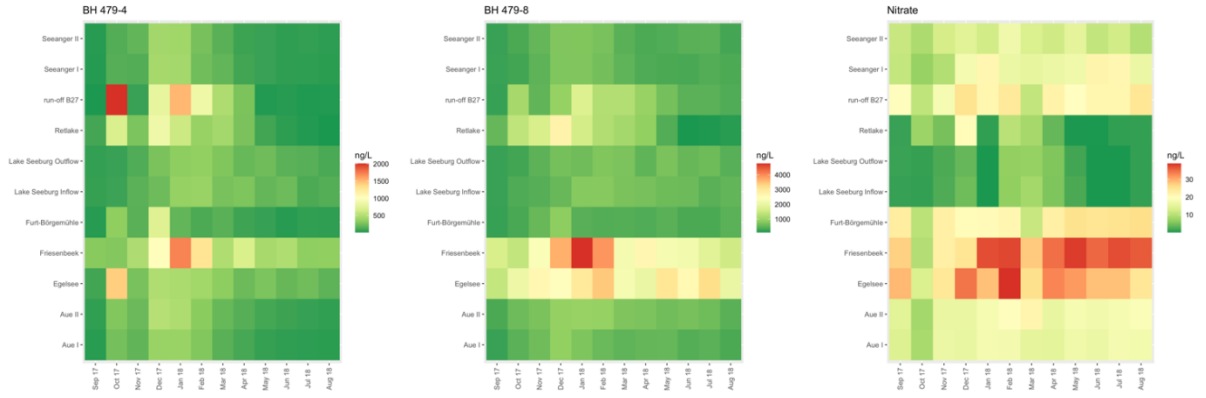

Fig. 2.4. Spatial distribution of Metazachlor's TPS BH 479–4 and BH 479–8 in ng/L. Instead of being evenly distributed over the catchment, clear hotspots are observable.

2.4. Conclusion

This study shows how to clearly identify dynamics within a catchment by relatively low personal and analytical effort and two major hotspots for pesticide input within the catchment could be allocated. This approach shows that expensive high-resolution monitoring with a large number of indicators is not mandatory to understand catchment dynamics. A careful catchment appraisal, probably including locals and citizens, is a key step to find relevant sampling spots and reduce the number of analytes.

The occurrence of pesticides, their TPs and nutrients are not necessarily coupled or show identical seasonal patterns. Especially a correlation between chloridazon's TPs desphenyl chloridazon and methyl desphenyl chloridazon and nitrate was of special interest for the studied area as both can be found in elevated concentrations in groundwater posing an increasing risk for drinking water production. The study could show that the input of chloridazon's TPs was decoupled from the areas of high nitrate input as both have different hotpots areas which is in accordance with Mottes et al. (2017) identifying two types of pollution in most catchments.

I) long-term chronic pollution of pesticides (and their metabolites) used over decades accumulating in the water cycle and soils such as chloridazon TPs and,

II) pesticides newly introduced or recently applied in the catchment, showing seasonal peak concentrations such as quinmerac and metazachlor. Both patterns could be assigned to two different hotspots within the catchments. Sources of high nutrient and compound fluxes are mostly smaller tributaries collecting run-off from adjacent fields. Also, soils can function as reservoirs for the historic application of pesticides and their transformation products and, hence, can function as diffusive sources slowly releasing these compounds over long periods of time. Targeted and low-cost measures in these hotspot areas, e.g., no pesticides/manure application before rainfalls, can probably reduce the input of pesticides and nutrients significantly leading to an improved water quality status. Due to the high dynamics there is probably no one-size-fits all approach for small lake systems and small catchments. However, the following recommendations for an agile monitoring approach are provided:

1. Catchment appraisal: define relevant pollutants/analytes and information-rich sampling spots (information-driven sampling rather than data driven).

2. Define water quality goals legislative guideline values or other catchment specific goals.

3. Choose information-rich indicators after a catchment appraisal, which can mean to include transformation products of compounds rather than the parent compounds.

4. Understand catchment dynamics, e.g., seasonal and spatial dynamics or pollution sources/hot spots.

5. Derive a measure where possible and most effective, define indicators to track the effectiveness of the measure.

6. Establish a long-term monitoring for catchment-specific indicators with a higher sampling rate when their maximum concentrations can be expected (risk-based approach) and further access changes in water quality.

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3. Effects of weather extremes on the nutrient dynamics of a shallow eutrophic lake as observed during a three-year monitoring study

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The formation of algal and cyanobacterial blooms caused by the eutrophication of water bodies is a growing global concern. To examine the impact of extreme weather events on blooms, eutrophication-related parameters (e.g., water temperature, nitrate, ammonium, nitrite, and soluble reactive phosphate (SRP)) were quantitatively assessed monthly over three years (2017–2019) at Lake Seeburg (Central Germany), a shallow eutrophic lake with regular cyanobacterial blooms. In addition, SRP concentrations in sediment pore water were assessed monthly for one year (2018). The monitoring period included a three-day extremely heavy rain event in 2017 as well as a severe drought in summer 2018. No such extreme weather conditions occurred in 2019. After the heavy rain event in 2017, anoxic water containing high levels of ammonium and SRP entered the lake from flooded upstream wetlands. This external nutrient spike resulted in a heavy but short (≈3 weeks) and monospecific cyanobacterial bloom. A different situation occurred during the exceptionally hot and dry summer of 2018. Especially favored by high water temperatures, SRP concentrations in sediment pore waters gradually increased to extreme levels (34.4 mg/L). This resulted in a strong and sustained internal SRP delivery into the water column (69 mg/m^2·day^{-1}), which supported the longest-lasting cyanobacterial bloom (≈3 months) within the 3-year monitoring period. Subsequent biomass decay led to oxygen-depleted conditions in the bottom waters, elevated ammonium, and, later, nitrate concentrations. Our observations demonstrate the particular effects of extreme weather events on nutrient dynamics and the phytoplankton composition in the lake. As the frequency and intensity of such events will likely increase in the future due to climate change, their impacts need to be increasingly considered, e.g., in future remediation strategies.

3.1. Introduction

Anthropogenic eutrophication of lake waters is a matter of growing global concern. The overabundance of nutrients leads to effects such as phytoplankton blooms and oxygen deficiency, which negatively impact lake ecosystems. Furthermore, cyanobacterial blooms can pose an immediate threat to animals and humans due to their production of hazardous toxins (Catherine et al., 2013; Huisman et al., 2018; Jones et al., 2021). Climate change and the associated increase in extreme weather events such as heavy rainfalls or heat waves will likely exacerbate negative eutrophication phenomena in lakes in the future (Jeppesen et al., 2007, 2021; Nürnberg, 2012; Paerl and Huisman, 2008).

Various changes in lake water bodies due to extreme weather events have been described in the literature. Heavy rain events can contribute to significant short-term changes such as nutrient inputs from soil erosion in the catchment (Kleinmann et al., 2006) or increased turbidity in the waterbody itself (Anh et al., 2002). Hot and dry periods can result in declining water levels, which is often associated with increased conductivity (Bonte and Zwolsman, 2010) and increased nutrient release from the sediment (Jeppesen et al., 2021). Both heavy rain events and dry periods can change the organism composition of lake waterbodies, often with a competitive advantage for cyanobacteria (Reichwald and Ghadouani, 2012).

Well-studied examples of lakes exhibiting these problems are the shallow lakes of Taihu (China) and Lake Okeechobee (FL, USA). Lake Taihu, the third-largest freshwater lake in China, with high concentrations of anthropogenic nutrients, recently experienced its largest cyanobacterial bloom, exacerbated by high rainfalls and a subsequent much warmer winter due to the El Niño effect (Qin et al., 2021). In Lake Okeechobee, the third-largest lake in the USA, three hurricanes caused increased nutrient loads, water levels, and turbidity that lasted two years and had a significant impact on the phytoplankton community and submersed aquatic vegetation (James et al., 2008).

To better protect vulnerable lake environments and design proper management strategies, it is necessary to understand how and in what time frames different lake ecosystems may be affected by, and respond to, such external forcing. Here, we report on nutrient and microorganism dynamics at Lake Seeburg, a small (0.89 km^2) and shallow (average depth 2 m) unstratified lake in central Germany. As a result of ongoing eutrophication, the lake has been suffering from recurrent cyanobacterial blooms in recent decades. The frequency and intensity of these blooms tend to increase, similar to various other inland lakes around the world (Taranu et al., 2015).

Small lakes, such as Lake Seeburg, are particularly exposed to nutrient inputs due to their low water volume and proximity to adjacent agricultural land (Lorenz et al., 2017). Although they account for

the largest share of inland water bodies in central Europe in terms of surface area, small lakes are strongly underrepresented in environmental studies. For example, more than 90% of all water systems in Germany have a catchment area of ≤10 km^2 and are, therefore, not considered by the European Water Framework Directive (WFD). This contrasts with the fact that small lakes often harbor even greater biodiversity than larger water bodies and, thus, play a particularly important ecological role (Biggs et al., 2007; Szöcs et al., 2017). Likewise, the high value of many small lakes to residential populations in terms of nature experience, recreation, and local economy makes it worthwhile to develop appropriate management and remediation strategies.

Our 3-year monitoring study of key nutrients allowed us to gain insight into the complex biogeochemical processes that govern the ecology of Lake Seeburg. In two of the three years of observation, extreme weather conditions occurred in the study area. Between July 24th and 26th, 2017, a heavy rain event with precipitation of ≈120 L/m^2 (almost twice the normal rainfall in a month) was recorded, leading to widespread floodings in the catchment area of Lake Seeburg (Becker et al., 2017). The total sum of rain for the month of July reached about 200 L/m^2 in the study area and was, thus, 2.7 times higher than average (Wetterkontor, 2021). In 2018, in contrast, there was a severe drought with very little rainfall between February and October (49% of the long-term average) and high average temperatures (+1.1 °C compared to the long-term average) (Wetterkontor, 2021). In this study, we report on the effects of these events on the seasonal and interannual nutrient dynamics and the associated varying microorganism composition of Lake Seeburg. Knowledge of the expected ecological consequences of such events enables early recognition of the resulting environmental impact and initiation of appropriate countermeasures.

3.2. Materials and methods

3.2.1. Sampling location

Lake Seeburg is located in central Germany, about 15 km E of the city of Göttingen (51°33’52’’ N, 10°09’52’’ E). It covers 0.89 km^2 and has a water volume of 2 million m^3, a mean water depth of 2 m, and a maximum water depth of 4 m (Streif, 1970). The lake is a water-filled sinkhole and was formed by subsurface leaching of Permian evaporites about 10.000 years ago (Streif, 1970). The lake has been a natural reserve since 1973 and is classified as a special flora–fauna habitat area and an EU bird reserve.

Lake Seeburg is used for non-commercial fishing and as an official swimming lake in summer (R13A50002403152002, EU Bathing Directive). The area surrounding the lake is only sparsely

populated with small villages, and no industry is located in the catchment. Residential wastewater is not allowed to be discharged into the lake, nor the inflow; the absence of such contamination has been recently confirmed (Warner et al., 2021). Most of the catchment area is used for agriculture; the resulting inputs of pesticides and their metabolites into the lake have recently been characterized (Warner et al., 2021).

The lake has only one significant inflow, the Aue creek. Before entering the lake, about 1.5 km upstream, the Aue creek passes the so-called Seeanger, a wetland with a central, few-decimeter-deep pond (Fig. 3.1; see also Fig. B1). The Seeanger wetland was formerly drained and used for agriculture but re-established in 2003 to renature the ecosystem. Other intentions were to reduce the nutrient input into Lake Seeburg and to create a flood plain and sediment trap for the Aue creek, reducing the particle load, especially after heavy rainfall events. Due to high nutrient inputs over the last decades, Lake Seeburg is currently considered to be strongly eutrophic to polytrophic, with recurring algal (i.e., cyanobacterial) blooms recorded since 2005 (Hartmann, 2007; NLWKN, 2010a).

To assess the nutrient dynamics of the lake, especially for N and P, we conducted a long-term monitoring campaign. Water sampling and analyses were carried out monthly at the main inflow (Aue creek), in the western part of the lake (pier), and in the eastern part near the main outflow over a period of 36 months between January 2017 and December 2019. Sediment sampling for pore water analysis was performed simultaneously with water sampling in the western part of the lake in 2018. The sampling locations are shown in Fig. 3.1.

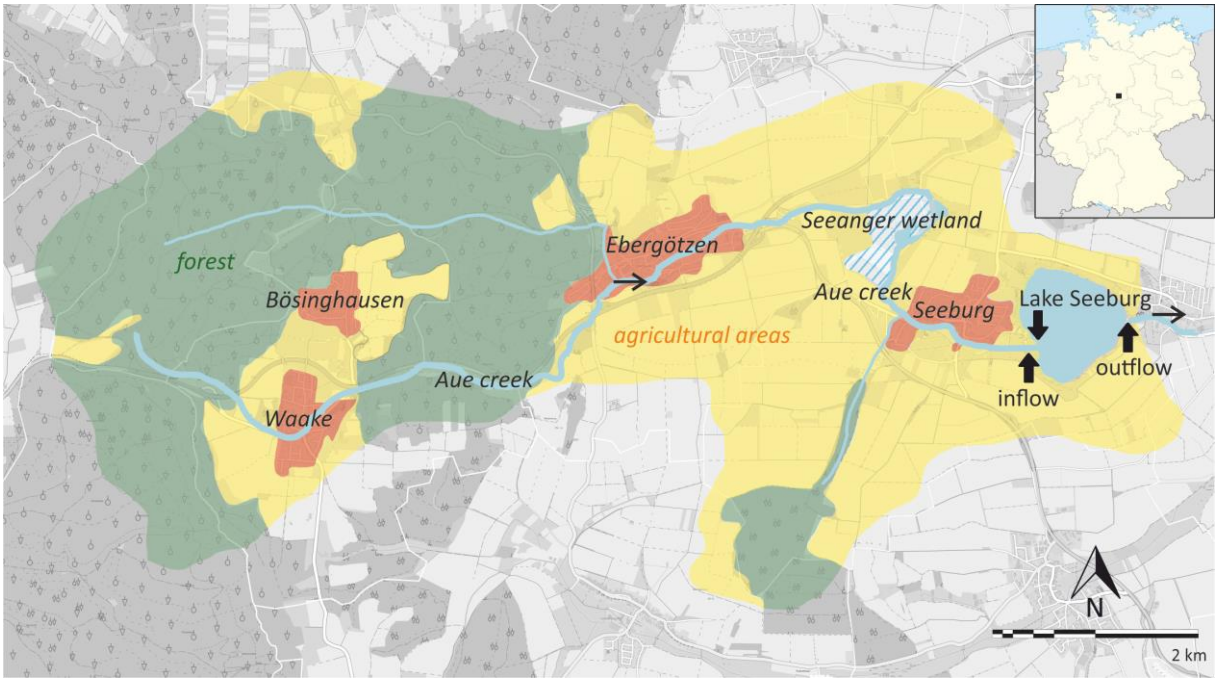

Fig. 3.1. Map of Lake Seeburg showing the catchment area and the sampling locations (arrows) at the main inflow (Aue creek), the western part of the lake (bathing pier), and the eastern part near the outflow. The shaded area represents the Seeanger wetland upstream of the main tributary (Aue creek). Simplified after NLWKN (2010b). For an enlarged map of the sampling points, see Fig. B1.

3.2.2. Analytical methods

At each sampling location, 100 mL of water was collected from the water surface using Zinsser Polyvials (Purell) from Zinsser Analytic. Push cores from lake sediments were taken and sectioned in 1–2 cm sub-samples. The top two centimeters were used as “surface sediments” in this study. Pore water was obtained by centrifuging, and subsequent analyses were identical to those of the lake water described below.

Pore- and lake-water samples were stored at 4 °C and analyzed within days after sampling. To fix the ammonium for later measurements, 5 mL of each sample was acidified with 5 µL of concentrated nitric acid. Temperature and pH were analyzed in situ using a multi-parameter portable meter (Multiline 3630 IDS, WTW GmbH) with a corresponding SenTix 940 electrode. Conductivity was measured in situ with a TetraCon 925 electrode, and oxygen concentration was measured with an FDO 925 electrode. For the calibration of the conductivity electrode, a 0.01 mol/L KCl calibration standard was used, and for the pH electrode, a technical buffer, according to ISO 7888 (both from WTW). The runoff measurements of the Aue creek were performed in situ using an OTT C2 hydrometric measuring blade with an OTT Z400 flowmeter from OTT HydroMet and a transverse distance of 10 cm.

Our study focused on bioavailable macronutrient fluxes, particularly soluble nitrogen and phosphorus species. Nitrite and soluble reactive phosphate (SRP) were analyzed via photometry according to EN ISO 6878 for SRP and EN ISO 26777, using a UviLine 9400 photometer by SI-Analytics. Nitrate and ammonium were analyzed by ion chromatography (IC) using an 883 Basic IC plus chromatograph by Metrohm. Prior to measurement, water samples were filtrated with 0.45 µm nylon filters by Carl Roth GmbH. For separation, a Metrosep A. Supp 5, 250 × 4.0 mm was used. The separation was performed at 25 °C, and the injection volume was set to 20 µL at a flow rate of 0.7 mL/min. The eluents were 3.2 mmol/L Na_2CO_3 and 1.0 mmol/L $NaHCO_3$.

Ammonium was analyzed via IC using an 820 IC separation unit, an 818 IC pump unit, an 837 IC degasser unit, and an 819 IC detector by Metrohm. Before measurement, filtered (mesh 0.22 µm) and acidified (0.1% HNO_3) water samples were diluted 1:2 with 3.0 mM HNO_3. For separation, a Metrosep C3, 250 × 4.0 mm was used. The column oven was performed at 40 °C; the injection volume was set to 20 µL at a flow rate of 1.0 mL/min. The eluent was 4.5 mmol HNO_3. IC-Standard tables are attached in the supplementary information Tab. B1).

Identification of microorganisms in the lake was performed microscopically using a Carl Zeiss Axio Scope.A1.

3.3. Results and discussion

The seasonal course of temperature, nitrite, ammonium, nitrate, and SRP between 2017 and 2019 is shown in Fig. 3.2. The minimum, maximum, and average concentrations at the sampling points are presented in Tab. 3.1. For detailed data, see Tab. B2. Due to the mostly high similarity of the data obtained from the western part (pier) and the eastern part (outflow) of Lake Seeburg, the results are jointly reported as “lake” in the following text unless otherwise noted.

Tab. 3.1. Minimum, maximum, and average temperatures and nutrient concentrations for the inflow (Aue creek), western (pier), and eastern (near the outflow) parts of Lake Seeburg.

		2017			2018			2019		
		min.	max.	average	min.	max.	average	min.	max.	average
Temperature [°C]	inflow	2.4 (January)	19.5 (August)	10.9	3.1 (January)	18.9 (August)	11.2	4.2 (February)	18.6 (September)	11.6
	lake (W), pier	2.5 (December)	22.5 (June)	15.1	2.5 (February)	25.9 (August)	13.7	3.7 (February)	25.6 (June)	14.0
	lake (E), outflow	2.6 (December)	23.0 (August)	15.3	2.6 (February)	26.0 (June)	13.5	3.8 (February)	25.3 (June)	14.0
Nitrate [mg/L]	inflow	1.22 (August)	21.47 (February)	14.78	14.81 (December)	21.55 (March)	18.23	8.25 (July)	21.40 (February)	14.08
	lake (W), pier	0.90 (October)	4.69 (February)	1.99	0.02 (July)	8.24 (March)	2.60	0.00 (September)	5.41 (January)	1.42
	lake (E), outflow	1.00 (October)	3.66 (December)	1.67	0.03 (July)	6.98 (March)	2.46	0.00 (July/December)	6.27 (February)	1.54
Ammonium [mg/L]	inflow	0.01 (July)	0.71 (August)	0.22	0.01 (November)	0.21 (May)	0.07	0.02 (February)	0.25 (June)	0.06
	lake (W), pier	0.01 (July)	0.63 (August)	0.18	0.01 (February)	0.33 (December)	0.08	0.02 (February)	0.22 (December)	0.06
	lake (E), outflow	0.01 (July)	0.58 (August)	0.20	0.01 (February)	0.36 (November)	0.09	0.01 (February)	0.21 (December)	0.05
Nitrite [mg/L]	inflow	0.01 (January)	0.37 (June)	0.11	0.04 (February)	0.48 (May)	0.13	0.03 (September)	0.42 (July)	0.11
	lake (W), pier	0.00 (May)	0.05 (March)	0.02	0.01 (July)	0.08 (May)	0.04	0.00 (June)	0.04 (January)	0.02
	lake (E), outflow	0.00 (May)	0.05 (March)	0.02	0.01 (June)	0.06 (December)	0.04	0.01 (June)	0.04 (January)	0.02
SRP [mg/L]	inflow	0.02 (December)	1.36 (August)	0.29	0.12 (March)	0.33 (December)	0.21	0.13 (April)	0.50 (July)	0.25
	lake (W), pier	0.01 (December)	0.78 (September)	0.23	0.02 (March)	0.68 (October)	0.21	0.02 (March)	0.43 (August)	0.16
	lake (E), outflow	0.01 (December)	0.65 (September)	0.20	0.01 (March)	0.69 (October)	0.21	0.02 (April)	0.37 (September)	0.14

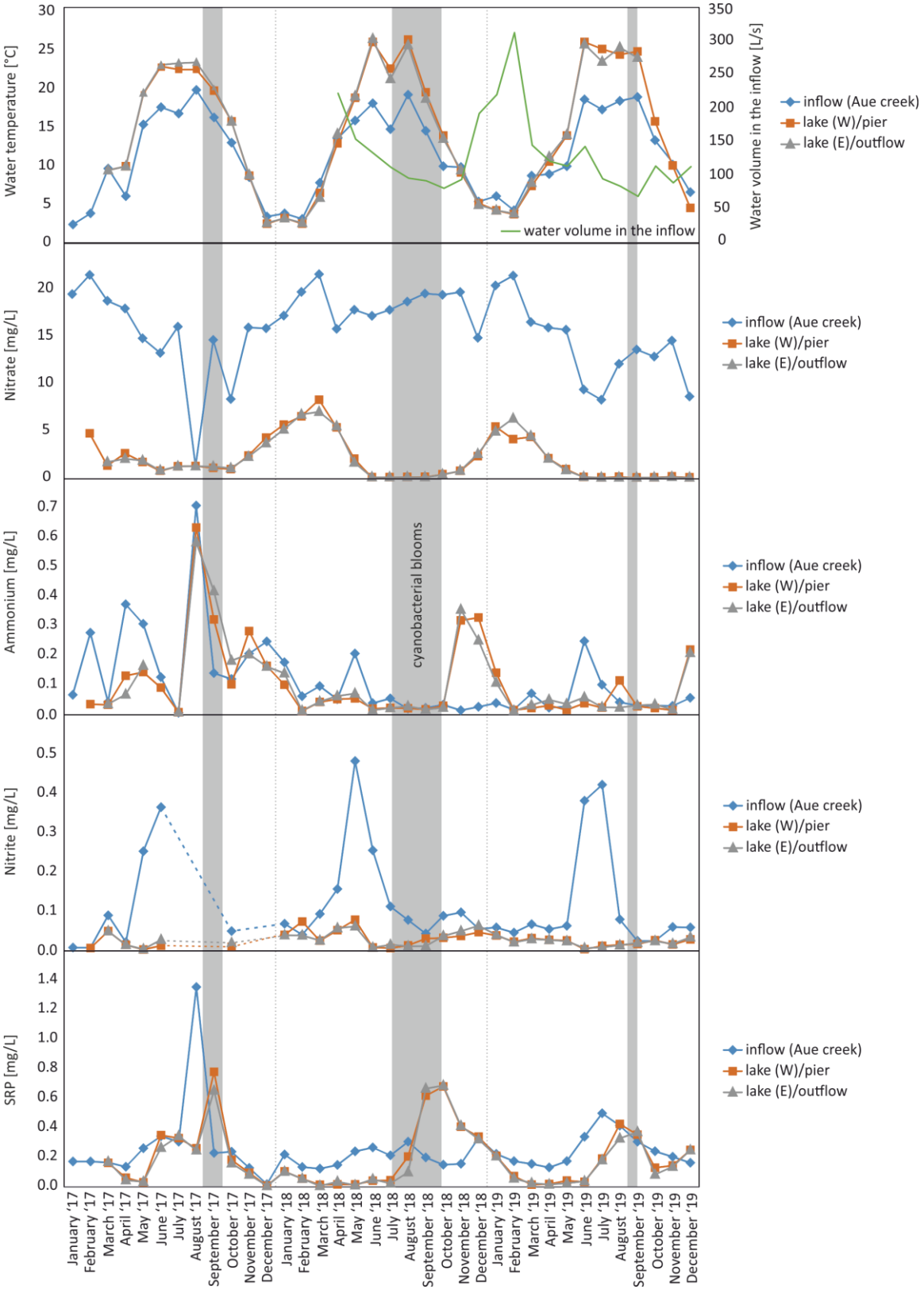

Fig. 3.2. Seasonal variability (2017–2019) of temperatures and nutrient concentrations for the inflow (Aue creek), western (pier), and eastern (near the outflow) parts of Lake Seeburg. The water volume in the inflow, measured between April 2018 and December 2019, is given in the top figure (green line). Episodes of cyanobacterial blooms are shaded in grey. For detailed concentration data, see Tab. B2. Dotted lines, no data available.

3.3.1. Temperature, precipitation, and runoff measurements

Temperatures in the inflow (Aue creek) varied between 2.4 °C in winter and 19.5 °C in summer. In the lake, temperatures ranged from 2.6–26.0 °C. While the peak temperatures in the inflow were relatively similar between the years, they differed in the lake. The hottest year was 2018 (26.0 °C in June), followed by 2019 (25.6 °C in June) and 2017 (23.0 °C in August). The annual means were 10.9–11.6 °C in the inflow and 13.7–15.3 °C in the lake. Again, the highest temperatures were observed in 2018. While the inflow and lake temperatures were similar during the winter, the lake water was consistently warmer from April through October.

Between April 2018 and December 2019, additional runoff measurements were taken in the Aue creek (Fig. 3.2, for detailed data, see Tab. B3). The inflow steadily decreased from 225 L/s in April to 84 L/s in October 2018. Over the winter months, the inflow increased to 315 L/s in February 2019 before it declined again with rising temperatures, stabilizing around 100 L/s between June and October 2019.

The observation period covered a year with a multi-day heavy rain event (2017), a very dry and hot year (2018), as well as a year with no major weather-related events (2019). After the 2017 heavy rain event, the slow drainage of the upstream Seeanger wetland resulted in continued flooding that lasted for several weeks. Concomitantly, the inflow into the lake increased and remained high until the following winter (own visual observations, measurements started later in 2018). The flooding of the Seeanger wetland was also associated with pronounced oxygen depletion in the flooded area and, consequently, in the inflow. Indeed, oxygen levels observed in the Aue creek were typically >6 mg/L throughout the three years but dropped to 0.22 mg/L in August 2017 (Tab. B2).

Unlike in 2017, there were no major rain events in the summers of 2018 and 2019, and thus, no large-scale flooding occurred in the Seeanger wetland. Instead, in 2018, a severe drought, with very little rainfall, between February and October (49% of the long-term average (Wetterkontor, 2021)) resulted in an ever-decreasing inflow into the lake throughout the summer (Fig. 3.2). Apart from a short cold snap in July, which was reflected in a temperature drop of the inflow and the lake water (Fig. 3.2), it was mostly warmer than average (+1.1 °C compared to the long-term average (Wetterkontor, 2021)). In comparison, 2019 represented a year with less extreme weather conditions. Again, it was warm (+0.9 °C compared to the long-term average); annual precipitation was slightly below the long-term average, with occasional light rain spread over the summer, as reflected by low inflow volumes with sporadic minor increases (Fig. 3.2).

3.3.2. Microorganisms and related biogeochemical processes

Cyanobacterial blooms were visually and microscopically observed at Lake Seeburg in all three years of monitoring (Fig. 3.3, A and B) but showed varying durations and intensities. In August and September 2017, blooming cyanobacteria dominated above all other species (own observations, see also (Bäthe et al., 2018)). Additionally, 2018 was the year with the longest and most intensive bloom, which began early in July and lasted for nearly three months until the first days of October. The shortest and least noticeable cyanobacterial bloom occurred in 2019 during the first two weeks of September. While Nostocales (*Anabaena* sp., Fig. 3.3, C) and, subordinately, Oscillatoriales (*Planktothrix agardhii*, *Pseudanabaena limnetica*) were predominant in 2017, the following two years showed a more mixed composition, with diverse forms of Oscillatoriales (*Planktothrix agardhii*, *Microcystis*, etc.) and Nostocales (*Anabaena* species) (own observations, see also (Bäthe et al., 2018)). In addition to the cyanobacteria, green algae (Chlamydomonadales, Chlorococcales) and diatoms (Centrales) occurred in increased abundance in the lake from May to October 2017, and accounted for about a quarter of the cyanobacterial biovolume. The maximum growth phase of the green algae was during May, August, and September (Cryptophyceae, Chlorococcales) and July/August (Centrales) (Bäthe et al., 2018). Whereas in (early) summer, green algae and diatoms are the dominant phytoplankton in the lake, cyanobacteria are typically most abundant in August/September. At this time of the year, their cell numbers can be >10 times higher than those of green algae (Bäthe et al., 2018).

Strikingly, in August 2017, after the heavy rain event, the Aue creek developed a severe lack of oxygen. This was obviously due to the intensified microbial decomposition of organic matter within the flooded organic-rich soils and overlying waters of the upstream Seeanger wetland. After the consumption of the available oxygen, anaerobic respiration processes took over, and, as a result, H_2S was formed via microbial sulfate reduction. The sulfide released caused a massive odor nuisance in the adjacent village of Seeburg. It also enabled the buildup of vast amounts of whitish feather-like biofilms of sulfide oxidizing bacteria (SOB) in the Aue creek over the entire distance between the Seeanger wetland and Lake Seeburg (Fig. 3.3, D - F). SOB typically thrive at suboxic/anoxic boundaries showing elevated H_2S concentrations (Friedrich et al., 2001). These conditions were toxic to all other oxygen-depending organisms and wiped out higher life in the creek for several weeks.

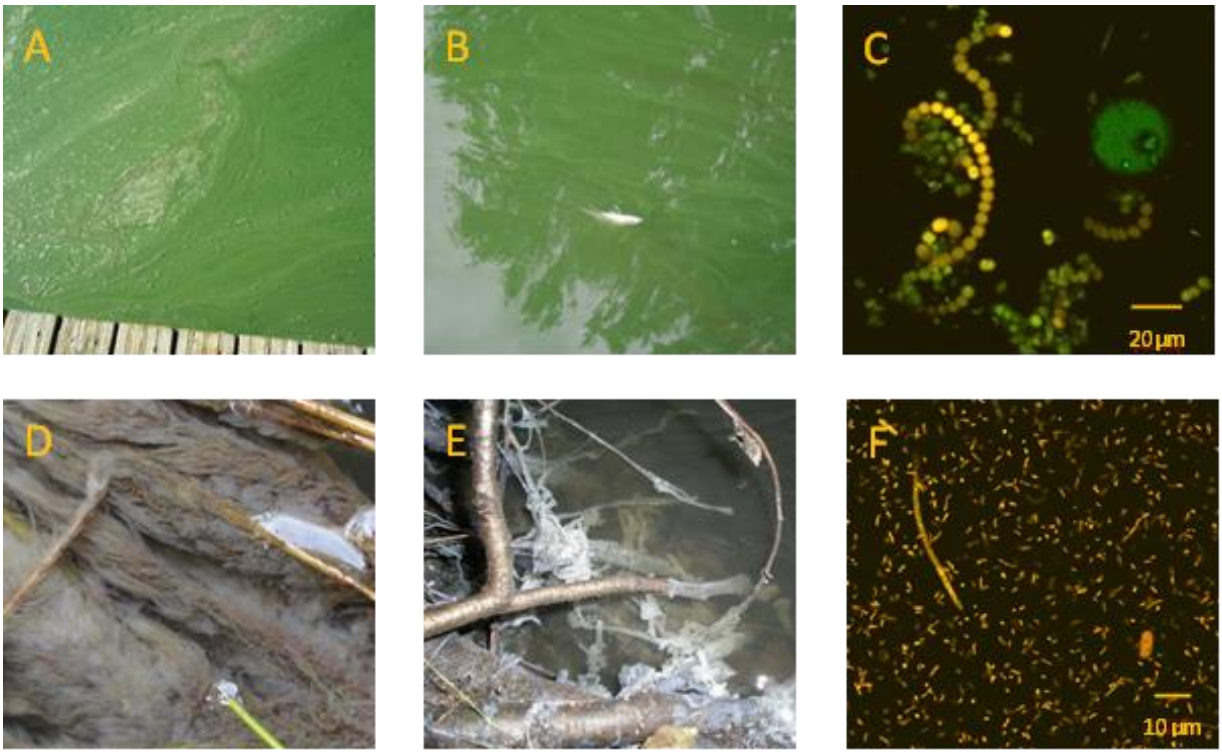

Fig. 3.3. A, B: Massive cyanobacterial bloom in Lake Seeburg (pier) in July 2018, with dead fish due to cyanobacterial toxins; B: see planks (≈12 cm) and dead fish (≈15 cm) for scale; C: Anabaena sp., dominating species in bloom 2017; D, E: microbial filaments (D) and thick biofilms (E) of sulfide oxidizing bacteria (SOB), which covered all available substrates in the Aue creek in August 2017 (image widths ≈15 cm); F: high abundance of sulfur-cycling microorganisms (SRB, SOB, including proteobacteria (purple sulfur bacteria)) in the sulfidic creek water after the rain event 2017. SOB with S-globules (observed via confocal laser scanning microscope); according to the size and surface pattern of the large bacterium (right corner), it can be assigned to purple sulfur bacteria.

3.3.3. Nutrient characterization

3.3.3.1. Nitrate

In the inflow (Aue creek), nitrate ranged from 8.3–21.5 mg/L, apart from a three-year low in August 2017 of 1.2 mg/L. In the lake, nitrate varied from below the detection limit to 8.2 mg/L (Fig. 3.2). The annual means ranged between 14.1–18.2 mg/L in the inflow and between 1.4–2.6 mg/L in the lake. Nitrate was, thus, the most significant nitrogen contributor during the observation period (Tab. B2, see Tab. B5 for water quality classifications according to Grage et al. (2014)).

The high and fairly steady nitrate inputs reaching the lake via the inflow (Fig. 3.2) can be attributed to discharges from the intensively farmed catchment area. The heavy rainfalls in July 2017 could have caused a dilution effect that may explain the notable drop of nitrate concentrations in the inflow in

August 2017 (however, increased nitrate discharges from farmland surface runoff often level up the dilution effect of rainfalls (Nettelmann, 2007)). In addition, nitrate levels in the inflow may have been attenuated by the intense microbial nitrate reduction that occurred in the oxygen-depleted flooded Seeanger wetlands upstream. This could also have contributed to the high ammonium levels observed during this period (Section 3.3.3.2) (Tobias et al., 2019).

Low nitrate concentrations in the lake compared to the inflow can be explained by the fact that nitrate is an essential nutrient for all aquaphytes, especially for green algae and diatoms (Ullrich, 1983). Consequently, the lake becomes nitrate-limited from about June to October, coinciding with the maximum growth phase of these algae (Jeppesen et al., 2007). In turn, the subsequent aerobic remineralization of phytoplankton biomass can plausibly explain the pronounced accumulation of nitrate in the lake during the autumn and winter of 2018 and 2019 (Fig. 3.2).

Different observations on external nitrate inputs after rain events have been reported in the literature. In a study of Lake Belau in northern Germany, which is similar in size to Lake Seeburg, a two-day storm event was recorded with twice the normal rainfall in a month. The storm caused major short-term changes in the lake, but increased allochthonous N inputs were not observed. One reason could be the constantly high nitrate load via the inflow (similar to Lake Seeburg), which could make additional input peaks less noticeable. Further aspects are the smaller catchment area and possible buffering by two upstream lakes (Schernewski, 2003). Unlike Lake Belau and Lake Seeburg, a positive correlation between precipitation and nitrate concentrations was reported for the eutrophic Lake Vico (Italy), where nitrate increased up to 20 mg/L after rain events (Garnier et al., 2010). The differences between these studies confirm that it is difficult to make sweeping statements about different, albeit similar, lake systems.

3.3.3.2. Ammonium

During the three years of monitoring, ammonium concentrations varied between 0.01–0.71 mg/L in the inflow and 0.01–0.63 mg/L in the lake (Fig. 3.2). The annual means were between 0.06–0.22 mg/L and 0.05–0.20 mg/L, respectively (Tab. B2, see Tab. B5 for water quality classifications).

Our data reveal that the extreme rain event in July 2017 had a strong impact on the ammonium concentrations of the lake system. From background levels near zero in July 2017, concentrations increased to peak concentrations as high as ≈0.7 mg/L in August 2017 in both the tributary and lake (Fig. 3.2). This can be interpreted as a result of the abovementioned anaerobic remineralization processes in the flooded upstream Seeanger wetlands (Sections 3.3.2 and 3.3.3.1). Evidently, this led to a high ammonium discharge via the Aue creek (along with sulfide, see above) and resulted in a

temporarily increased ammonium concentration in the lake. In the two following years, however, no such heavy rainfall events occurred, and thus, no comparable ammonium peaks were recorded.

Unlike Lake Seeburg, no elevated ammonium inputs were observed for Lake Belau after a two-day storm event (see Section 3.3.3.1) (Schernewski, 2003). However, it has to be considered that its inflow, before entering Lake Belau, discharges into two other lakes, which may, therefore, act as a buffer for ammonium. In the western Lake Superior in North America, two heavy rain events in 2012 (250 mm of rainfall in two days) and 2016 (220 mm of rainfall in two days) resulted in additional ammonium inputs that accounted for only up to 1% (2016) of the total annual inputs (Cooney et al., 2018). The much greater ammonium increase at Lake Seeburg after a similar rain event may point to a major role of the flooded Seeanger wetland as a source of reduced nitrogen species.

Our data further indicate a regular increase in ammonium concentrations in Lake Seeburg in the aftermath of cyanobacterial blooms, i.e., in autumn and winter (Fig. 3.2). This may be explained by the release of ammonium from the decaying cyanobacterial biomass under oxygen-limited conditions. Similarly, in column experiments with lake water from Lake Taihu (China), strongly elevated ammonium concentrations (up to 53.3 mg/L) were recorded during the anaerobic degradation of cyanobacterial blooms (Zhu et al., 2013).

Numerous cyanobacteria have the ability to fix atmospheric nitrogen and convert it into bioavailable modifications (Herrero et al., 2001; Stewart and Lex, 1970). Whereas eukaryotic phytoplankton require bioavailable nitrogen as well as phosphorus, nitrogen-fixing cyanobacteria are limited only by the latter. In late summer 2017, cyanobacteria from the nitrogen-fixing order Nostocales (especially *Anabaena* sp.) were the dominant aquatic organisms in Lake Seeburg ((Bäthe et al., 2018), see also Section 3.3.4). The decay of these blooms released major amounts of ammonium into the lake water. Subsequent microbial ammonium oxidation (i.e., nitrification) most likely contributed to the elevated nitrate concentrations in the lake over the winter months of 2017/2018 (Section 3.3.2; Fig. 3.2).

3.3.3.3. Nitrite

The nitrite concentrations varied between 0.01–0.48 mg/L in the inflow and near-zero to 0.08 mg/L in the lake. The mean values were between 0.11–0.13 mg/L and 0.02–0.04 mg/L, respectively. In the inflow, maximum concentrations occurred as annually repeating peaks in late spring or early summer. With one exception (February 2018), nitrite concentrations in the lake were lower than those in the inflow (Tab. B2, see Tab. B5 for water quality classifications). No data were available during the heavy rain event.

A noteworthy feature of the nitrite distributions at Lake Seeburg is annual peaks in the inflow occurring in early summer (Fig. 3.2). These nitrite distributions might result from the increased microbial decomposition of dead plant material accumulated in the upstream Seeanger wetland, where the high availability of such material in spring is evident (own observation). As the first step in nitrification, ammonium resulting from the decay of organic material is aerobically oxidized to nitrite (Keeney, 1973). The energy so obtained is more than four times higher than for the subsequent aerobic oxidation of nitrite to nitrate (Alexander, 1978). Consequently, oxygen deficiency arising in wetland environments as a result of intense decomposition processes would hamper the (energetically less favorable) oxidation of nitrite to nitrate. Notably, the marked nitrite spike is only observed in the inflow but not in the lake itself (Fig. 3.2). This can plausibly be explained by the lower availability of organic matter and a higher amount of available oxygen in the lake water, which would promote a more rapid turnover of nitrite and, thus, complete oxidation of ammonium to nitrate.

3.3.3.4. Soluble reactive phosphate (SRP)

SRP in the inflow ranged from 0.02–0.50 mg/L, apart from a strikingly high peak observed in August 2017 after the rain event (1.36 mg/L). In the lake, concentrations varied widely from 0.01–0.78 mg/L. Mean values were between 0.21–0.29 mg/L and 0.14–0.23 mg/L, respectively. Concentrations in the lake were typically lower than in the inflow; however, higher values regularly occurred around September in all three monitoring years (Fig. 3.2, Tab. B2, see Tab. B5 for water quality classifications).

The remarkably high SRP peak observed in the inflow in August 2017 most likely resulted from the extreme rain event in July 2017 (Fig. 3.2, Section 3.3.1). The enhanced biodegradation processes in the upstream flooded Seeanger wetland resulted in oxygen-depleted conditions, leading to the release of high amounts of SRP from the degraded organic matter and formerly iron-bound phosphate. Phosphate speciation analyses of the wetland soils showed almost equal proportions of organically bound phosphate and mineralized (iron-bound) phosphate in the sample fractions. It can be estimated that approximately 64.3 kg/day of SRP entered the lake during the rain event (see Tab. B6 for calculations). In the absence of further major flooding events, SRP concentrations in the inflow consistently remained at much lower levels for the rest of the observation period (e.g., 2.1 kg/day one year later in July 2018).

At Lake Belau, heavy rain resulted in additional P inputs of 5 kg/day, about 3–4 times the pre-event levels (Schernewski, 2003). At Lake Gollin, another north German lake with similar characteristics, SRP concentrations increased to nearly 0.3 mg/L (annual mean 0.004 mg/L) after a heavy rain event with flooding (Kazanjian et al., 2019). Similar observations were also made at two shallow eutrophic

lakes in Spain, where SRP concentrations increased to maximum concentrations of up to 0.28 mg/L after heavy rain events (annual mean 0.04 mg/L) (De Vicente et al., 2006). These findings, as well as our results from Lake Seeburg, demonstrate that high external phosphorus inputs after heavy rain events are a widespread problem in lake environments worldwide.

Unlike in 2017, the marked late summer SRP peaks in Lake Seeburg were not related to major external input events in 2018 and 2019. Obviously, high SRP concentrations in Lake Seeburg may build up independently from short-term inputs.

Increased SRP concentrations in the water column of lakes are generally observed during the final stages of cyanobacterial blooms in late summer (Rose et al., 2017; Xie and Xie, 2002). One explanation discussed in the literature is the release of sedimentary phosphorus by carps (Huser et al., 2016, 2022). However, the fish population in Lake Seeburg is controlled by the local anglers' club through stocking (walleye, pike, trout) and selective removal (carp, whitefish). Therefore, bottom-dwelling fish should not have a crucial effect on sedimentary nutrient release. As Lake Seeburg is very shallow and used as a swimming lake, it is also possible that human activity may cause some sediment disturbance and promote nutrient release, but this should be limited to small areas of the lake during the summer season. Overall, therefore, the sedimentary release of phosphorus through chemical processes (Bormans et al., 2016; Schindler, 2012; Schindler et al., 2016) and the degradation of phytoplankton biomass are most likely to be of critical importance (Zhang et al., 2018). Both processes contribute to the late summer SRP maximum in Lake Seeburg, which is shown by pore water analyses in parallel with the water sampling in 2017 and during the warm and dry year of 2018.

In 2017, a constant increase in pore water SRP was observed from 0.15 mg/L in April to 8.3 mg/L in August, which later dropped significantly to 0.3 mg/L in October. In the following year, 2018, the pore water SRP concentration increased markedly, with its annual maximum in the water column. During the peak cyanobacterial bloom, pore water values were raised to an extreme 34.4 mg/L (Fig. 3.4); note that there was hardly any SRP present in the lake water earlier in summer because of a direct uptake by green algae and diatoms (Bäthe et al., 2018; Jansson et al., 1990).

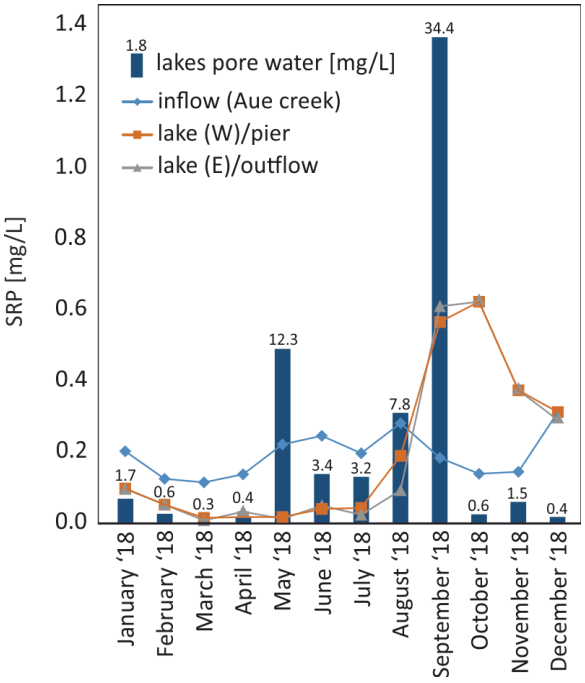

Fig. 3.4. Seasonal variability of soluble reactive phosphate (SRP) in the pore water of Lake Seeburg surface sediments compared to the Aue creek (inflow), the western part (pier), and the eastern part (outflow) in 2018. Note the different scales of surface and pore water. For detailed concentrations, see Tab. B4.

The observed sedimentary SRP release is probably coupled to benthic biodegradation, which leads to the remineralization of biomass-bound nutrients and the depletion of pore water oxygen. Under fully oxic conditions (such as in oligotrophic lakes), phosphorus released from decaying organic material is typically bound to sedimentary iron hydroxides and, thus, removed from the lake cycle for a long period of time (Randall et al., 2019). However, the iron-bound phosphorus association becomes unstable as soon as suboxic to anoxic conditions emerge (Nowlin et al., 2005). As a consequence, iron-bound sedimentary SRP is released.

In addition to the O_2 concentration (↓) and temperature (↑), further drivers for the transformation of dissolved, organic, and inorganic phosphorus species (and thus, the SRP levels) are pH value (especially pH >8) and redox conditions (Chen et al., 2014; Mortimer, 1941; Søndergaard et al., 2003; Wu et al., 2014). In summer, high lake water temperatures favor the growth of cyanobacteria (Pearl and Huisman, 2008). Due to the particularly high maximum water temperatures during the 2018 drought (Fig. 3.2), the growth of cyanobacteria was enhanced. Phytoplankton (e.g., green algae, cyanobacteria) increase the pH value in the water body during their maximum growth phase through their CO_2/HCO_3^- consumption, and their photosynthetic activity can lead to oxygen oversaturation (Aizawa and Miyachi, 1986; Gao et al., 2014; Morales-Williams et al., 2017). Due to the sheer amount of cyanobacteria in late summer, we consider them to be primarily responsible for the significant

increases in pH and oxygen in Lake Seeburg (late summer pH ≈9; oxygen >12 mg/L; Tab. B2). In the decay stage, the decomposition of the cyanobacterial biomass requires large amounts of oxygen, resulting in oxygen depletion in the water column and the sediment. Similar to the bloom formation, the decay of the cyanobacteria was certainly promoted by high water temperatures in 2018. Consequently, oxygen concentrations in the surface water of Lake Seeburg regularly decreased to values <7 mg/L immediately after cyanobacterial blooms (Tab. B2). Close to the sediment–water interface, the oxygen concentrations are considerably lower (ca. 2–3 mg/L). The calculated amount of sediment-released SRP during the cyanobacterial bloom in 2018 was 69 $mg/m^2 \cdot day^{-1}$, corresponding to 61.4 kg/day in the whole lake (see Tab. B7; calculations according to (Scholtysik et al., 2020)). In a comparison of core incubations from seven small and shallow eutrophic lakes under oxic and anoxic conditions, the P release rate ranged from 0.02 to 83 mg/m^2 per day (Paytan et al., 2017). In the shallow eutrophic Lake Hiidenvesi (Finland), a maximum sedimentary release rate of 57.6 mg/m^2 per day, a value very similar to Lake Seeburg, was observed for two weeks in summer (Horppila and Nurminen, 2001). This internal phosphorus release from the sediment, caused by cyanobacteria, plays a major role in maintaining the lake's eutrophic status (Cao et al., 2016; Cottingham et al., 2015; Hupfer and Lewandowski, 2008; Nürnberg, 2012; Randall et al., 2019; Wu et al., 2019; Zhang et al., 2018).

3.3.4. Influences of extreme weather events on the nutrient and phytoplankton community composition in the lake

Due to the heavy rainfall event in 2017, anoxic water enriched with ammonium and, especially, SRP (64.3 kg/day) entered the lake through the inflow (Section 3.3.4 and Tab. B6). The strong nutrient inputs obviously induced a cyanobacterial bloom that was relatively short-lived (≈3 weeks) but very intense, showing high cell densities of Nostocales (*Anabaena spiroides*, 168,000/mL, 63% of the biovolume of the lake) and Oscillatoriales (P*lanktothrix agardhi,* 78.000/mL; *Pseudanabaena limnetica,* 48.000/mL) (Bäthe et al., 2018). The intensity of the cyanobacterial bloom in the wake of the 2017 heavy rain event was considerably higher and much less diverse, as previously observed in Lake Seeburg. Anabaena species, which dominate the overall phytoplankton community, are typical for eutrophic to hypertrophic lakes. As *A. spiroides* is neurotoxin-producing (anatoxin-a(s)), toxic to all kinds of wildlife in the lake (e.g., zooplankton, fishes, and crabs; Fig. 3.3, B), there is a clear tendency towards worse conditions (Catherine et al., 2013). A phytoplankton monitoring study conducted in September 2006, which may be taken as a background reference, reported a broader diversity of cyanobacteria, where the abovementioned species were also present but in much lower cell densities (*Anabaena compacta* and *Anabaena sp.,* 13.000/mL; *Planktothrix agardhii,* 41.000/mL;

Pseudanabaena limnetica, 26.000/mL) and in co-occurrence with other phytoplankton communities such as Chlorophyceae (cryptophyceae, Bacillariophyceae, and euglenophyceae (Bäthe and Coring, 2007)).

In the hot and dry year of 2018, the water volume of the inflow decreased significantly during summer, and, thus, only small amounts of nutrients entered the lake (Section 3.3.1). On the other hand, the warm weather conditions influenced early-blooming Bacillariophyceae in May and enhanced degradation and remineralization processes in the lake; thus, a remarkably high SRP re-dissolution from the sediment (61.4 kg/day) was observed (Section 3.3.3.4 and Tab. B7). This sustained re-dissolution fostered a cyanobacterial bloom that was more diverse than in the year before and lasted much longer (≈3 months).

In 2019, in the absence of extreme weather events, only a minor cyanobacterial bloom occurred, whose impact was significantly smaller than in previous years. The bloom was the shortest (only a few days) and had a lower total number of organisms and a higher diversity.

3.4. Conclusions

Like many other lakes worldwide, Lake Seeburg suffers from severe eutrophication. Our long-term (3 years) observation of bioavailable nutrients revealed, as expected, steady background inputs of bioavailable nitrogen and phosphorous species from the farmed catchment area. In addition, our data indicate a critical role of weather extremes in the dynamics of these nutrients and the formation of hazardous phytoplankton blooms. Following a three-day very heavy rain event in July 2017, high amounts of ammonium and SRP were discharged into the lake from the upstream Seeanger wetland, which has been restored as a nutrient retention trap for Lake Seeburg. In this case, the wetland even represented a strong nutrient source and failed to serve its intended purpose. In addition to such exogenous inputs, internal dynamics between the surface sediment and the water column exert significant control over nutrient distribution in Lake Seeburg. In particular, the release of sediment-bound phosphorus in late summer promotes the additional growth of cyanobacteria. Again, extreme weather conditions can be an important driver of this process, which becomes particularly intense under very hot and dry weather conditions, such as those experienced during the severe drought of the summer of 2018. Our observations also suggest that the duration and composition of the resulting cyanobacterial blooms depend on the nature of the nutrient input involved (short-lived and monospecific after spike-like external inputs; long-lived and more diverse with sustained internal release), but this requires further investigation. As the frequency and intensity of heat waves and heavy rain events are expected to increase due to climate change, their effects on the nutrient dynamics of lake ecosystems will need to be understood in more detail. Only with accurate

knowledge of the potential impacts can appropriate and sustainable management strategies be implemented in the future.

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4. Qualitative reconstruction of eutrophication at a shallow eutrophic lake using sedimentary stenols and their degradation products

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Biomarkers are widely used to reconstruct the sources of organic matter or past biogeochemical processes. However, the preservation of biomarkers in the aquatic environment and, consequently, the extent to which biomarker signals from the water column are reflected in the sedimentary record is still not fully understood.Here we assessed major extractable lipid biomarkers (hydrocarbons, sterols and fatty acids) in Lake Seeburg, a shallow eutrophic lake that increasingly suffers from cyanobacterial blooms, due to continued anthropogenic nutrient inputs over the last decades. Over the course of one year (2018/19), the distributions of these compounds were analyzed in the inflow, the lake water, and the underlying surface sediments (0-2 cm) to assess their origin and transfer into the lake deposits.Via principal component analysis (PCA), the biomarkers studied were clustered into 5 groups with similar characteristics. These groups comprised (i) biomarkers delivered via the inflow, (ii) autochthonous biomarkers formed in the lake by eukaryotes or (iii) bacteria, (iv) compounds accumulating in the surface sediment, and (v) C_{27} to C_{29} stenols together with their degradation products, C_{27} to C_{29} 5α(H)-stanols. Their seasonal partition clearly revealed that C_{27} stenols mainly derived from autochthonous sources within the lake, whereas C_{29} stenols largely reflect allochthonous material reaching the lake via the inflow. To check whether the recent trophic level change of Lake Seeburg may be reflected by the carbon number distributions of sedimentary sterols, additional analyses were performed on two short sediment cores. To compensate for a slower stenol-stanol conversion with increasing carbon number, as indicated by our data, the major stenols were summed with their corresponding 5α(H)-stanols. It was found that the trend of C_{27} and C_{29} sterols with depth is clearly inverse, with highest C_{27} to C_{29} ratios observed at the tops, and lowest ratios at the bottom of the cores.We interpret these signals to reflect the increasing trend of eutrophication of Lake Seeburg and thus, enhanced autochthonous organic matter production in the lake over the last decades. The abundances of C_{27} vs. C_{29} stenols, summed with their respective degradation products, are considered as suitable proxies to qualitative reconstruct the historical eutrophication trends.

4.1. Introduction

Lipid biomarkers reflecting characteristic precursor biota provide important information on the sources of organic matter or past biogeochemical processes (Cranwell et al., 1987; Volkman et al., 1998; Zhang et al., 2018). Therefore, sedimentary biomarkers have been widely used to reconstruct modern and ancient lake environments (Meyers, 2003; Naeher et al., 2012; van Bree et al., 2014). For instance, terrestrial organisms such as higher plants deliver different lipids into sediments than aquatic phytoplankton (Huang and Meinschein, 1979; Volkman, 1986; Castañeda and Schouten, 2011); therefore, a shift from terrestrial to more aquatic dominated distributions may indicate increasing eutrophication of a lake system over time (Huang and Meinschein, 1979).

The biomarker composition of a wide variety of lake sediments have been reported in the literature (Meyers, 2003; Pearson et al., 2007). Studies additionally reporting the biomarker distributions of the lake water column are less common (Thiel et al., 1997; Naeher et al., 2012; van Bree et al., 2018). However, studying the seasonal biomarker distribution of the water column provides immediate insights into the composition of planktonic organisms and their organic matter production within the lake. In combination with biomarker measurements in the sediment, statements can be made about which compounds tend to be degraded at an early stage in the water column or, by contrast, are particularly resistant to degradation. By revealing such lake-specific biomarker sedimentation characteristics, such integrated biomarker studies may allow for more accurate retrospective interpretations of trophic conditions from the sedimentary record.

Here we report on biomarker dynamics in Lake Seeburg, a small (0.89 km^2) and shallow (average depth 2 m) unstratified lake in Central Germany. Lakes like Lake Seeburg are especially susceptible to eutrophication, due to their small water volume and the increased nutrient input over the last decades. The exchange of nutrients from decaying organic material between the sediment and the water column is much more extensive compared to deep lakes. The main reasons are the missing thermocline (which normally acts as a physicochemical barrier), the large ratio of the sediment surface to water body, and the high turbidity associated with wind-driven sediment resuspension of organic and inorganic matter (Lorenz et al., 2017). As a result, eutrophication processes increased during recent decades and regular cyanobacterial blooms have been observed in Lake Seeburg since 2005 which occur with increasing frequency and intensity (own observations).

Our integrated study of key biomarkers in the inflow, water column, and surface sediment of Lake Seeburg provided a comprehensive view on the seasonal biomarker composition in the lake system. Examining the relationship between the water column and sediment provided insight into how the distribution of biomarkers from the water column is actually reflected in the earliest depositional

record. Among the compounds studied, sterols emerged as relatively degradation-resistant biomarkers that reasonably reflect the production in the water column of Lake Seeburg as well as allochthonous inputs. Based on this, we examined their distributions in deeper (≈50 cm) sediment layers of Lake Seeburg and assessed the use of sterols as potential eutrophication indicators.

4.2. Materials and methods

4.2.1. Sampling location

Sampling was conducted at Lake Seeburg, a shallow eutrophic lake in Central Germany located about 15 km east of Göttingen (51°33'52'' N, 10°09'52'' E). The lake covers an area of 0.89 km², has a water volume of 2 million m³, an average depth of 2 m and a maximum depth of 4 m (Streif, 1970). Since 1973 the lake is a natural reserve, classified as a special flora-fauna habitat (FFH) and an EU bird reserve. The lake is used for fishing and as an official swimming lake. The catchment area of Lake Seeburg is characterized by agriculture (for a recent study on pesticide metabolites in Lake Seeburg and its catchment see (Warner et al., 2021). Increasing eutrophication within the last decades led to almost annual, partly severe, cyanobacteria blooms since 2005, which also occurred during our study in September 2019.

Sampling campaigns were conducted between May and December 2019 (water samples) and between August 2019 and June 2020 (surface sediments). Water samples were collected using 10 L Niskin bottles at two-week (summer, fall) and four-week intervals at the main inflow of the lake (Aue creek), in the western part of the lake (pier) and the eastern part near the main outflow. The location for surface sediment sampling (0-1 cm, 1-2 cm) coincided with those for water sampling; sampling locations are shown in Fig. 4.1.

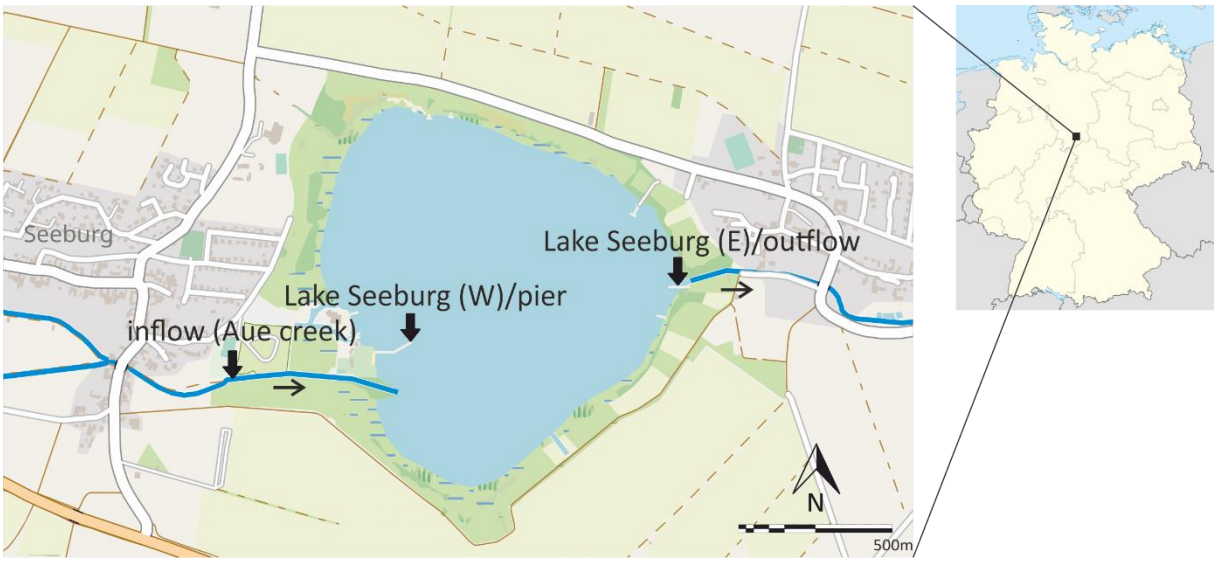

Fig. 4.1. Map of Lake Seeburg with sampling locations indicated by bold arrows.

To obtain surface sediments, push cores were taken monthly in summer and autumn and every two to four months in winter and spring.

For water column sampling, 0.5-2 L of lake surface water were immediately transferred to the home laboratory, and filtered with glass microfiber filters (pore size 0.7 µm; GE Healthcare Life Science, Whatman). The filters were freeze-dried for 30 hours, and stored at -20 °C until further analysis. Sediment sub-samples were centrifuged for separation from the pore water, freeze-dried for 48 hours, and ground in a swing mill.

4.2.2. Organic carbon analysis

Total organic carbon (C_{org}) was analyzed by a LECO RC-612 multiphase carbon analyzer. To calculate C_{org} values, the peak areas of the samples were compared to those of certified standards (12% $CaCO_3$ by IVA Analysetechnik, No. 502-029 and No. 502-030 by LECO Corporation)

4.2.3. Extraction and derivatization of biomarkers

About 2 g of the freeze-dried sediment was extracted three times each with 10 ml (filter samples: 5 ml) dichloromethane (DCM)/methanol (MeOH) (2:1), DCM/MeOH (3:1), and DCM (ultrasonication, 15 min) and centrifuged at 1500 rpm for 15 min. The supernatants were combined and the resulting total organic extract (TOE) was evaporated to near-dryness (nitrogen, 40 °C). From an aliquot of the TOE, fatty acids were transesterified to their GC-amenable methyl ester derivatives (FAME) using 3 ml trimethylchlorosilane (TMCS)/MeOH (1:9, v:v; 70 °C, 90 min). FAMEs and other neutral lipids were separated from the reaction mixture by repeated (3x) liquid-liquid extraction with 2 ml portions

of *n*-hexane. The *n*-hexane phases were pipetted off, combined, near-dried under nitrogen, and placed on a glass column containing 0.7 g silica gel (60-230 µm). The hydrocarbon fraction was separated with 7 ml *n*-hexane, FAMEs were eluted with 7 ml DCM, and the alcohol (OH) fraction with 7 ml DCM/acetone (9:1). To convert alcohols to their trimethylsilyl (TMS) derivatives, the OH fractions were derivatized with 100 µl BSTFA (70 °C, 1 h). All glass- and steel ware for sample preparation were heated at 450 °C to 550 °C for at least two hours prior to use.

4.2.4. Gas chromatography – mass spectrometry (GC-MS)

Fractions were analyzed using a Thermo Fisher Trace 1310 GC coupled to a Thermo Fisher Quantum XLS Ultra MS. Samples were injected via a Thermo TriPlus RSH autosampler. Compounds were separated using a Phenomenex silica capillary column (Zebron ZB-5MS, 30 m, 0.1 µm film thickness, inner diameter 0.25 mm). The GC oven temperature was programmed from 80 °C (6 min) to 320 °C at 5 °C/min (20 min isothermal). Helium was used as carrier gas (1.5 ml/min). Electron ionization mass spectra were recorded in full scan mode (mass range m/z 50 – 600) at 70 eV electron energy. Components were identified by comparison with standard compounds (Supelco 37 Fame standard) and comparison of the mass spectra with the NIST MS Search 2.0 library. Semi-quantification was achieved by comparison of GC-MS peak areas with those of internal standards of known concentration (*n*-icosane D42, *n*-nonadecanoic acid methyl ester).

4.2.5. Data analysis

To reduce the complexity of the data set, the individual sampling dates were grouped into the four seasons covered by our study. Due to the strong similarity of biomarker concentrations obtained from the western and eastern parts of the lake, the respective water column and sediment data were averaged. For principal component analyses (PCA) the biomarker data in each seasonal group were standardized; the mean of each group was subtracted and then divided by the standard deviation (Pondell and Canuel, 2020). By creating more comparable unit-free values in the same order of magnitude within the seasons and sampling locations, the different types of data become more comparable. Statistical analysis and visualization of the biomarker data was performed using R-Studio, version 4.1.0. The PCA were performed using the "ggfortify" and “cluster” packages.

4.3. Results and discussion

During the monitoring period, 39 biomarker data sets were generated from the inflow and the lake water, and 22 biomarker data sets from the sediment. The mean seasonal concentrations of

phytoplankton-related biomarkers in the inflow, the lake water and the surface sediment are shown in Tab. 4.1. For detailed data, see Tab. C1 in the supplement. Based on the PCA analysis in Fig. 4.2, we distinguish five biomarker groups that contain the characteristics of 26 out of 30 biomarkers.

Tab. 4.1. Biomarkers used in this study, their origin and mean seasonal concentrations in the inflow, lake and surface sediment [µg/g_{Corg}].

	Component	Specific for	Reference*	Inflow [µg/g_{Corg}]				Lake [µg/g_{Corg}]				Sediment [µg/g_{Corg}]			
				Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter
Hydrocarbons	*n*-C_{17}	Algae, cyanobacteria	Coates et al. (2014), Zhang et al. (2018)	1	4	20	8	30	44	135	122	4	9	9	5
	n-C_{23}	Aquatic macrophytes	Ficken et al. (2000)	4	2	1	< 1	10	3	1	2	6	16	7	3
	n-C_{27}	Land plants	Eglinton & Hamilton (1967)	15	25	30	12	< 1	3	1	< 1	56	103	79	30
	n-C_{29}	Land plants	Eglinton & Hamilton (1967)	11	26	33	5	< 1	< 1	< 1	< 1	65	105	94	36
	n-C_{31}	Land plants	Eglinton & Hamilton (1967)	1	2	6	< 1	< 1	< 1	< 1	< 1	9	19	12	6
	HBI 1 ($C_{25:2}$)	Diatoms	Kaiser et al. (2016)	< 1	< 1	< 1	< 1	< 1	< 1	4	< 1	3	14	5	2
	HBI 2 ($C_{25:2}$)	Diatoms	Kaiser et al. (2016)	< 1	< 1	< 1	< 1	1	2	< 1	< 1	4	31	13	5
	Σ Phytadienes	Zooplankton	Grossi et al. (1998)	15	17	29	21	238	268	313	316	86	202	112	61
	Tetrahymanol	Ciliates	Harvey & McManus (1991)	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	3	5	3	1
	Hop(17,21)ene	Biohopanoids	Innes et al. (1998)	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	26	26	23	18
Sterols	27^{0}	Degradation	Nakakuni et al. (2017)	13	< 1	< 1	< 1	15	24	41	4	150	522	220	79
	27^{5}	Zooplankton, microalgae	Volkman (2003)	298	59	66	189	306	429	223	325	279	631	233	125
	$27^{5,22}$	Zooplankton, microalgae	Volkman (2003)	< 1	< 1	< 1	< 1	45	10	41	49	20	34	111	165
	28^{0}	Degradation	Nakakuni et al. (2017)	< 1	1	< 1	< 1	< 1	6	13	7	114	305	141	73
	28^{5}	Microalgae	Volkman (2003)	23	4	< 1	< 1	62	56	98	54	140	234	119	102
	$28^{5,22}$	Microalgae	Volkman (2003)	10	2	< 1	< 1	154	47	19	69	102	287	104	39
	29^{0}	Degradation	Nakakuni et al. (2017)	2	4	< 1	< 1	< 1	< 1	3	< 1	435	438	236	297
	29^{5}	Land plants	Huang & Meinschein (1979)	210	71	114	243	144	79	81	68	882	1042	528	559
	$29^{5,22}$	Land plants	Huang & Meinschein (1979)	37	12	< 1	< 1	59	20	30	8	84	203	83	64
Fatty acids	*i*-15:0	SO_4-reducing bacteria	Rütters et al. (2001)	85	81	70	141	312	161	82	128	108	139	115	76
	ai-15:0	SO_4-reducing bacteria	Rütters et al. (2001)	61	69	67	137	86	61	23	68	118	201	143	97
	16:0	Algae, diatoms	Taipale et al. (2013)	705	839	718	1210	3234	4497	4727	2036	1692	1097	1213	1106
	18:2n6c	Cyanobacteria	Los &Mironov (2015)	38	103	105	162	294	489	531	260	226	212	189	78
	18:3n3c	Cyanobacteria	Los &Mironov (2015)	< 1	81	94	131	1291	2734	2336	1152	74	93	77	31
	18:1ω7c	Algae, cyanobacteria	Los &Mironov (2015)	111	243	183	263	645	1367	1168	575	472	312	337	224
	20:4n6c	Macroalgae, diatoms	Volkman et al. (1989), Howell et al. (2003)	20	18	18	48	508	451	844	652	28	161	71	18
	20:5n3c	Diatoms	Fujibayashi et al. (2016)	6	15	18	17	48	103	57	42	47	183	121	33
	20:0	Land plants	Bianchi & Canuel (2011)	27	56	65	70	12	31	15	26	174	139	209	526
	22:0	Land plants	Bianchi & Canuel (2011)	57	101	117	200	42	57	13	57	232	251	224	225
	24:0	Land plants	Bianchi & Canuel (2011)	54	96	110	80	43	85	23	107	220	391	345	282

*) Selection, further references in the text

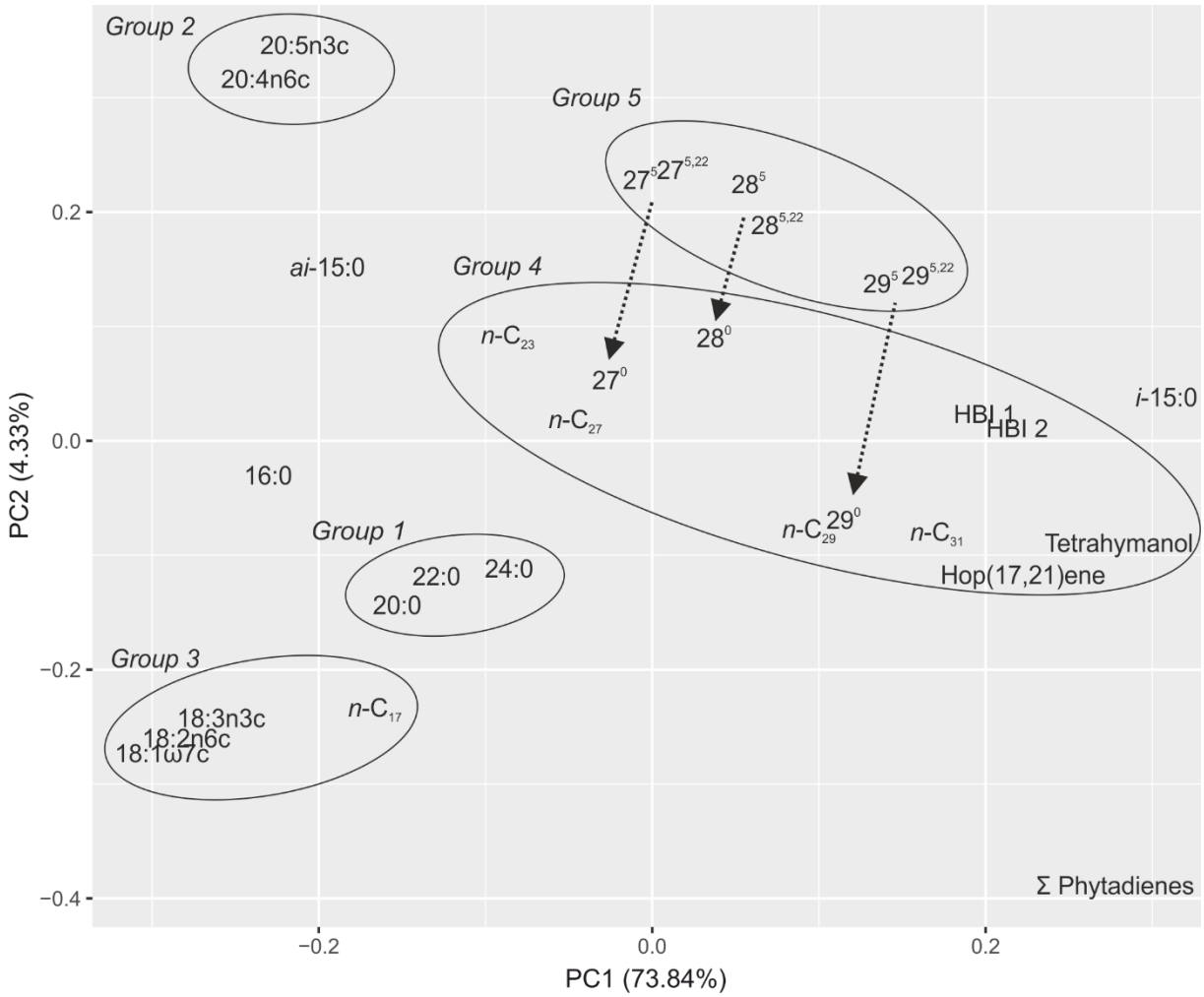

Fig. 4.2. PCA-plot containing the biomarker data of the inflow, the lake and the sediment between May 2019 and June 2020. Group 1: fatty acids from terrestrial sources, mainly introduced via the inflow. Group 2: fatty acids from eukaryotic phytoplankton (mainly diatoms, plus other algae). Group 3: biomarkers from bacterial phytoplankton (cyanobacteria). Group 4: biomarkers prevailing in the surface sediment. Group 5: sterols; dashed arrows show the transition of primary water column compounds to their sedimentary degradation products (into Group 4).

4.3.1. Group 1: fatty acids from terrestrial sources, mainly discharged via the inflow

Group 1 is comprised of long-chain saturated *n*-fatty acids (20:0, 22:0, 24:0). These compounds are, with respect to organic carbon, most abundant in the sediment. In the water column they typically show higher concentrations in the inflow than in the lake. With one exception (20:0 in winter, for an explanation see Section 4.3.2), the abundances of individual homologues in the surface sediment increase with carbon chain length.

The data clearly indicate that long-chain *n*-fatty acids are allochthonous compounds that enter Lake Seeburg via the inflow. Their most likely origin is higher land plants (Harvey, 1994; Colombo et al., 1997; Bianchi and Canuel, 2011). The fact that these compounds accumulate in the sediment indicates a degradation rate even lower than bulk organic matter. The apparently high stability of these compounds and their chain length distributions plausibly relate to observations that the degradation of fatty acids in sediments typically decreases with chain length and degree of saturation (Sun et al., 2000; Grossi et al., 2003; Bianchi and Canuel, 2011).

4.3.2. Group 2: fatty acids from eukaryotic phytoplankton, mainly diatoms plus other algae

Group 2 contains the long-chain unsaturated fatty acids 20:4n6c and 20:5n3c. In the inflow the concentrations of both biomarkers are constantly below those of the lake and the sediment. 20:4n6c shows its highest abundance in autumn. The concentrations of 20:5n3c are below the former, and its maximum is observed in summer.

The data indicate an autochthonous origin within the water column of Lake Seeburg. The most likely source of both 20:4n6c and 20:5n3c is diatoms which are known to contain these compounds as major fatty acids (Volkman et al., 1989; Dunstan et al., 1993; Pond et al., 1998; Fujibayashi et al., 2016).

Indeed, diatoms occur in Lake Seeburg almost year-round with a maximum in summer. In July 2017, almost 40% of the biovolume in Lake Seeburg consisted of Centrales (*Aulacoseira granulata*) and, in lower abundance, Pennales (Bäthe et al., 2018). Especially Centrales synthesize 20:5n3c (Dunstan et al., 1993), explaining the high concentrations of this biomarker in summer. 20:4n6c probably has a more mixed origin. Although this fatty acid is produced by diatoms (Volkman et al., 1989), contributions from macroalgae and microeukaryotes are also possible (Howell et al., 2003). Such a more diverse origin seems plausible, as the seasonal maximum of 20:4n6c coincides with the peak accumulation of phytoplankton biomass in the lake in autumn (Bäthe et al., 2018).

The decreasing concentrations of both biomarkers in the lake as well as in the surface sediment towards winter/spring are striking and indicate rapid degradation. Particularly high degradation rates of 20:4 and 20:5 have been reported to occur at the sediment-water interface, whereby the double bonds of the (poly-) unsaturated fatty acids are attacked (Canuel and Martens, 1996; Bianchi and Canuel, 2011). In addition to complete decomposition, reductive conversion of 20:4n6c and 20:5n3c can lead to elevated concentrations of 20:0 in the surface sediment, as it has been observed in winter (see Section 4.3.1).

4.3.3. Group 3: biomarkers from bacterial phytoplankton (cyanobacteria)

The third group consists of 18:1ω7c, 18:2n6c, 18:3n3c, and *n*-heptadecane (*n*-C_{17}). All these biomarkers have in common that they are much more abundant in the lake water than in the sediment and especially in the inflow. In the lake water, peak concentrations occur in summer/autumn (Tab. 4.2). Due to a moderate occurrence of *n*-C_{17} in the inflow in autumn, this biomarker has overlaps with group 1 (see Section 4.3.1). In the surface sediment, concentrations of 18:1ω7c and 18:2n6c are slightly lower, whereas 18:3n3c is significantly lower than in the water column.

Tab. 4.2. Absolute concentrations of n-C_{17}, 18:1ω7c, 18:2n6c and 18:3n3c in the lake water [µg/L]. These compounds can be attributed to cyanobacteria (see text for discussion). Note peak concentrations in autumn.

biomarker [µg/L]	spring	summer	autumn	winter
n-C_{17}	0.1	0.4	4.0	0.3
18:2n6c	0.6	3.9	13.4	1.1
18:3n3c	2.7	21.4	57.7	4.8
18:1ω7c	1.3	10.7	28.8	2.4

The compounds of this group can be attributed to N_2 fixing heterocystous cyanobacteria (unsaturated C_{18} fatty acids: (Vargas et al., 1998; Los and Mironov, 2015; Bauersachs et al., 2017); *n*-C_{17}: (Meyers and Ishiwatari, 1993a; Coates et al., 2014; Zhang et al., 2018). Indeed, cyanobacteria from the nitrogen-fixing order Nostocales (especially *Anabaena* sp.) had been observed as the dominant aquatic organism in Lake Seeburg during a former bloom in August and September 2017, both in terms of biovolume (about 35 mm^3/L) and cell number (about 160,000/ml) (Bäthe et al., 2018).

However, the seasonal course of these cyanobacterial biomarkers indicates their rapid removal from the lake water and efficient microbial degradation that takes place already in the water column. As discussed above, (poly-) unsaturated fatty acids can be more easily utilized by microorganisms and are therefore degraded in the sediment up to ten times faster than their saturated counterparts (Meyers et al., 1980; Bauersachs et al., 2017). This is consistent with our observation that the concentrations of group 3 fatty acids are lower in the surface sediment than in the lake water (18:1ω7c, 18:2n6c; see Tab. 4.1). Remarkably, the most unsaturated C_{18} fatty acid, 18:3n3c, is highly abundant in the lake water but nearly absent in the surface sediment of Lake Seeburg throughout

the year. This indicates rapid degradation of 18:3n3c still in the water column, which is consistent with reports from other environments (Baltic Sea, (Wittenborn et al., 2020)).

4.3.4. Group 4: biomarkers prevailing in the surface sediment

The fourth group consists of the alkanes *n*-C_{23} (major source: aquatic macrophytes, (Ficken et al., 2000) , *n*-C_{27}, *n*-C_{29} and *n*-C_{31} (land plants, (Eglinton and Hamilton, 1967; Cranwell et al., 1987), the stanols 27^0, 28^0 and 29^0 (degradation products of unsaturated sterols, particularly 27^5, 28^5 and 29^5 (Bogus et al., 2012; Nakakuni et al., 2017), two diunsaturated highly branched C_{25} isoprenoid hydrocarbons (HBI I and HBI II, diatoms, (Kaiser et al., 2016), tetrahymanol (Harvey and Mcmanus, 1991) and Hop-(17,21)-ene (early diagenetic product of biohopanoids, (Innes et al., 1998). All Group 4 components have in common that they do not, or only sparsely, occur in the inflow and in the lake water column. In the surface sediment, in contrast, concentrations are high throughout the year, usually with a maximum in summer.

Tetrahymanol may be largely originating in the surface sediment, which is certainly a preferred habitat of tetrahymanol-producing bacterivorous ciliates. Likewise, the major occurrence of hop-17(21)-ene in the sediment can be plausibly explained by biodegradation of bacterial bacteriohopanepolyols or other primary hopanoids. Yet, it is difficult to explain why long-chain *n*-alkanes and HBIs are almost exclusively found in the surface sediment, but not in the water column. Possibly, HBI-producing diatoms have been scarce in the year of sampling whereas they were more abundant in previous year(s). However, none of the known HBI-producing diatoms (Bianchi and Canuel, 2011) were found during a recent phytoplankton survey in Lake Seeburg (Bäthe et al., 2018). In the case of the long-chain *n*-alkanes adulteration by sampling appears possible. While major plant particles such as leaves were excluded from the water samples, this could only be done to a limited extent in the surface sediment due to the partial decomposition of the plant material. This may have led to a higher abundance of long-chain n-alkanes in the sediment samples.

4.3.5. Group 5: sterols and their degradation products

Group 5 includes the major unsaturated sterols (stenols) 27^5, 28^5, 29^5, $27^{5,22}$, $28^{5,22}$, and $29^{5,22}$ (Fig. 4.3). To check their distribution in the lake water vs. the surface sediment, the ratios of the individual sterol concentrations (lake water vs. the surface sediment with respect to total organic carbon, $\mu g/gC_{org}$) are shown in table 3. It is interesting to see that these numbers strongly decrease with increasing carbon chain length (e.g. from 1.33 (27^5) to 0.51 (28^5) and 0.13 (29^5)), indicating a

relative accumulation of higher molecular weight stenols in the sediment. The di-unsaturated stenols show a similar decreasing trend with increasing chain length, but less clearly.

As for the stenols a comparable trend is evident for saturated sterols (stanols). The average (annualized) ratio of lake water to sediment concentrations of stanols (in $\mu g/gC_{org}$) decrease with chain length from 0.10 (27^0) to 0.05 (28^0) and 0.00 (29^0, i.e. this compound occurs in the sediment, but is virtually absent in the water column; Tab. 4.3). Notably, all stanol ratios are significantly smaller than those observed for the corresponding stenols, indicating that these compounds are predominantly formed in the sediment (Fig. 4.3, see also sedimentary group 4, Section 4.3.4).

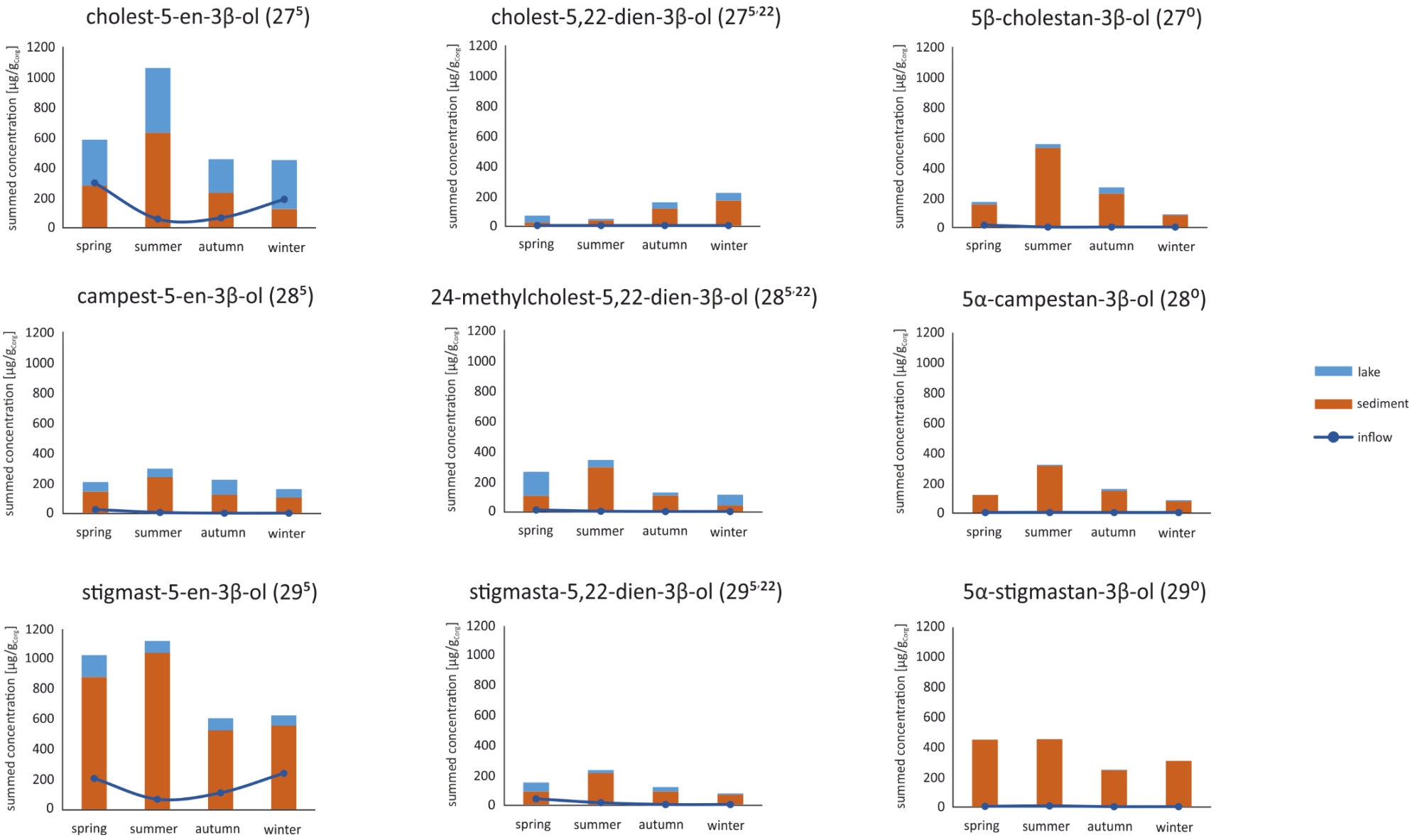

Fig. 4.3. Mean concentrations of the major stenols 27^5, 28^5, 29^5, $27^{5,22}$, $28^{5,22}$ and $29^{5,22}$ and their putative degradation products 27^0, 28^0 and 29^0 (stanols) over the course of the year in the inflow, lake and sediment of Lake Seeburg. The data suggest a more pronounced water column degradation of 27^5 as compared to 28^5 and, in particular, 29^5 (and their corresponding di-unsaturated compounds). See text for further discussion. Lake water and sediment concentrations are summed.

Tab. 4.3. Ratios of sterol concentrations (based on µg/g_{Corg}) in the lake water column vs. the surface sediment.

water/sediment	spring	summer	autumn	winter	average
27^{5}	1.10	0.68	0.96	2.59	1.33
28^{5}	0.44	0.24	0.82	0.53	0.51
29^{5}	0.16	0.08	0.15	0.12	0.13
$27^{5,22}$	2.25	0.28	0.36	0.30	0.80
$28^{5,22}$	1.51	0.16	0.19	1.79	0.91
$29^{5,22}$	0.70	0.10	0.36	0.12	0.32
27^{0}	0.10	0.05	0.18	0.05	0.10
28^{0}	0.00	0.02	0.09	0.10	0.05
29^{0}	0.00	0.00	0.01	0.00	0.00

27^{5} and $27^{5,22}$ are formed by a variety of eukaryotic phyto- and zooplankton, micro- and macroalgae (Huang and Meinschein, 1979; Parrish et al., 2000; Pearson et al., 2007). At Lake Seeburg, arthropods (*Daphnia pulex*) dominate the mesozooplankton in the entire lake, especially in spring (own observations). Indeed, *Daphnia* filtered from lakes water show nearly exclusively 27^{5}, and subordinately $27^{5,22}$ (see Fig. C1 for a GC-MS chromatogram). We therefore assume that mesozooplankton is a main source of C_{27} sterols at Lake Seeburg. Notably, arthropods such as *Daphnia* are unable to synthesize sterols directly, but transform other phytosterols into cholesterol (Martin-Creuzburg and Merkel, 2016). Such transformation of algal sterols into cholesterol by arthropod mesozooplankton may be a reason for the overall low abundance of typical algal sterols, namely C_{28} pseudohomologs, in Lake Seeburg.

29^{5} and $29^{5,22}$ are mostly reported to originate from terrestrial higher plants, but may also occur in some algae (Huang and Meinschein, 1979; Volkman, 1986; Mudge et al., 1999; Rampen et al., 2010). In Lake Seeburg, an allochthonous terrestrial contribution is most likely more significant, as C_{29}-sterol producing algae (Volkman, 1986) play only a minor role (Bäthe et al., 2018) and both, 29^{5} and $29^{5,22}$ have their highest concentrations in the inflow (Tab. 4.1).

28^{5} and $28^{5,22}$ are less specific. They originate mainly from algae, partly from higher plants and occasionally also from zooplankton (Huang and Meinschein, 1979; Mudge et al., 1999; Volkman, 2003; Pearson et al., 2007). However, at Lake Seeburg C_{28}-stenols are barely present in the inflow, which indicates a dominating autochthonous origin, most likely from eukaryotic phytoplankton.

Stanols are not typically produced in living organisms, although minor amounts were reported from a few dinoflagellates and diatoms (Robinson et al., 1984; Volkman et al., 1990; Rampen et al., 2010). The most likely, and often proposed origin of stanols is microbial degradation of stenols. While under

oxic conditions stenols are mainly degraded/destroyed (Bogus et al., 2012), they can be chemically reduced to stanols under sub-/anoxic conditions (Nakakuni et al., 2017).

In the sediment of Lake Seeburg, stanols are by an order more abundant than in the water column. The high amount of organic material deposited at a high sedimentation rate (about 5 mm per year) could quickly lead to sub- to anoxic conditions in the surface sediment and thus promote the degradation of stenols to stanols. Low amounts of stanols observed in the water column mainly coincide with the cyanobacterial bloom. These stanols may be explained by (i) temporary sub-/anoxic zones occurring during the bloom e.g. in sinking aggregates or fecal pellets, (ii) resuspension of sedimentary stanols, or (iii) a direct origin from planktonic algae, particularly dinoflagellates (however, only a few individuals per milliliter of the Dinoflagellate *Peridinium* occur in spring and summer, and no dinoflagellates were observed in the lake water in autumn and winter (Bäthe et al., 2018)).

4.3.6. Stenols as eutrophication markers

Due to their occurrence in all eukaryotes and their good preservation in sediments, sterols are excellent biomarkers for the reconstruction of the eutrophication history of aquatic environments (Parrish et al., 2000). For instance, the ratio of C_{27} to C_{29} stenols has been seen as a possibility to reconstruct the eutrophication level of a water body (Gaskell and Eglinton, 1976; Huang and Meinschein, 1979; Wang et al., 2004). In water bodies suffering from eutrophication due to increased nutrient supply, autochthonous production of organic matter and thus, contributions of C_{27} and C_{28} sterols vs higher-plant derived allochthonous C_{29} sterols increases. As a consequence, the C_{27} to C_{29} ratio will increase with eutrophication.

On the other hand, it was shown in degradation studies that 27^{5} and $27^{5,22}$ may degrade faster than 29^{5} and $29^{5,22}$ (Sun and Wakeham, 1998; Muri et al., 2004; Bauersachs et al., 2017). These different degradation rates of individual stenols have to be considered in any interpretation as eutrophication markers (Wakeham, 1989; Meyers and Ishiwatari, 1993b; Sun and Wakeham, 1998; Muri et al., 2004). Our study at Lake Seeburg supports the slower stenol-stanol conversion with increasing carbon number. While 27^{0} is present in the sediment throughout the year (max. of 41 µg/g C_{org} in autumn), concentrations drop from 28^{0} (≤13 µg/g C_{org}) to 29^{0} (≤3 µg/g C_{org}) (see Section 4.3.5).

To check whether a trophic level change over time may be reflected by the carbon number distributions of sedimentary sterols in Lake Seeburg, we performed additional sterol analyses on two short (≈30 and 50 cm) sediment cores sampled at the western (bathing pier) and northern (reed belt, near the shore) part of the lake. To compensate for the slower stenol-stanol conversion with

increasing carbon number, as indicated by our data, the major stenols were summed with their corresponding stanols (Fig. 4.4, data in Tab. C4). Further degradation products of sterols, namely steroid hydrocarbons (Schwarzbauer and Jovančićević, 2016) were only occasionally found in low abundances (cholesta-3,5-diene and cholest-2-ene, <1 % of the respective sterols), or absent (steranes) and were therefore not considered in the calculations.

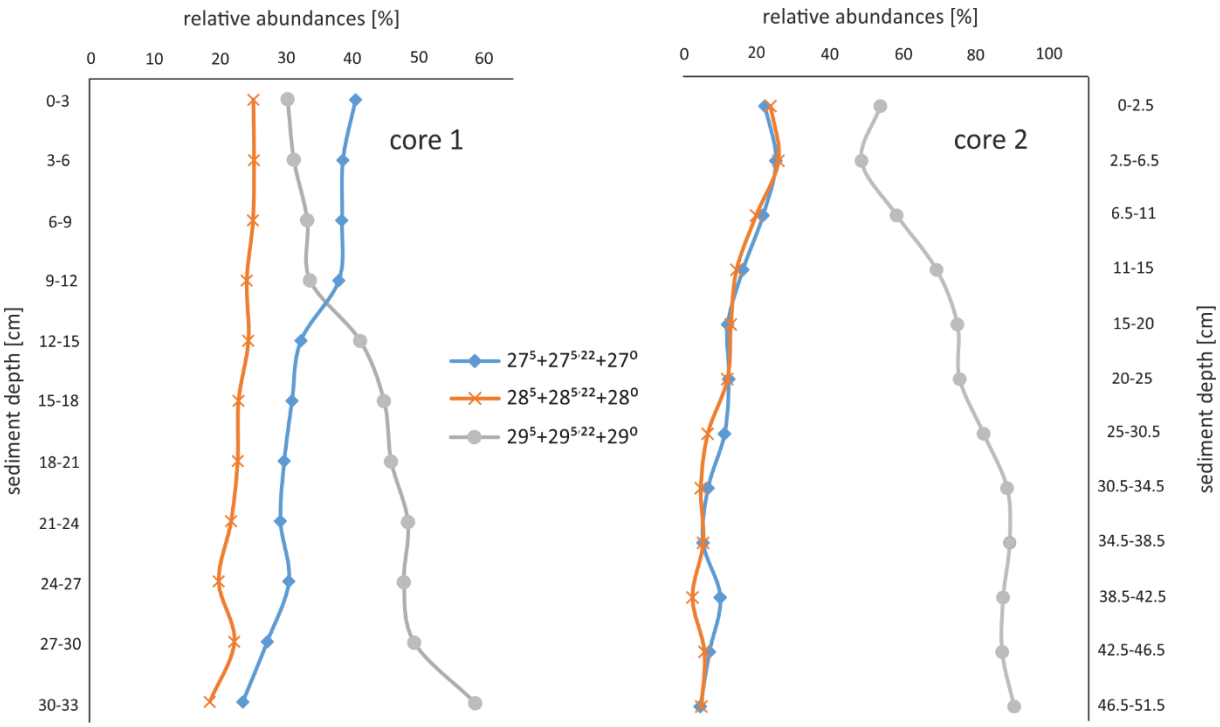

Fig. 4.4. Relative abundances of major C_{27}, C_{28}, and C_{29} sterols in short sediment cores from Lake Seeburg. Core 1 (left) is located in the western part of the lake, core 2 (right) in the northern part (nearshore, close to reed belt).

From the bottom to the top of core 1, summed C_{27}-sterols (stenols plus 27^0) increase from 25% to 50% while summed C_{29}-sterols decrease from 59% to 30%. C_{28} sterols, in comparison, remain roughly constant. Core 2 behaves similar but shows even higher overall proportions of C_{29} sterols that range from 90% (bottom) to 50% (top). These higher contents of C_{29} sterols of core 2 may be explained by the proximity of the sampling point to the reed belt, and thus, higher contributions of higher plant derived organic matter. Nevertheless, both cores show a similar overall behavior of sterol carbon number distributions. The trend of summed C_{27} and C_{29} sterols (original-compounds plus degradation products) with depth is clearly inverse, which may be interpreted to reflect increasing eutrophication and thus, autochthonous contributions in the lake environment over the last decades.

Together with the observation of an increasing deterioration of the trophic status, we consider the ratios of C_{27} to C_{29} stenols plus their degradation products (particularly stanols) as a possibility to track the historical eutrophication trend of a lake. However, to derive precise information from

sterols about past trophic stages in lake environments, it will be important to investigate further possible degradation mechanisms and products through long-term experiments.

4.4. Conclusion

Via principal component analysis (PCA) lipid biomarkers were clustered into five groups, each with similar distribution in the inflow, the lake and the surface sediment. Long-chain saturated *n*-fatty acids (20:0, 22:0, 24:0) were attributed to an allochthonous input from the inflow. Two long-chain unsaturated fatty acids (20:4n6c and 20:5n3c) most likely originate from diatoms. The fatty acids 18:1ω7c, 18:2n6c, 18:3n3c, and n-heptadecane (*n*-C_{17}) were attributed to bacterial phytoplankton (cyanobacteria). They were formed in the lake (only *n*-C_{17} is slightly present in the inflow), but show signs of early degradation in the water, resulting in moderate concentrations in the surface sediment. The biomarkers nearly exclusively found in the sediment were considered to be formed there (tetrahymanol), to be degradation products (stanols 27^0, 28^0 and 29^0, and hop-(17,21)ene), to have likely been entered more frequently in the past (HBI I and HBI II), or to be possibly distorted due to sampling effects (*n*-alkanes *n*-C_{27}, *n*-C_{29} and *n*-C_{31}). Although the stenols show a similar behavior among each other, they are attributed to different sources (C_{27}, autochthonous; C_{29}, allochthonous).

The subsequent sterol study on two sediment cores was designed to determine if a change in trophicity is reflected by the carbon number distribution of the sedimentary sterols. A possible bias due to a slower degradation rate of the stenols with increasing carbon number was reduced by summation with their degradation products, especially with the corresponding 5α(H)-stanols. While the proportions of predominantly allochthonous C_{29} sterols decreased with decreasing sediment depth, the proportions of autochthonous C_{27} (and C_{28}) sterols increased significantly. This is consistent with the observed eutrophication trend in Lake Seeburg over the last decades. Increasing eutrophication led to enhanced production of autochthonous organic matter in recent decades, resulting in an increase in the C_{27} (and C_{28}) stenols. Therefore we consider the C_{27} vs. C_{29} stenoles plus their degradation products as suitable biomarker proxies to aid in the qualitative reconstruction of historical eutrophication trends.

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5. Conclusion, outlook and possible measures at Lake Seeburg

5.1. Conclusion

The aim of this thesis was to better understand the dynamics of anthropogenic eutrophication processes in lakes compared to conventional monitoring strategies. Therefore, pesticides, bioavailable nutrients, and biomarkers were tested at Lake Seeburg to assess if and how they can be used for a deeper understanding of the overall eutrophication dynamics in spatial and especially temporal terms. The following findings were obtained in the individual studies:

The results of the pesticide and nutrient monitoring in the first study indicate that common rigid monitoring strategies need to be expanded or replaced by more flexible, event-based samplings. Using a broad spectrum of pesticides, two main factors of spatial and temporal pollution were identified at Lake Seeburg. Pesticides applied in the past are discharged into adjacent water bodies at a relatively constant rate throughout the year, correlating with nitrate inputs. In contrast, currently applied pesticides tend to cause high peaks in adjacent water bodies during or shortly after heavy rain events, correlating with soluble reactive phosphate (SRP) inputs. The sources of high nutrient and pesticide inputs are primarily smaller tributaries collecting runoff from adjacent agricultural fields. Beside the observation that pesticides are discharged from agricultural fields into surrounding water bodies, especially after heavy rain events, pesticide measurements have proven to be an excellent tool for obtaining in-depth information on the spatial and temporal dynamics of watersheds. Expensive high-resolution monitoring with a large number of indicators is not essential to understanding watershed dynamics. Instead, a careful catchment appraisal, preferably involving residents and citizens, is an important step in finding relevant sampling sites and in reducing the number of analytes.

The second study reveals that Lake Seeburg, like many other lakes worldwide, suffers from severe eutrophication. Bioavailable nitrogen and phosphorus species are steadily discharged from farmed catchment areas into the lake. Especially extreme weather events lead to massively increased nutrient inputs with subsequent negative effects. During the heavy rainfall event, high allochthonous nutrient inputs via the inflow were observed; during the period of severe drought, autochthonous inputs through sediment re-dissolution were the primary concern. Both favored the formation of cyanobacterial blooms, primarily through their triggered nutrient inputs. After the heavy rain event, the bloom was short but intense and mainly monospecific, and more diverse but long-lasting after the heat wave. Despite their different composition, the consequences are similarly negative in several respects (e.g. formation of anoxic zones, a massive increase in pH, death of higher

organisms). Since an increase in the intensity and frequency of exceptional weather events is to be expected, they need to be considered in more detail. Only with precise knowledge of their temporal and spatial effects on the overall nutrient dynamics, can the long-term consequences of climate change be assessed and adapted measures implemented at an early stage.

The third study aimed to complement the studies of current lake dynamics with information on the past to reconstruct how the current eutrophic status developed. It was shown that sterols are suitable biomarkers to qualitatively describe the change of organic matter sources and thus, indirectly, the eutrophication history of Lake Seeburg. In the sediment, the relative decrease with depth of autochthonous C_{27} stenols, as compared to allochthonous C_{29} stenols, can be interpreted as a clear indicator of increasing eutrophication over time. A possible bias due to a slower degradation rate of stenols with increasing carbon number can be corrected by summing with their early diagenetic saturated degradation products, especially with the stanols. Due to a constant shift from C_{29} to C_{27} dominant sterols in the sediments of Lake Seeburg, a continuous increase in eutrophication over the last decades can be assumed.

In summary, all three different substance groups (pesticides, bioavailable nutrients and biomarkers) can be used for a more precise spatial and temporal characterization of the overall eutrophication dynamics of the lake. The first study (mainly on pesticides) contributed to improve common monitoring strategies and to better characterize the catchment areas in spatial and temporal aspects. The second study (mainly on nutrients) clearly showed the negative effects of extreme weather events (heavy rainfall and dry periods). Finally, the third study (mainly on biomarkers) identified sedimentary sterols as suitable biomarkers for the reconstruction of the eutrophication level of a water body over time. The first and especially the second study confirmed the need for detailed pre-studies to understand the overall lake dynamics in terms of eutrophication (e.g. possible peak inputs of nutrients after extreme weather events). Based on the detailed studies, timely optimized and more cost-efficient monitoring of identified nutrient hotspots can be conducted, in order to gain a deeper understanding of eutrophication problems of the lake ecosystem. To reconstruct how the current eutrophic status emerged, biomarkers can be used to provide additional information on the historical course of eutrophication.

5.2. Outlook

In recent decades, water bodies around the world have been subject to increasing eutrophic pressure, which was also the case in our study object Lake Seeburg (see Section 4). Problems with eutrophication, primarily caused by the intensive use of fertilizers, are very likely to increase in the future due to a growing world population, increasing global affluence, and other socioeconomic

factors (Alcamo et al., 2007). Globally, the use of fertilizers is predicted to increase by 2050 (Bouwman et al., 2013; Lim et al., 2021). The intensified use of fertilizers alone, with the associated inputs of nutrients into surrounding water bodies, will further cause eutrophication problems.

However, it is not only the rising use of fertilizers that could increase eutrophication in water bodies in the future; climate change will also have a negative impact (O'Neil et al., 2012; Smith and Schindler, 2009). Rising anthropogenic CO_2 levels, a higher intensity of extreme weather events, and rising water temperatures are already favoring changes in the composition of aquatic organisms. The occurrence of heat-adapted cyanobacteria increases, resulting in greater numbers of blooms with associated negative effects (Orihel et al., 2017; Paerl and Huisman, 2008; Visser et al., 2016). As our second study in Section 3 points out, both heavy rainfall events and the intensity of dry periods lead to cyanobacterial blooms, albeit in different ways, but with similar negative consequences for the lake ecosystem. To better understand the expected impacts on individual lake ecosystems (not all findings can be equally applied to all water bodies), further studies are needed for the future.

Overall, this thesis demonstrates the need to create greater awareness that the precious resource of water is under high anthropogenic pressure. Especially due to climate change and the growing use of fertilizers, water bodies must be protected more intensively to secure the supply of fresh water. As a first step, the affected water bodies need to be monitored to identify impending negative impacts in time and detail. However, based on our findings in Section 2, optimizations in the common monitoring strategies are necessary to save costs, to validate sources of contamination, and to capture the growing impacts of the increasing global population and climate change more accurately. Only with an accurate understanding of the potential impacts, including its catchment and its seasonal variabilities, can appropriate and sustainable remediation of individual water bodies be implemented in the future.

5.3. Possible measures at Lake Seeburg

At Lake Seeburg, a significant reduction in nutrient inputs from the catchment is needed, especially after heavy rain events. Otherwise, any measures taken in the lake itself may become ineffective as ongoing external nutrient inputs will promote a return of the previous eutrophic state (Kiani et al., 2020; Pokorný and Hauser, 2002; Søndergaard et al., 2003). Our data show that the Seeanger wetland served as a retention basin for a few days after heavy rain events, due to initial flooding. However, the eutrophication-relevant nutrients built up quickly in the flooded wetland and still entered the lake after a time delay of several weeks. As the Seeanger wetland was originally intended as a sedimentation trap, regular dredging should be considered and at least partly conducted. Since the construction of the wetland in 2004, the area has been a special habitat for

flora and fauna and is also recognized as such by the EU. Therefore, special consideration must be given to the impact of dredging on the ecology. Additional options to prevent sediments and nutrients from entering Lake Seeburg include slope-parallel tillage of agricultural land in the catchment area, the cultivation of soil-holding plants close to the water bodies, the conversion of slopes into grassland for grazing animals, or the construction of additional sedimentation ponds.

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Appendices

Appendix A

Supplementary information for Section 2:

Seasonal and spatial dynamics of selected pesticides and nutrients in a small lake catchment - Implications for agile monitoring strategies

Tab. A1. IC standards for cations and anions.

		1 [mg/L]	2 [mg/L]	3 [mg/L]	4 [mg/L]	5 [mg/L]	6 [mg/L]	7 [mg/L]	8 [mg/L]	9 [mg/L]	10 [mg/L]
standards for anions	**NO_3**	100	80	60	40	20	20	10	5	2	1
	Cl	100	80	60	40	20	20	10	5	2	1
	SO_4	100	80	60	40	20	20	10	5	2	1
	F	5	4	3	2	1	2	1	0.5	0.2	0.1
	PO_4	5	4	3	2	1	2	1	0.5	0.2	0.1
	Br	5	4	3	2	1	2	1	0.5	0.2	0.1
standards for cations	**Ca**	200	100	80	40	20	10	5	2	1	-
	Mg	100	50	40	20	10	5	2	1	0.5	-
	Na	200	100	80	40	20	10	5	2	1	-
	K	100	20	15	10	5	2	1	0.5	0.2	-
	Li	-	-	-	-	-	2	1	0.5	0.2	-
	Sr	-	-	-	-	-	2	1	0.5	0.2	-
	Ba	-	-	-	-	-	2	1	0.5	0.2	-

Tab. A2. UPLC-MS/MS parameters.

compound	quantifier	qualifier	RT	IS	ESI	DL [ng/L]	origin
atrazine	216 → 103	216→ 174	5.35	atrazine D_5	+	0.4	Ehrenstorfer
desisopropyl atrazine	174 → 95	174 → 103	3.16	atenolol D_7	+	1.4	Ehrenstorfer
desethyl atrazine	188 → 103	188 → 146	3.96	atrazine D_5	+	11	Ehrenstorfer
metazachlor	277 → 210	277→ 134	5.44	atrazine D_5	+	5	Ehrenstorfer
BH 479-4	274→ 134	274→ 162	3.53	melamin ^{13}C	+	10	BASF
BH 479-8	324 → 69	324 → 120	3.74	atrazine D_5 atenolol D_7	+/-	10	BASF
BH 479-12	302→ 116	302 → 162	2.82	atenolol D_7	-	2	BASF
quinmerac	222 → 141	222→ 204	3.36	atrazine D_5	+	5	Ehrenstorfer
BH 518-5	238 → 102	238 → 164	3.57	melamin ^{13}C	+	5	BASF
BH 518-2	252 → 234	252 → 234	1.43	chloridazon D_5	+	5	BASF
chloridazon	221 → 91	221 → 104	3.75	chloridazon D_5	+	0.3	Ehrenstorfer
desphenyl chloridazon	145 → 101	145 → 117	0.84	chloridazon D_5	+	0.3	BASF
methyldesphenyl chloridazon	160 → 129	160 → 87	1.38	chloridazon D_5	+	1.3	BASF
metolachlor	285 → 253	285 → 117	6.01	atrazine D_5	+	5	Ehrenstorfer
metolachlor oxanilic acid	298 → 202	298 → 160	5.00	atrazine D_5		5	BASF
metolachlor sulfonic acid	352 → 230	352 → 208	4.53	atrazine D_5		5	BASF
sulfadimidin	279→ 124	279 → 186	2.76	atrazine D_5	+	2	Acros
acesulfam	161 → 87	161 → 82	0.95	melmin ^{13}C	-	4.2	-
caffeine	195 → 110	195 → 138	2.67	atenolol D_7	+	3.2	ACROS
nicotine	163 → 130	163 → 117	1.10	melamin ^{13}C	+	5	ACROS
paraxanthin	181 → 96	181 → 124	2.39	paraxanthin D_6	+	8.1	BASF
valsartan acid	265 → 165	267 → 16206	4.11	ibuprofen D_3	-/+	1	Ehrenstorfer

Tab. A3. In situ parameters temperature, oxygen, conductivity and pH at the water sampling positions.

Sampling point	Termperature [°C] min[a]	max[b]	average	median	Sampling point	Oxygen [mg/L] min[a]	max[b]	average	median
1	4.9 (Feb)	16.4 (Aug)	10.2	9.7	**1**	9.40 (Aug)	12.47 (Feb)	10.89	10.86
2	2.5 (Feb)	26.7 (Aug)	12.5	12.9	**2**	4.75 (Nov)	16.04 (Aug)	10.59	10.21
3	2.6 (Feb)	22.5 (Aug)	12.0	12.6	**3**	3.36 (Aug)	12.78 (Apr)	8.19	7.89
4	2.9 (Feb)	19.9 (Aug)	11.4	12.0	**4**	6.58 (Oct)	11.69 (Apr)	8.93	9.09
5	3.1 (Feb)	18.9 (Aug)	11.4	13.1	**5**	7.05 (Nov)	14.10 (Apr)	9.50	9.00
6	2.5 (Feb)	25.9 (Aug)	14.0	14.6	**6**	6.74 (Nov)	14.15 (Jul)	11.11	11.87
7	2.6 (Feb)	26.0 (Jun)	13.9	14.7	**7**	6.41 (Nov)	13.50 (Jan)	10.75	11.77
a	5.0 (Feb)	13.5 (Aug)	10.0	10.9	**a**	4.76 (Mar)	9.80 (Dec)	8.23	8.81
b	2.0 (Feb)	15.2 (Jun)	9.5	9.7	**b**	3.96 (Aug)	11.98 (Feb)	8.53	8.93
c	4.5 (Feb)	16.8 (Aug)	10.3	10.4	**c**	7.95 (Oct)	11.81 (Feb)	10.00	10.16
d	4.2 (Feb)	18.8 (Aug)	11.5	12.7	**d**	7.03 (Oct)	13.78 (Apr)	9.58	8.74

Sampling point	Conductivity [µS/cm] min[a]	max[b]	average	median	Sampling point	pH min[a]	max[b]	average	median
1	692 (Oct)	962 (Nov)	888	899	**1**	7.92 (Mar)	8.42 (Jul)	8.26	8.28
2	684 (Oct)	889 (Dec)	853	866	**2**	7.43 (Sep)	8.71 (Aug)	7.97	7.90
3	791 (Oct)	899 (Nov)	845	843	**3**	7.55 (Sep)	8.18 (Apr)	7.79	7.80
4	744 (Oct)	907 (Nov)	844	841	**4**	7.49 (Oct)	8.22 (Jul)	7.87	7.91
5	702 (Oct)	873 (Nov)	806	809	**5**	7.23 (Feb)	8.37 (Apr)	7.91	7.87
6	536 (Aug)	737 (Mar)	660	674	**6**	7.68 (Nov)	9.34 (Sep)	8.39	8.34
7	509 (Aug)	737 (Apr)	658	671	**7**	7.64 (Nov)	9.01 (Sep)	8.33	8.31
a	582 (Oct)	775 (Dec)	692	694	**a**	7.30 (Oct)	8.10 (Aug)	7.65	7.60
b	634 (Oct)	957 (Oct)	746	734	**b**	7.51 (Aug)	8.08 (Apr)	7.73	7.67
c	461 (Sep)	662 (Dec)	530	528	**c**	7.20 (Oct)	8.16 (Oct)	7.64	7.66
d	373 (Jul)	440 (Dec)	401	391	**d**	7.30 (Oct)	8.18 (Apr)	7.70	7.70

[a] Minimum concentration, [b] Maximum concentration

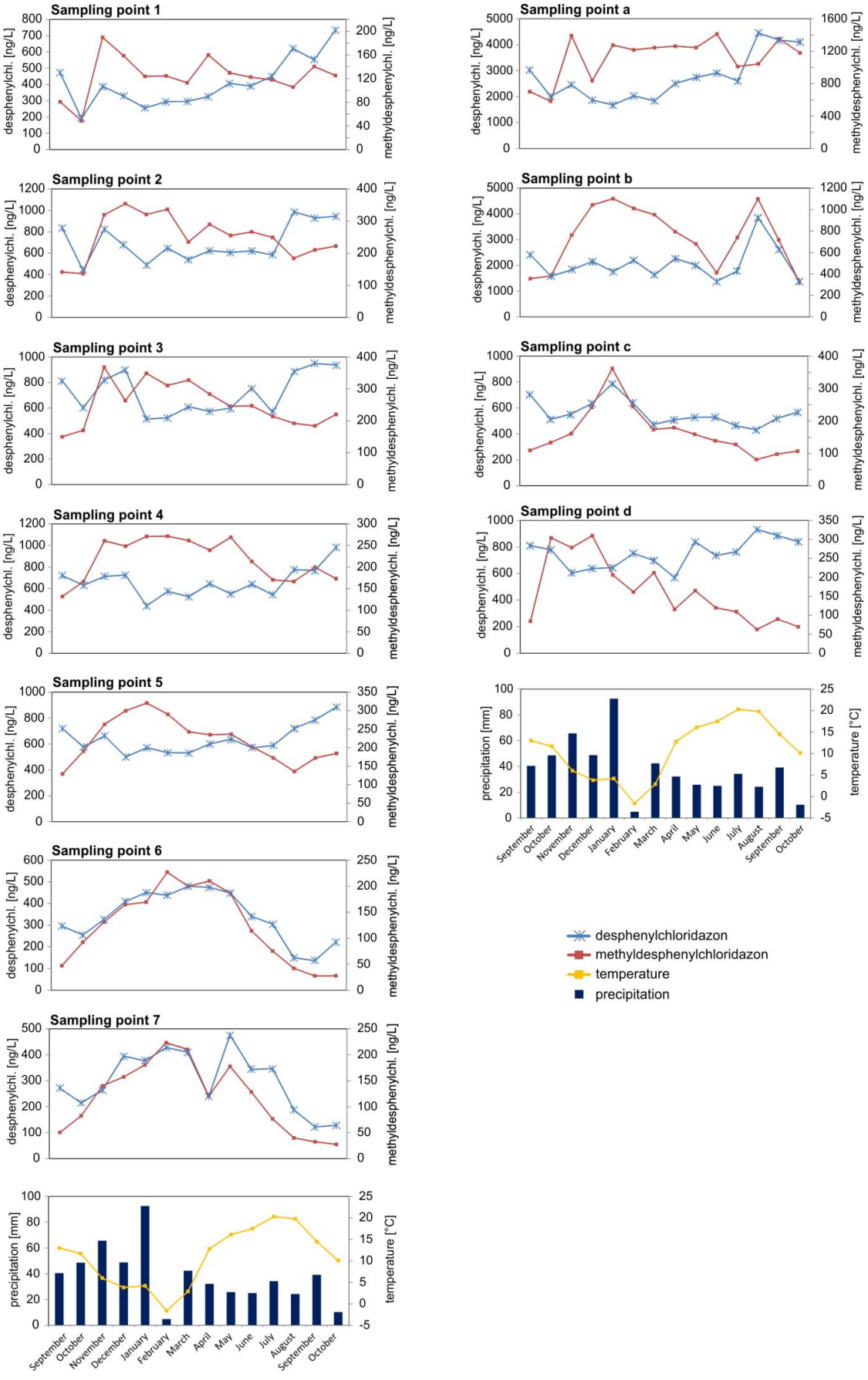

Fig. A1. Seasonal dynamics of desphenyl chloridazon, methyldesphenyl chloridazon, temperature and precipitation in the studied area.

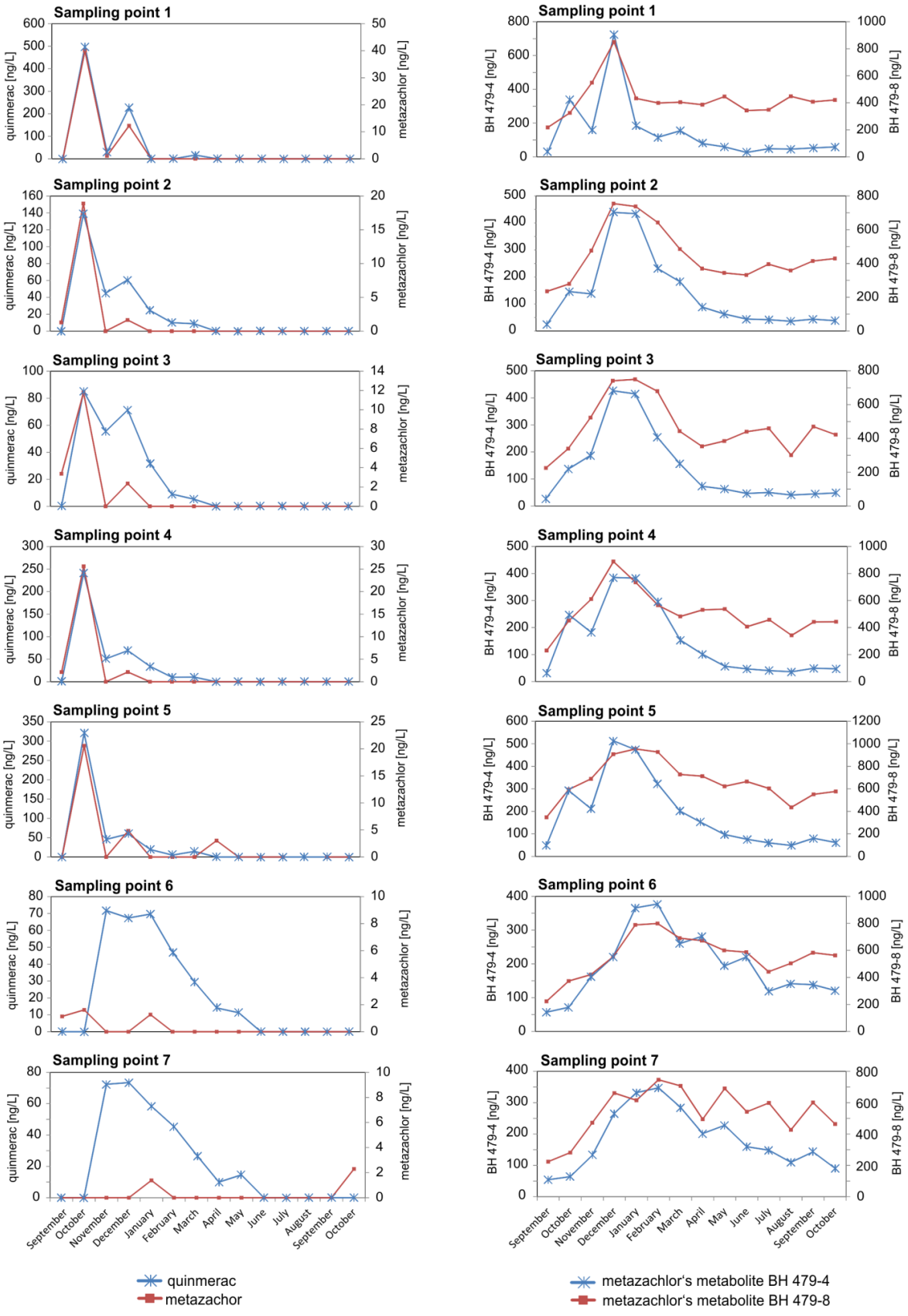

Fig. A2. Seasonal dynamics of quinmerac and metazachlor with its metabolites in the studied area.

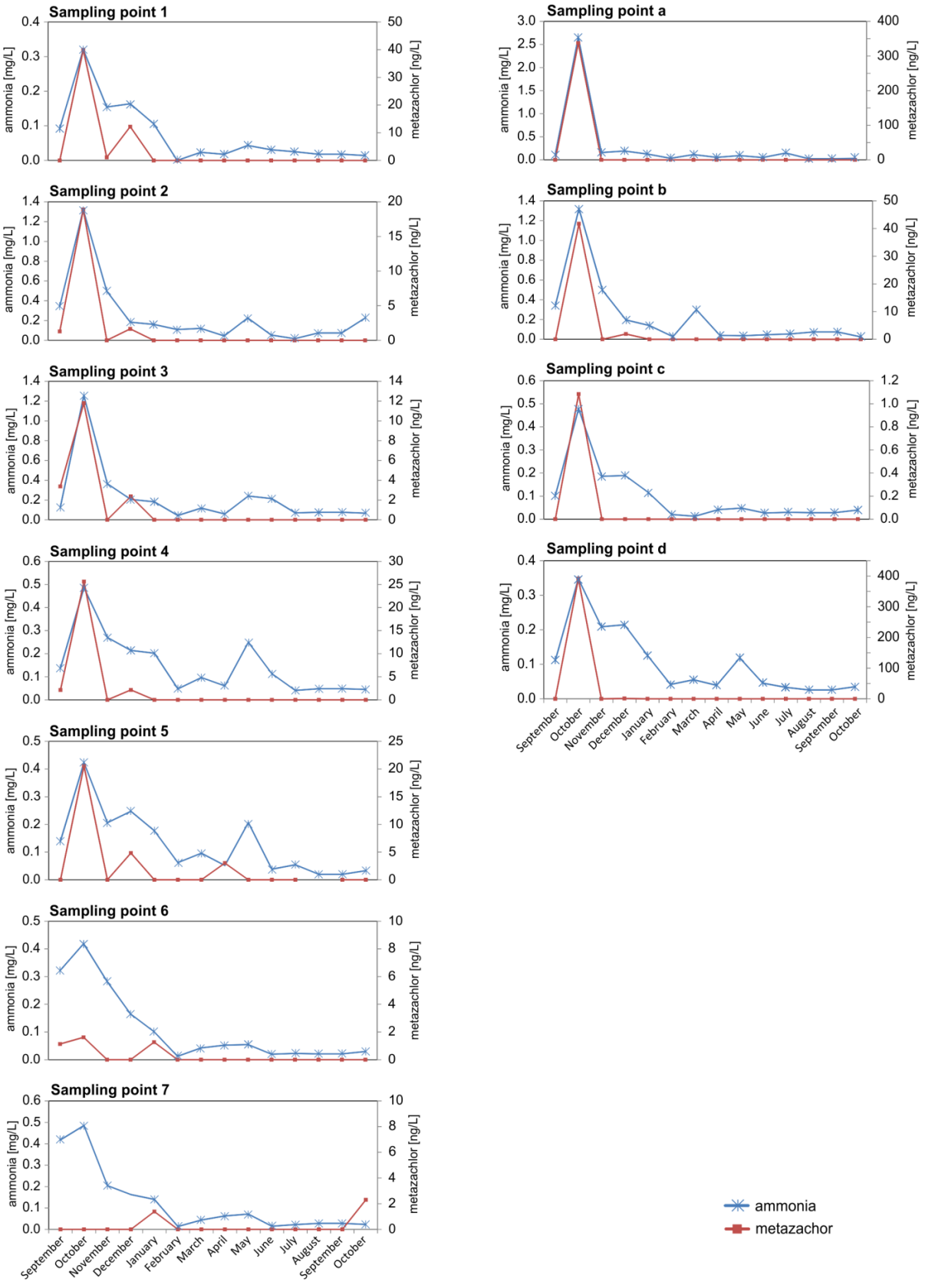

Fig. A3. Seasonal dynamics of ammonium and metazachlor in the studied area.

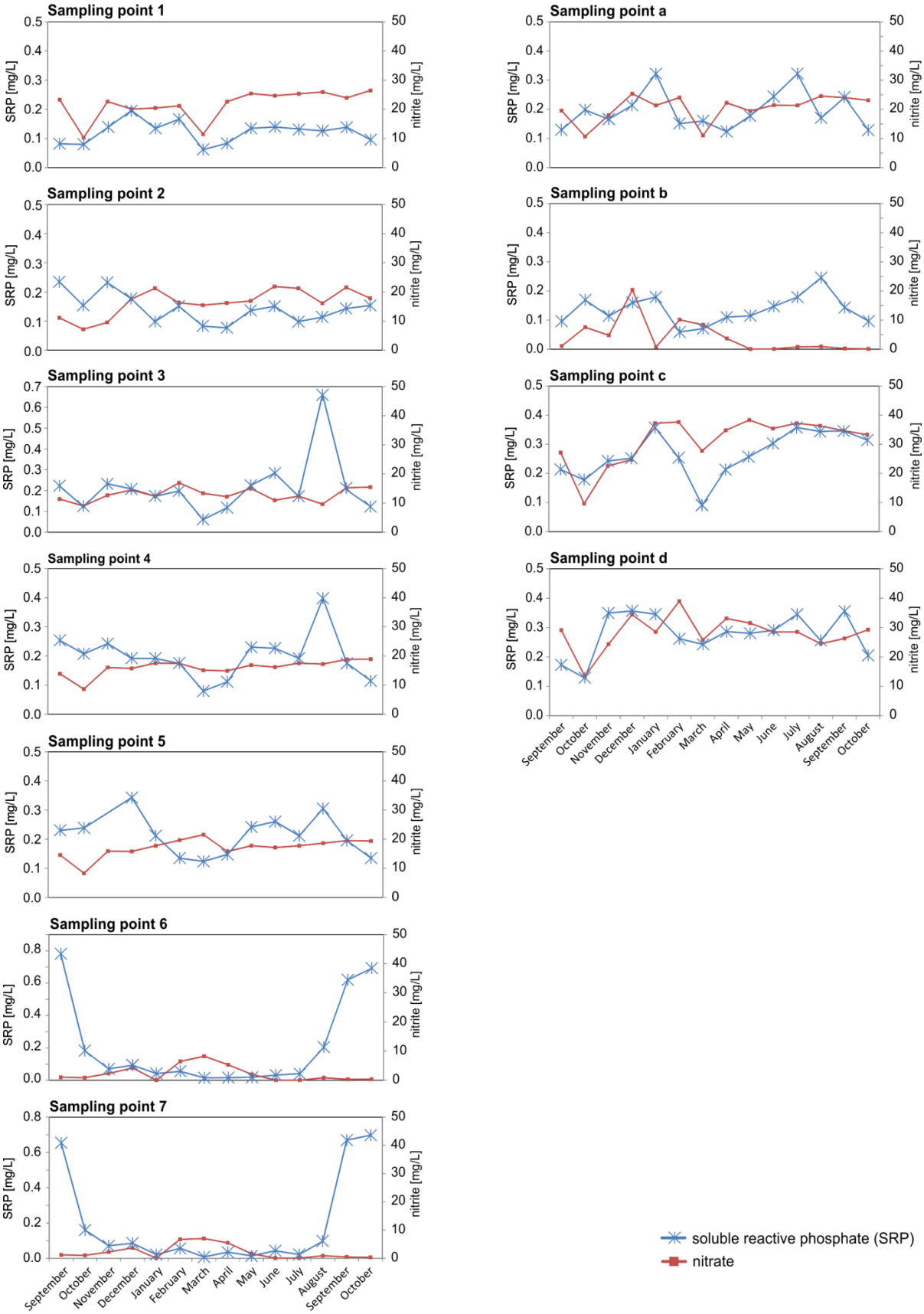

Fig. A4. Seasonal dynamics of soluble reactive phosphate (SRP) and nitrate in the studied area.

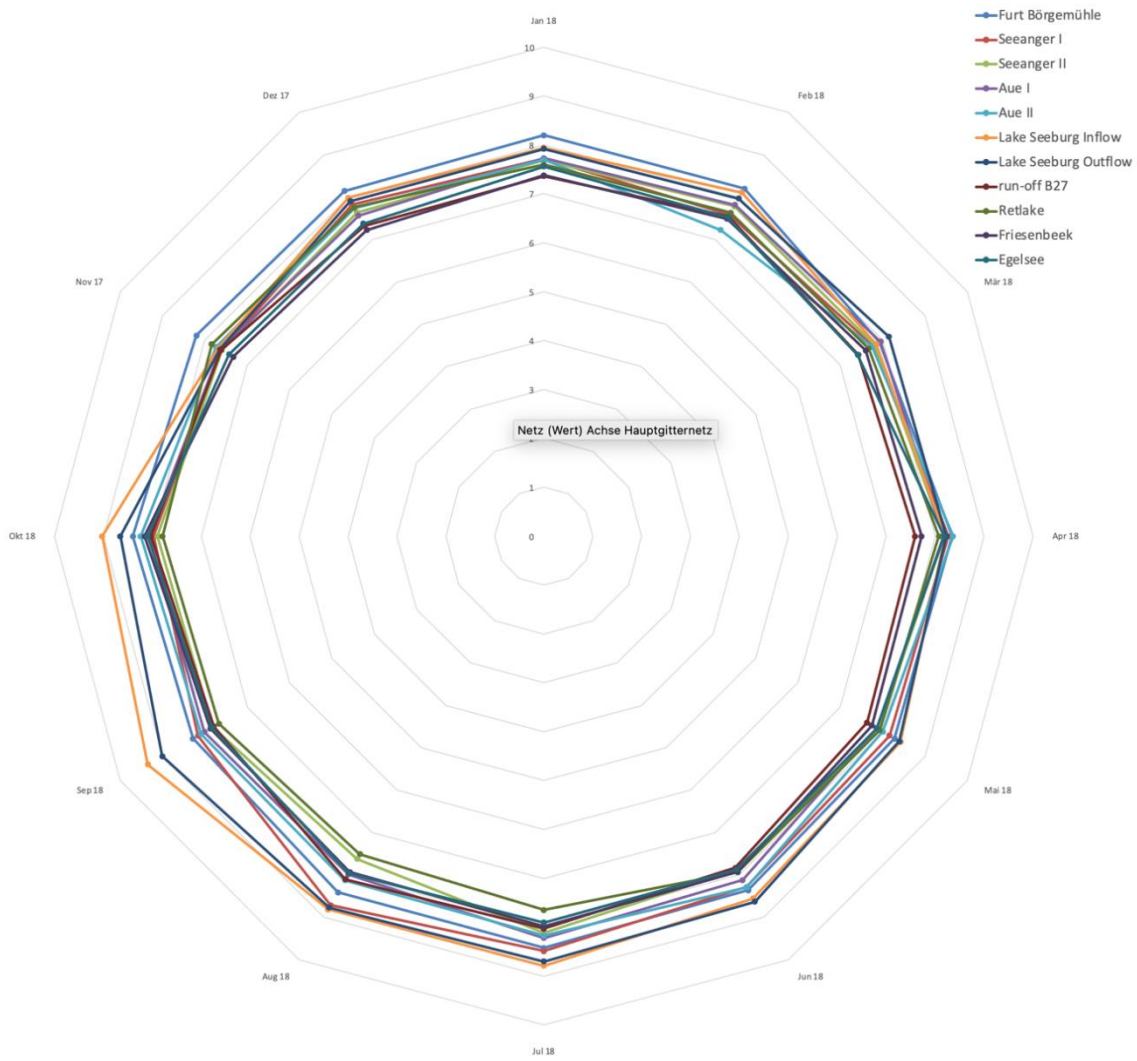

Fig. A5. Radar chart of all EC values in [µS/cm]. For further information please refer to Tab. 2.3.

Appendix B

Supplementary information for Section 3:

Effects of weather extremes on the nutrient dynamics of a shallow eutrophic lake as observed during a three-year monitoring study

Fig. B1. Map of Lake Seeburg showing the sampling locations (arrows) at the main inflow (Aue creek), the western part of the lake (bathing pier) and the eastern part near the outflow. The shaded area represents the Seeanger wetland upstream of the main tributary (Aue creek).

Tab. B1: Standards used for IC analyses of cations and anions.

		1 [mg/L]	2 [mg/L]	3 [mg/L]	4 [mg/L]	5 [mg/L]	6 [mg/L]	7 [mg/L]	8 [mg/L]	9 [mg/L]	10 [mg/L]
standards for anions	**NO_3**	100	80	60	40	20	20	10	5	2	1
	Cl	100	80	60	40	20	20	10	5	2	1
	SO_4	100	80	60	40	20	20	10	5	2	1
	F	5	4	3	2	1	2	1	0.5	0.2	0.1
	PO_4	5	4	3	2	1	2	1	0.5	0.2	0.1
	Br	5	4	3	2	1	2	1	0.5	0.2	0.1
standards for cations	**Ca**	200	100	80	40	20	10	5	2	1	
	Mg	100	50	40	20	10	5	2	1	0.5	
	Na	200	100	80	40	20	10	5	2	1	
	K	100	20	15	10	5	2	1	0.5	0.2	
	Li	-	-	-	-	-	2	1	0.5	0.2	
	Sr	-	-	-	-	-	2	1	0.5	0.2	
	Ba	-	-	-	-	-	2	1	0.5	0.2	

Tab. B2. Compilation of the data obtained at the sampling positions in 2017.

Date	Location	Temperature °C	pH	Oxigen mg L^{-1}	Alkalinity meq L^{-1}	SRP mg L^{-1}	Nitrite mg L^{-1}	Nitrate mg L^{-1}	Ammonium mg L^{-1}	Calcium mg L^{-1}	Chloride mg L^{-1}
January '17	Inflow (Aue creek)	2.4	8.3		4.64	0.172	0.008	19.440	0.066	134.6	46.7
	Lake (W, pier)										
	Lake (E, outflow)										
February '17	Inflow (Aue creek)	3.8	7.9		4.56	0.172	0.008	21.469	0.277	139.0	29.4
	Lake (W, pier)		8.0		3.8		0.007	4.687	0.035	112.3	32.5
	Lake (E, outflow)										
March '17	Inflow (Aue creek)	9.5	8.2		4.36	0.166	0.090	18.736	0.042	128.0	32.0
	Lake (W, pier)	9.3	8.5		3.14	0.163	0.050	1.278	0.033	95.4	31.9
	Lake (E, outflow)	9.3	8.6		3.24	0.171	0.050	1.654	0.035	96.8	31.8
April `17	Inflow (Aue creek)	6.0	8.3	14.57	4.02	0.136	0.022	17.909	0.374	120.6	28.7
	Lake (W, pier)	9.8	8.2	11.70	3.22	0.062	0.015	2.581	0.131	98.3	31.7
	Lake (E, outflow)	9.8	8.2	12.11	3.32	0.046	0.015	2.009	0.068	100.3	31.5
May '17	Inflow (Aue creek)	15.1	7.9	8.06	3.8	0.262	0.253	14.760	0.307	110.1	25.5
	Lake (W, pier)	19.0	8.3	9.14	3.14	0.031	0.003	1.654	0.144	96.3	31.9
	Lake (E, outflow)	19.1	8.2	8.77	3.34	0.035	0.004	1.819	0.166	95.8	32.2
June '17	Inflow (Aue creek)	17.3	8.1	7.60	3.76	0.344	0.365	13.212	0.127	126.8	21.7
	Lake (W, pier)	22.5	8.4	9.16	2.86	0.351	0.013	0.708	0.091	91.2	31.2
	Lake (E, outflow)	22.7	8.4	9.48	2.74	0.266	0.028	0.750			31.1
July '17	Inflow (Aue creek)	16.5	8.0	8.17	4.32	0.306		15.988	0.006	125.2	28.0
	Lake (W, pier)	22.1	8.6	12.33	3.46	0.330		1.204	0.008	90.6	31.7
	Lake (E, outflow)	22.9	8.6	12.62	3.3	0.346		1.205	0.008	91.2	31.6
August '17	Inflow (Aue creek)	19.5	7.3	0.22	4.44	1.355		1.215	0.708	107.2	23.1
	Lake (W, pier)	22.1	8.7	10.45	2.88	0.262		1.224	0.634	73.3	26.5
	Lake (E, outflow)	23.0	8.7	12.34	2.84	0.249		1.221	0.584	73.9	26.5
September '17	Inflow (Aue creek)	16.0	7.7	7.61	4.06	0.230		14.591	0.140	119.9	28.8
	Lake (W, pier)	19.4	8.4	8.13	3.12	0.780		1.032	0.322	78.2	26.2
	Lake (E, outflow)	19.8	8.5	9.46	2.96	0.654		1.178	0.418	77.6	26.3
October '17	Inflow (Aue creek)	12.8	7.5	7.47	3.72	0.239	0.050	8.323	0.120	104.4	24.8
	Lake (W, pier)	15.5	8.3	7.54	2.84	0.183	0.010	0.896	0.102	81.3	26.5
	Lake (E, outflow)	15.5	8.1	7.3	2.92	0.161	0.020	1.004	0.183	81.3	26.4
November '17	Inflow (Aue creek)	8.4	7.7	7.05	4.48	0.128		15.902	0.206	129.5	29.0
	Lake (W, pier)	8.6	7.7	6.74	3.16	0.096		2.339	0.283	90.5	27.1
	Lake (E, outflow)	8.7	7.6	6.41	3.1	0.084		2.209	0.205	90.8	27.1
December '17	Inflow (Aue creek)	3.4	7.7	11.26	4.8	0.018		15.824	0.247	121.3	34.2
	Lake (W, pier)	2.5	8.0	12.28	3.58	0.008		4.234	0.165	99.0	28.1
	Lake (E, outflow)	2.6	7.9	12.51	3.46	0.007		3.659	0.163	98.2	27.4

Tab. B2 (continued). Compilation of the data obtained at the sampling positions in 2018.

Date	Location	Temperature °C	pH	Oxigen mg L^{-1}	Alkalinity meq L^{-1}	SRP mg L^{-1}	Nitrite mg L^{-1}	Nitrate mg L^{-1}	Ammonium mg L^{-1}	Calcium mg L^{-1}	Chloride mg L^{-1}
January '18	Inflow (Aue creek)	3.8	7.7	11	4.48	0.220	0.069	17.163	0.177	122.0	28.3
	Lake (W, pier)	3.2	7.9	12.2	3.72	0.105	0.040	5.618	0.101	102.2	26.7
	Lake (E, outflow)	3.2	7.9	13.5	3.76	0.103	0.040	5.105	0.140	102.2	26.7
February '18	Inflow (Aue creek)	3.1	7.2	12.16	3.98	0.135	0.041	19.673	0.062	132.3	32.2
	Lake (W, pier)	2.5	8.1	12.95	4.06	0.055	0.074	6.493	0.012	111.8	29.3
	Lake (E, outflow)	2.6	8.0	12.89	3.90	0.056	0.039	6.692	0.013	112.1	29.5
March '18	Inflow (Aue creek)	7.7	7.7	10.08	4.06	0.124	0.093	21.551	0.096	109.8	39.4
	Lake (W, pier)	6.4	7.9	12.08	3.90	0.015	0.026	8.244	0.042	102.9	35.0
	Lake (E, outflow)	5.8	8.2	12.05	3.92	0.007	0.026	6.975	0.044	102.5	35.2
April '18	Inflow (Aue creek)	13.3	8.4	14.1	4.20	0.149	0.157	15.754	0.052	114.9	32.1
	Lake (W, pier)	12.7	8.2	10.97	4.04	0.017	0.052	5.318	0.052	108.9	31.5
	Lake (E, outflow)	13.9	8.2	11.07	3.98	0.036	0.058	5.463	0.063	107.9	31.9
May '18	Inflow (Aue creek)	15.6	8.0	8.13	4.30	0.241	0.482	17.785	0.207	123.6	31.1
	Lake (W, pier)	18.5	8.4	12.2	3.94	0.017	0.079	2.010	0.055	99.5	33.8
	Lake (E, outflow)	18.7	8.4	13.17	3.82	0.011	0.062	1.608	0.071	105.2	33.4
June '18	Inflow (Aue creek)	17.8	8.3	9.19	4.00	0.267	0.255	17.139	0.038	120.6	28.0
	Lake (W, pier)	25.6	8.6	11.66	3.38	0.042	0.008	0.025	0.020	93.0	32.5
	Lake (E, outflow)	26.0	8.6	11.83	3.28	0.052	0.008	0.029	0.015	90.7	32.6
July '18	Inflow (Aue creek)	14.5	8.2	8.81	3.66	0.214	0.112	17.765	0.054	112.7	28.0
	Lake (W, pier)	22.2	8.8	14.15	2.78	0.045	0.007	0.024	0.022	75.0	32.9
	Lake (E, outflow)	20.9	8.7	12.51	2.74	0.024	0.016	0.028	0.022	79.0	32.9
August '18	Inflow (Aue creek)	18.9	8.1	7.61	3.96	0.306	0.078	18.640	0.020	118.8	27.6
	Lake (W, pier)	25.9	8.8	11.4	1.74	0.206	0.014	0.043	0.021	54.6	33.7
	Lake (E, outflow)	25.2	8.8	11.7	1.40	0.099	0.012	0.047	0.028	46.6	34.0
September '18	Inflow (Aue creek)	14.3	8.1	8.38	3.88	0.199	0.044	19.504	0.023	127.4	27.0
	Lake (W, pier)	19.2	9.3	12.69	2.64	0.618	0.031	0.062	0.017	71.6	34.3
	Lake (E, outflow)	18.4	9.0	7.75	2.70	0.667	0.012	0.037	0.017	70.1	34.4
October '18	Inflow (Aue creek)	9.8	8.2	10.06	3.94	0.150	0.089	19.366	0.033	127.1	27.0
	Lake (W, pier)	13.7	9.0	10.5	3.08	0.681	0.033	0.342	0.029	76.3	33.8
	Lake (E, outflow)	13.3	8.7	8.4	3.06	0.687	0.038	0.314	0.023	68.8	33.9
November '18	Inflow (Aue creek)	9.7	8.1	9.06	4.20	0.156	0.098	19.657	0.014	126.1	26.9
	Lake (W, pier)	9.0	8.0	6.3	3.10	0.408	0.038	0.696	0.319	84.6	32.9
	Lake (E, outflow)	9.3	7.9	4.53	3.22	0.414	0.050	0.711	0.356	86.3	32.9
December '18	Inflow (Aue creek)	5.3	8.0	10.58	3.30	0.333	0.056	14.812	0.026	111.7	30.6
	Lake (W, pier)	5.1	8.5	11.6	3.22	0.341	0.047	2.274	0.329	90.0	31.5
	Lake (E, outflow)	4.9	8.5	12.01	3.20	0.323	0.064	2.523	0.251	91.8	32.1

Tab. B2 (continued). Compilation of the data obtained at the sampling positions in 2019.

Date	Location	Temperature °C	pH	Oxygen mg L^{-1}	Alkalinity meq L^{-1}	SRP mg L^{-1}	Nitrite mg L^{-1}	Nitrate mg L^{-1}	Ammonium mg L^{-1}	Calcium mg L^{-1}	Chloride mg L^{-1}
January '19	Inflow (Aue creek)	6.0	8.1	10.42	4.02	0.224	0.059	20.357	0.039	134.2	38.4
	Lake (W, pier)	4.2	8.5	12.33	3.42	0.210	0.039	5.410	0.141	97.1	31.3
	Lake (E, outflow)	4.2	8.8	12.95	3.38	0.208	0.041	4.894	0.108	98.6	32.7
February '19	Inflow (Aue creek)	4.2	7.7	11.87	3.64	0.174	0.046	21.396	0.017	119.6	42.5
	Lake (W, pier)	3.7	8.1	12.71	3.08	0.073	0.023	4.078	0.015	101.4	33.5
	Lake (E, outflow)	3.8	8.2	13.87	3.20	0.057	0.022	6.271	0.012	101.9	34.8
March '19	Inflow (Aue creek)	8.6	7.6	11.53	3.96	0.156	0.068	16.471	0.071	118.7	29.6
	Lake (W, pier)	7.3	8.5	12.55	3.22	0.015	0.032	4.312	0.022	102.6	33.6
	Lake (E, outflow)	7.7	8.5	12.58	3.14	0.025	0.030	4.427	0.032	103.4	33.9
April '19	Inflow (Aue creek)	8.8	8.2	13.43	4.18	0.132	0.055	15.887	0.023	115.1	30.1
	Lake (W, pier)	10.4	8.4	11.67	3.26	0.020	0.028	2.059	0.031	99.9	32.4
	Lake (E, outflow)	11.0	8.4	12.38	3.20	0.017	0.028	2.031	0.050	98.1	33.5
May '19	Inflow (Aue creek)	9.8	8.3	11.58	3.72	0.175	0.063	15.666	0.027	113.9	28.3
	Lake (W, pier)	13.7	8.4	9.93	2.84	0.043	0.026	0.897	0.016	101.0	32.6
	Lake (E, outflow)	13.8	8.5	11.91	3.10	0.025	0.025	0.777	0.035	100.0	32.7
June '19	Inflow (Aue creek)	18.3	8.0	6.42	3.26	0.340	0.381	9.339	0.249	93.7	22.0
	Lake (W, pier)	25.6	8.9	9.64	3.08	0.034	0.004	0.041	0.038	97.7	30.8
	Lake (E, outflow)	25.3	8.8	8.96	2.98	0.039	0.007	0.060	0.058	98.2	30.9
July '19	Inflow (Aue creek)	17.0	7.8	6.36	4.12	0.499	0.422	8.253	0.101	116.0	21.0
	Lake (W, pier)	24.7	8.3	8.07	3.62	0.191	0.013	0.004	0.023	95.7	23.6
	Lake (E, outflow)	23.1	8.2	7.32	3.54	0.181	0.009	0.000	0.025	95.1	23.1
August '19	Inflow (Aue creek)	18.1	7.9	6.54	3.80	0.415	0.080	12.048	0.042	122.7	26.4
	Lake (W, pier)	24.0	8.5	6.85	3.52	0.427	0.015	0.073	0.115	97.7	30.7
	Lake (E, outflow)	24.9	8.6	7.39	3.42	0.329	0.014	0.000	0.024	96.7	30.9
September '19	Inflow (Aue creek)	18.6	8.0	7.06	4.04	0.307	0.025	13.567	0.031	123.4	26.1
	Lake (W, pier)	24.4	8.9	11.4	3.56	0.354	0.017	0.000	0.027	97.6	31.3
	Lake (E, outflow)	23.6	8.7	8.72	3.62	0.373	0.020	0.001	0.031	98.8	31.1
October '19	Inflow (Aue creek)	13.1	8.1	8.28	4.20	0.242	0.025	12.815	0.030	119.6	24.6
	Lake (W, pier)	15.5	8.9	11.25	2.82	0.130	0.027	0.006	0.022	79.3	30.7
	Lake (E, outflow)	15.5	9.0	12.26	2.82	0.084	0.025	0.003	0.034	76.9	30.8
November '19	Inflow (Aue creek)	10.3	7.9	9.41	4.32	0.204	0.060	14.517	0.029	126.0	25.9
	Lake (W, pier)	9.9	8.7	10.30	2.90	0.145	0.016	0.108	0.015	81.2	29.9
	Lake (E, outflow)	10.4	8.7	10.56	2.80	0.137	0.017	0.063	0.017	80.3	30.1
December '19	Inflow (Aue creek)	6.5	7.9	10.54	4.50	0.163	0.059	8.585	0.056	128.0	21.8
	Lake (W, pier)	4.5	8.3	11.60	3.28	0.251	0.029	0.004	0.220	85.0	24.6
	Lake (E, outflow)	4.4	8.2	11.38	3.10	0.250	0.034	0.000	0.209	86.2	24.0

Tab B3. Lake inflow between April 2018 and December 2019.

Date	Waterflow $L\ s^{-1}$
April '18	225
May '18	157
June '18	136
July '18	115
August '18	99
September '18	95
October '18	84
November '18	97
December '18	195
January '19	223
February '19	315
March '19	148
April '19	124
May '19	117
June '19	146
July '19	98
August '19	87
September '19	72
October '19	117
November '19	92
December '19	116

Tab. B4: Soluble reactive phosphate (SRP) concentrations in the pore water of the lake sediment in 2018.

Date	SRP $mg\ L^{-1}$
January '18	1.677
February '18	0.614
March '18	0.003
April '18	0.359
May '18	12.303
June '18	3.441
July '18	3.232
August '18	7.767
September '18	34.369
October '18	0.579
November '18	1.468
December '18	0.398

Tab. B5: Quality classification for nutrients according to the "Bund/Länder-Arbeitsgemeinschaft Wasser" (LAWA), (abbreviated from https://www.nlwkn.niedersachsen.de/download/92683, last accessed 12.05.2021, according to Grage et al., 2014).

Nutrient	Quality class						
[mg/L]	I	I-II	II	II-III	III	III-IV	IV
NO_3^--N	≤ 1	≤ 1.5	≤ 2.5	≤ 5	≤ 10	≤ 20	> 20
NO_2^--N	≤ 0.01	≤ 0.05	≤ 0.1	≤ 0.2	≤ 0.4	≤ 0.8	> 0.8
NH_4^+-N	≤ 0.04	≤ 0.1	≤ 0.3	≤ 0.6	≤ 1.2	≤ 2.4	> 2.4
PO_4^{3-}	≤ 0.05	≤ 0.08	≤ 0.15	≤ 0.3	≤ 0.6	≤ 1.2	> 1.2
PO_4^{3-}-P	≤ 0.02	≤ 0.04	≤ 0.1	≤ 0.2	≤ 0.4	≤ 0.8	> 0.8

Nitrate:

- inflow: III-IV
- lake: II (mean), III (max)

Ammonium:

- inflow: II (mean 2017), I-II (mean 2018/2019), III (max)
- lake: II (mean 2017), I-II (mean 2018/2019))

Nitrite:

- inflow: II-III (mean), III (max 2017), III-IV (max 2018/2019)
- lake: I-II

Soluble reactive phosphate (SRP)

- inflow: II-III (mean), IV (max 2017), III (max 2018/2019)
- lake: II-III (mean), III-IV (max 2017/2018), III (max 2019)

Tab. B6: Calculations of soluble reactive phosphate (SRP) in- and outputs and dissolutions from the sediment.

	Water volume in- and outflow [L/s]	SRP conc. (inflow) [mg/L]	SRP conc. (outflow) [mg/L]	Inflow [kg/day]	Outflow [kg/day]	Difference [kg/day]	Redissolution from sediment [g/m²day][2)]	Redissolution from sediment [kg/day] [2)]
July 2017 [1)]	550	1.355	0.249	64.3	11.8	52.6		
January 2018		0.220	0.103				0.0032	2.85
February 2018		0.135	0.056				0.0011	0.98
March 2018		0.124	0.007				-0.000016	-0.014
April 2018	225	0.149	0.036	2.9	0.7	2.2	0.00068	0.61
May 2018	157	0.241	0.011	3.3	0.1	3.1	0.025	22.25
June 2018	136	0.267	0.052	3.1	0.6	2.5	0.007	6.23
July 2018	115	0.214	0.024	2.1	0.2	1.9	0.0065	5.785
August 2018	99	0.306	0.099	2.6	0.8	1.8	0.0155	13.8
September 2018	95	0.199	0.667	1.6	5.5	-3.8	0.069	61.4
October 2018	84	0.15	0.687	1.1	5.0	-3.9	-0.0002	-0.178
November 2018	97	0.156	0.414	1.3	3.5	-2.2	0.002	1.78
December 2018	195	0.333	0.323	5.6	5.4	0.2	0.0003	0.267
January 2019	223	0.224	0.208	4.3	4.0	0.3		
February 201	315	0.174	0.057	4.7	1.6	3.2		
March 2019	148	0.156	0.025	2.0	0.3	1.7		
April 2019	124	0.132	0.017	1.4	0.2	1.2		
May 2019	117	0.175	0.025	1.8	0.3	1.5		
June 2019	146	0.34	0.039	4.3	0.5	3.8		
July 2019	98	0.499	0.181	4.2	1.5	2.7		
August 2019	87	0.415	0.329	3.1	2.5	0.6		
September 2019	72	0.307	0.373	1.9	2.3	-0.4		
October 2019	117	0.242	0.084	2.4	0.8	1.6		
November 2019	92	0.204	0.137	1.6	1.1	0.5		
December 2019	116	0.163	0.250	1.6	2.5	-0.9		

[1)] The maximum flow through a weir (550 L/s) downstream of the Seeanger wetland was consistently reached during the heavy rain event.
[2)] For calculation see table 7.

Tab. B7. Calculation of the amount of soluble reactive phosphate (SRP) released from the sediment into the pore water during the cyanobacterial bloom in 2018. Calculation according to Scholtysik et al., 2020.

$$J_P = \frac{\varphi}{\theta^2} * D_P * \frac{\Delta C_P}{\Delta z}$$

$$\Phi = \frac{\frac{\omega}{\rho(\text{water})}}{\frac{\omega}{\rho(\text{water})} + \frac{1-\omega}{\rho(\text{sediment})}} = \frac{\frac{0.7}{1}}{\frac{0.7}{1} + \frac{1-0.7}{2.43}} = 0.85$$

$$\rho(\text{sediment}) = \frac{1}{\frac{LOI}{\rho(\text{org})} + \frac{1-LOI}{\rho(\text{min})}} = \frac{1}{\frac{0.10}{1.4} + \frac{1-0.1}{2.65}}\ g\ cm^{-3} = 2.43\ g\ cm^{-3}$$

$$\theta = \sqrt{1 - ln\Phi^2} = \sqrt{1 - \ln(0.84)^2} = 0.98$$

$$J_P = \frac{\varphi}{\theta^2} * D_P * \frac{\Delta C_P}{\Delta z} = \frac{0.84}{0.98^2} * 4.7 * 10^{-5} * \frac{34.4 - 0.69}{0.02} g\ m^{-2}\ day^{-1} = 0.069\ g\ m^{-2}\ day^{-1} = 61.4\ kg\ day^{-1} in\ the\ hole\ lake$$

where:

- J_P is the diffusion rate of P (g m^{-2} day^{-1})
- ϕ is the porosity
- ρ is the density [g cm^{-3}]
- θ is the tortuosity
- D_P is the molar diffusion coefficient of Phosphate in the sediment (5.5 *10^{-6} cm^2 s^{-1} or 4.7 *10^{-5} m^2 s^{-1})*

Appendix C

Supplementary information for Section 4:

Qualitative reconstruction of eutrophication at a shallow eutrophic lake using sedimentary stenols and their degradation products

Tab. C1. Compilation of the biomarker data obtained in the inflow.

Concentration [µg/gC_{org}]	Inflow											
0: < limit of detection	09.05.2019	10.06.2019	19.06.2019	02.07.2019	15.07.2019	30.07.2019	12.08.2019	30.08.2019	09.09.2019	12.09.2019	04.11.2019	09.12.2019
n-C_{17}	0	0	3	3	6	3	2	7	19	20	5	11
n-C_{23}	0	11	3	0	3	4	2	3	3	0	0	1
n-C_{27}	0	22	23	15	21	35	29	26	32	29	13	10
n-C_{29}	0	15	18	14	24	36	27	28	36	30	0	10
n-C_{31}	0	0	3	0	0	3	4	5	9	3	0	0
HBI 1 (C25:2)	0	0	0	0	0	0	0	0	0	0	0	0
HBI 2 (C25:2)	0	0	0	0	0	0	0	0	0	0	0	0
Σ Phytadienes	10	7	27	7	25	14	19	20	27	32	32	10
Tetrahymanol	0	0	0	0	0	0	0	0	0	0	0	0
Hop(17,21)en	0	0	0	0	0	0	0	0	0	0	0	0
27^{0}	0	19	21	0	0	0	0	0	0	0	0	0
27^{5}	352	348	195	26	114	34	106	12	57	76	186	191
$27^{5,22}$	0	0	0	0	0	0	0	0	0	0	0	0
28^{0}	0	0	0	0	0	0	0	3	0	0	0	0
28^{5}	16	30	23	0	0	0	22	0	0	0	0	0
$28^{5,22}$	0	17	13	0	0	0	10	0	0	0	0	0
29^{0}	0	0	7	0	12	0	8	2	0	0	0	0
29^{5}	147	315	167	29	130	49	136	11	110	117	306	181
$29^{5,22}$	36	52	23	17	29	2	10	1	0	0	0	0
i-15:0	51	99	105	63	77	97	100	67	70	69	213	69
ai-15:0	34	63	85	52	84	73	79	57	65	69	213	61
16:0	762	590	762	341	1755	553	924	623	651	785	1836	584
18:2n6c	34	35	45	37	184	82	129	81	89	121	240	84
18:3n3c	0	0	0	26	215	44	64	57	75	112	186	76
18:1ω9c	84	120	130	73	636	136	200	171	150	216	373	153
20:4n6c	59	0	0	16	23	15	21	14	19	17	80	15
20:5n3c	17	0	0	10	15	15	21	14	19	17	27	8
20:0	0	35	45	26	77	58	64	52	61	69	80	61
22:0	0	85	85	63	123	111	114	95	112	121	293	107
24:0	0	77	85	58	115	111	107	90	108	112	53	107

Tab. C2. Compilation of the biomarker data obtained in the lake (I/II).

Concentration [µg/gC_{org}]	Lake											
0: < limit of detection	09.05.2019	10.06.2019	19.06.2019	02.07.2019	15.07.2019	30.07.2019	12.08.2019	30.08.2019	09.09.2019	12.09.2019	01.10.2019	09.12.2019
n-C_{17}	29	21	28	17	44	32	42	20	14	32	11	67
n-C_{23}	23	10	11	5	7	4	0	2	3	2	1	6
n-C_{27}	0	0	0	7	16	0	0	0	0	3	1	0
n-C_{29}	0	0	0	0	0	0	0	0	0	0	0	0
n-C_{31}	0	0	0	0	0	0	0	0	0	0	0	0
HBI 1 (C25:2)	0	0	0	0	0	0	0	1	3	7	6	0
HBI 2 (C25:2)	8	0	0	4	5	9	0	0	0	0	0	0
Σ Phytadienes	241	105	219	248	411	150	259	137	264	330	175	108
Tetrahymanol	0	0	0	0	0	0	0	0	0	0	0	0
Hop(17,21)en	0	0	0	0	0	0	0	0	0	0	0	0
27^{0}	0	30	0	42	12	0	19	59	75	97	29	12
27^{5}	393	258	131	471	127	2501	141	217	255	378	284	469
$27^{5,22}$	59	58	17	6	9	35	12	9	16	22	110	27
28^{0}	0	0	0	18	0	0	0	11	20	15	25	21
28^{5}	56	71	66	40	30	109	47	59	40	46	237	31
$28^{5,22}$	182	114	128	39	9	46	78	21	17	22	56	62
29^{0}	0	0	0	0	0	0	0	3	8	13	0	0
29^{5}	135	246	75	58	70	82	75	54	33	39	189	45
$29^{5,22}$	44	39	54	11	6	16	37	38	16	27	99	0
i-15:0	303	257	403	252	98	238	180	201	90	73	158	160
ai-15:0	70	86	91	92	84	98	63	39	18	21	58	80
16:0	3794	2153	5102	5411	2816	3067	4689	10332	5404	6281	3666	2145
18:2n6c	415	183	412	483	438	296	545	826	414	373	265	256
18:3n3c	1807	606	2202	2752	2197	2112	3133	4682	2429	2406	1050	1001
18:1ω7c	904	303	1101	1375	1099	1056	1567	2341	1214	1203	524	501
20:4n6c	680	600	277	717	303	621	454	753	607	668	1439	538
20:5n3c	37	80	30	189	39	191	86	141	53	55	94	48
20:0	0	11	17	33	20	23	27	41	14	16	20	32
22:0	51	34	35	53	66	43	54	57	16	11	22	75
24:0	61	17	35	95	102	62	81	64	28	29	32	117

Tab. C2 (continued). Compilation of the biomarker data obtained in the lake (II/II).

Concentration [µg/gC_{org}]	Lake												
0: < limit of detection	09.05.2019	10.06.2019	19.06.2019	02.07.2019	15.07.2019	30.07.2019	12.08.2019	30.08.2019	09.09.2019	12.09.2019	01.10.2019	04.11.2019	09.12.2019
n-C_{17}	0	44	58	49	75	5	40	114	359	374	22	126	172
n-C_{23}	15	0	0	2	2	0	3	0	0	0	0	0	0
n-C_{27}	0	0	0	3	0	0	0	0	0	0	0	0	0
n-C_{29}	0	0	0	0	0	0	0	0	0	0	0	0	0
n-C_{31}	0	0	0	0	0	0	0	0	0	0	0	0	0
HBI 1 (C25:2)	0	0	0	0	0	0	0	0	0	0	12	0	0
HBI 2 (C25:2)	0	0	0	0	0	0	0	0	0	0	0	0	0
Σ Phytadienes	424	156	283	285	540	147	274	227	469	348	293	331	508
Tetrahymanol	0	0	0	0	0	0	0	0	0	0	0	0	0
Hop(17,21)en	0	0	0	0	0	0	0	0	0	0	0	0	0
27^{0}	9	23	29	27	4	16	36	27	6	17	19	0	0
27^{5}	617	220	219	239	113	186	127	172	56	180	182	172	333
$27^{5,22}$	62	48	24	2	4	8	5	5	5	22	67	110	11
28^{0}	0	0	0	0	0	0	0	34	0	0	15	0	0
28^{5}	94	35	49	72	42	57	49	55	21	48	197	88	42
$28^{5,22}$	261	82	158	54	18	120	59	24	5	15	1	92	54
29^{0}	0	0	0	0	0	0	0	0	0	0	0	0	0
29^{5}	178	146	84	127	93	91	78	60	23	55	146	98	61
$29^{5,22}$	74	116	27	22	0	38	0	29	12	17	8	23	0
i-15:0	256	216	435	191	108	56	167	123	45	40	83	83	140
ai-15:0	85	94	88	60	59	22	63	32	4	6	28	53	70
16:0	2997	2018	3338	4263	4316	1016	4499	4556	5178	4982	2849	2134	1829
18:2n6c	356	122	277	508	610	103	529	548	991	903	241	307	219
18:3n3c	1180	442	1509	2792	3730	621	3041	2279	4138	3089	902	1378	1075
18:1ω7c	590	221	752	1396	1866	310	1520	1139	2069	1544	451	690	533
20:4n6c	704	456	330	302	238	103	543	477	184	433	1732	1041	376
20:5n3c	50	52	40	181	35	12	69	85	27	49	66	44	35
20:0	14	9	22	53	41	9	31	27	15	12	11	12	35
22:0	57	28	44	68	79	34	59	55	8	9	10	18	79
24:0	71	28	44	119	110	64	81	68	9	22	17	39	166

Tab. C3. Compilation of the biomarker data obtained in the surface sediment (I/II).

Concentration [µg/gC_{org}]	Sediment										
0: < limit of detection	12.08.2019	12.08.2019	12.09.2019	12.09.2019	12.09.2019	12.09.2019	01.10.2019	01.10.2019	01.10.2019	01.10.2019	09.12.2019
n-C_{17}	14	4	6	24	8	1	6	18	4	1	0
n-C_{23}	25	7	6	17	5	2	7	18	2	1	1
n-C_{27}	148	57	39	125	129	45	42	205	35	10	11
n-C_{29}	154	56	37	122	237	73	50	189	35	9	12
n-C_{31}	27	11	6	19	22	9	8	24	3	5	4
HBI 1 (C25:2)	22	6	6	15	1	0	7	12	0	0	0
HBI 2 (C25:2)	50	12	14	35	4	0	14	37	2	1	0
Σ Phytadienes	302	101	104	274	129	35	80	224	40	11	7
Tetrahymanol	9	2	4	8	2	0	3	10	0	1	1
Hop(17,21)en	38	14	39	23	21	46	14	24	12	9	8
27^{0}	790	253	297	435	17	28	257	646	37	45	12
27^{5}	1012	250	277	461	68	106	193	655	50	51	0
$27^{5,22}$	55	13	13	26	164	244	6	34	195	209	2
28^{0}	437	172	182	432	11	18	124	320	16	27	17
28^{5}	385	82	128	352	29	42	74	263	31	36	12
$28^{5,22}$	445	130	148	243	18	28	87	267	18	21	9
29^{0}	634	241	220	342	176	224	200	482	86	160	44
29^{5}	1508	575	502	773	388	528	410	1137	174	310	89
$29^{5,22}$	314	93	112	181	17	24	74	223	16	20	11
i-15:0	176	102	172	127	107	146	70	151	78	71	23
ai-15:0	244	158	253	186	107	139	98	213	74	76	32
16:0	1243	950	2079	1439	1091	1678	693	1625	620	480	260
18:2n6c	263	161	248	227	344	266	113	186	73	56	38
18:3n3c	0	0	0	0	0	0	0	0	0	0	0
18:1ω7c	543	252	610	536	529	594	217	509	199	155	66
20:4n6c	166	156	146	155	84	63	21	43	31	25	3
20:5n3c	202	164	179	208	234	171	40	92	25	17	5
20:0	155	122	139	114	310	382	76	163	281	209	96
22:0	301	200	223	175	318	360	128	259	174	156	185
24:0	442	340	359	283	472	554	175	374	293	247	210

Tab. C3 (continued). Compilation of the biomarker data obtained in the surface sediment (II/II).

Concentration [µg/gC_{org}]	Sediment										
0: < limit of detection	09.12.2019	09.12.2019	09.12.2019	11.02.2020	11.02.2020	11.02.2020	11.02.2020	22.06.2020	22.06.2020	22.06.2020	20.06.2020
n-C_{17}	15	1	1	11	8	0	0	3	11	1	2
n-C_{23}	6	2	1	8	7	1	1	4	20	0	1
n-C_{27}	40	50	19	55	61	2	1	65	153	3	5
n-C_{29}	54	57	22	60	80	0	1	76	174	3	6
n-C_{31}	11	5	7	12	11	0	0	9	27	0	1
HBI 1 (C25:2)	3	0	1	5	4	0	0	1	8	1	0
HBI 2 (C25:2)	11	1	0	13	12	0	0	3	12	0	1
Σ Phytadienes	134	21	17	180	115	12	1	56	206	45	37
Tetrahymanol	1	1	1	1	0	0	0	1	11	0	1
Hop(17,21)en	20	11	7	37	20	19	20	30	28	36	9
27^{0}	187	61	22	191	101	10	49	76	450	24	50
27^{5}	244	139	35	299	120	104	62	126	667	256	66
$27^{5,22}$	18	959	160	29	8	32	110	12	62	6	0
28^{0}	98	46	13	100	66	55	191	57	349	18	31
28^{5}	158	76	20	197	77	81	194	82	369	53	55
$28^{5,22}$	81	33	12	121	53	0	0	62	287	36	24
29^{0}	170	677	134	196	110	247	799	213	978	177	372
29^{5}	401	977	223	623	299	474	1385	659	2310	260	300
$29^{5,22}$	83	35	15	86	46	54	184	60	254	0	20
i-15:0	99	64	37	144	116	73	55	108	135	119	71
ai-15:0	144	84	49	181	176	47	66	142	171	94	63
16:0	1745	573	293	2550	1556	1164	708	2081	1590	2059	1038
18:2n6c	87	142	41	137	116	26	40	208	181	277	238
18:3n3c	0	0	0	0	0	0	0	0	0	0	0
18:1ω7c	397	243	98	515	337	113	188	517	430	867	375
20:4n6c	28	33	17	31	32	0	0	31	38	21	23
20:5n3c	62	31	9	104	53	0	0	55	77	31	25
20:0	1896	199	208	197	156	509	949	284	233	78	100
22:0	169	194	124	259	211	315	343	374	306	137	109
24:0	226	215	129	331	282	305	556	401	336	14	129

Tab. C4. Compilation of the biomarker data from the sediment cores. Core 1 was sampled at the bathing pier, core 2 at northern part of the lake.

Biomarker	Depth [cm], core 1										
[peak area]	0-3	3-6	6-9	9-12	12-15	15-18	18-21	21-24	24-27	27-30	30-33
27^{0}	6033	7329	7264	4021	2032	1191	800	773	771	979	741
27^{5}	8438	7878	7386	3632	2426	1399	984	997	1242	1530	960
$27^{5,22}$	961	938	906	469	218	133	72	100	91	90	93
28^{0}	2354	2438	2730	1508	1178	685	522	492	481	847	554
28^{5}	3308	4195	3606	1864	1319	778	551	548	525	889	547
$28^{5,22}$	3600	3600	3500	1616	956	501	313	318	316	351	278
29^{0}	3042	3674	3899	2278	2040	1522	1097	1265	1248	1764	1698
29^{5}	5632	6162	6482	3280	2822	1766	1325	1373	1519	2381	2281
$29^{5,22}$	2800	3600	2739	1700	950	520	369	340	480	478	374

Biomarker	Depth [cm], core 2											
[peak area]	0-2.5	2.5-6.5	6.5-11	11-15	15-20	20-25	25-30.5	30.5-34.5	34.5-38.5	38.5-42.5	42.5-46.5	46.5-51.5
27^{0}	3410	8873	6480	1813	768	185	161	102	76	53	221	163
27^{5}	4795	12568	9005	1467	732	258	151	98	65	33	199	141
$27^{5,22}$	612	132	922	178	90	0	0	0	0	0	0	0
28^{5}	3800	7143	2892	927	702	159	123	140	141	20	337	326
$28^{5,22}$	5633	15029	12087	2157	1001	270	60	0	0	0	0	0
29^{0}	5778	10665	13164	6152	4387	1381	1212	1337	1085	416	2179	2529
29^{5}	10977	17914	20093	6121	3984	1072	949	1211	1136	278	2582	3219
$29^{5,22}$	4647	13047	10850	2549	1558	267	138	137	170	60	484	387

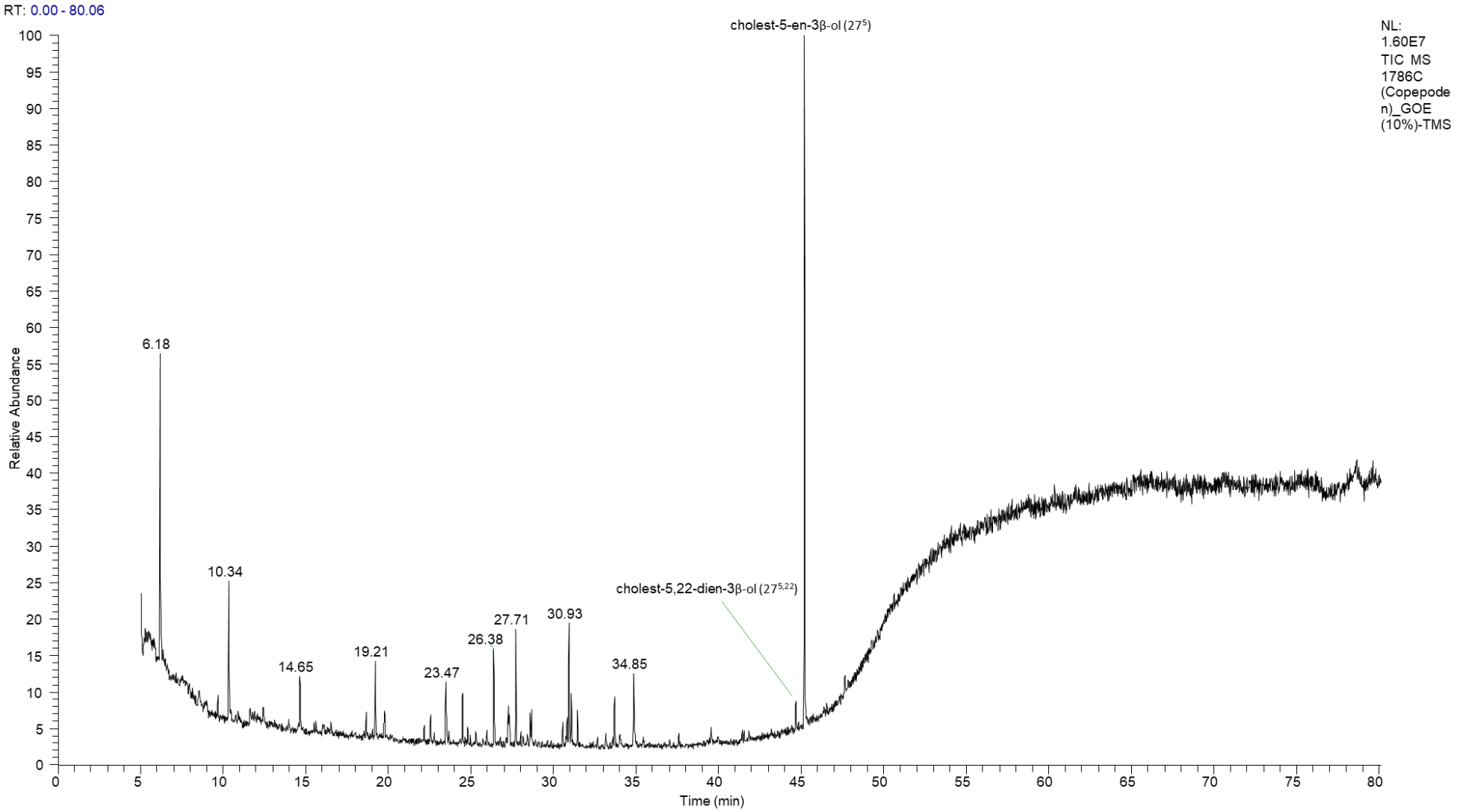

Fig. C1. GC-MS chromatogram of arthropods (daphnia) at Lake Seeburg.

Scientific curriculum vitae

Personal data

Name: Sebastian Zeman-Kuhnert

Date of birth: 08.04.1992

Place of birth: Nürnberg

Education

Oct. 2018 - present	**PhD Geoscience** (Georg-August-University Göttingen, Geowissenschaftliches Zentrum, Abteilung Geobiologie) Thesis title: "Use of selected anthropogenic pesticides, nutrients, and biomarkers to spatially and temporally characterize eutrophication dynamics at a shallow lake (Lake Seeburg)" Supervisors: Prof. Dr. Volker Thiel, Prof. Dr. Christine Heim, PD Dr. Michael Hoppert
Oct.2015 - Sept. 2018	**MSc Geoscience** (Georg-August-University Göttingen) Thesis title: "Verwendung der nicht-relevanten Metaboliten des Herbizids Chloridazon als Prozessindikator in der aquatischen Umwelt"
Oct. 2012 – Sept. 2015	**BSc Geoscience** (Georg-August-University Göttingen)
May 2011	**Abitur** (Clavius-Gymnasium Bamberg)

Conference participation

Talk on "Goldschmidt 2021": Zeman-Kuhnert S., Thiel V., Heim C. (2021). Quantitativ remediation study to avoid orthophosphate dynamics between sediment and water column at a shallow eutrophic lake. DOI: https://doi.org/10.7185/gold2021.5752

Publications

Warner, W., Zeman-Kuhnert, S., Heim, C., Nachtigall, S., Licha, T., 2021. Seasonal and spatial dynamics of selected pesticides and nutrients in a small lake catchment - implications for agile monitoring strategies. Chemosphere 281, 130736. https://doi:10.1016/j.chemosphere.2021.130736.

Zeman-Kuhnert, S.; Thiel, V.; Heim, C., 2022. Effects of weather extremes on the nutrient dynamics of a shallow eutrophic lake as observed during a three-year monitoring study. Water 14, 2032. https://doi.org/10.3390/w14132032.

Zeman-Kuhnert, S.; Heim, C.; Thiel, V., (manuscript in preparation). Qualitative reconstruction of eutrophication at a shallow eutrophic lake using sedimentary stenols and their degradation products. To be submitted to “Organic Geochemistry”.

Field trips

09.06.2014 - 15.06.2014	Italienische Westalpen (Ivrea Zone)
26.07.2014 - 02.08.2014	Hallig Hooge
18.08.2014 - 27.08.2014	Südost-Schweden
13.02.2015 - 26.02.2015	Oman
24.04.2015 - 26.04.2015	Tschechien (Egerrift)
18.07.2015 - 25.07.2015	Süddeutschland
02.03.2016 - 15.03.2016	Mexiko
15.08.2017 - 29.08.2017	Albanien

Mappings

24.03.2014 - 04.04.2014	Grundlagenkartierung im Hildesheimer Wald
15.03.2016 - 15.04.2016	Freiwilliges Masterkartierprojekt in Uruguay (30 Geländetage)