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Research article

Impact of copper sulphate treatment on cyanobacterial blooms and subsequent water quality risks

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ABSTRACT

Control of algal blooms and associated biologically-induced water quality risks in drinking reservoirs is problematic. Copper sulphate ($CuSO_4$) treatment is one intervention that has been utilised for >100 years. Evidence indicates a favourable short-term reduction in Cyanobacterial biomass (e.g. bloom termination), but here we indicate that it may also increase longer-term water quality risk. In 2022, we investigated the impacts of $CuSO_4$ spraying on Cyanobacterial communities and nutrient levels within a drinking water supply reservoir using environmental DNA (eDNA) to assess community shifts, alongside monitoring nutrient fractions, orthophosphate (OP) and total phosphate (TP), post-treatment. $CuSO_4$ application successfully reduced Cyanobacterial abundance, however elimination of Cyanobacteria resulted in a shift in bacterial dominance favouring Planctomycetota throughout the summer and a combination of Actinobacteriota and Verrucomicrobiota, throughout autumn. As Cyanobacterial abundance recovered post-treatment, Cyanobacterial genera demonstrated greater diversity compared to only three Cyanobacterial genera present across samples pre-treatment, and included taxa associated with water quality risk (e.g. taste and odour (T&O) metabolite and toxin producers). The increase in Cyanobacteria post-treatment was attributed to an increase in biologically available nutrients, primarily a significant increase in OP. Overall, findings suggest that the significant shift in biodiversity likely induces a less stable ecosystem with greater plasticity of response to changing environmental and biogeochemical variables. Legacy implications of $CuSO_4$ spraying, in terms of shifts in ecosystem and nutrient balance over time, may have implications for drinking water quality, but importantly also for reservoir management options. As such, the effects of $CuSO_4$ spraying should be considered carefully before consideration as a contender for in-reservoir biological control.

1. Introduction

Harmful algal blooms (HABs) are a frequent issue in drinking water reservoir management. The control of biomass, which can result in filter blocking or treatment breakthrough, can be a significant problem for water companies. Additionally, the taxa associated with these blooms are often those responsible for water quality risks, such as toxins and taste and odour (T&O) metabolite production. Cyanobacteria, a bacterial phylum considered to be the main producer of volatile T&O compounds in freshwater environments (Suurnäkki et al., 2015), are a predominant cause of water quality and treatment risk in drinking water supply reservoirs. For many consumers, T&O is one means of assessing the safety of their drinking water (Kehoe et al., 2015; McGuire, 1995), hence it's common for water companies to experience customer complaints related to T&O (Webber et al., 2015). Despite there being no risk to human health from ingestion of the two major T&O-causing compounds, geosmin (trans-1,10-dimethyl-trans-9 decalol-$C_{12}H_{22}O$) and MIB (2-methyl isoborneol-$C_{11}H_{20}O$) (Dionigi et al., 1993; Martins et al., 2021; Pirbazari et al., 1993), water companies are under increasing pressure to address these complaints. Treatment breakthrough and customer complaints relating to T&O events in drinking water induce considerable cost to water companies, an issue which is likely to increase in the future due to increased temperature and other climatic variables as the result of climate change, as well as synergy with increased

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nutrient supply from agricultural sources (Davis et al., 2009; Taranu et al., 2015; Zhang et al., 2017). Reduced summer rainfall and increased average temperature favours the development of warm, shallow reservoirs that promote Cyanobacteria abundance (Hooper et al., 2023; Winston et al., 2014). The presence of natural organic matter (i.e. organic compounds derived from plant and animal decay) is innately present in all water sources but additional loading of nutrients, for example ammonium and inorganic phosphorous from agricultural practices and fertilizer run-off, can exacerbate T&O issues (Perkins et al., 2019). Furthermore, extreme weather events, in particular excessive summer rainfall and storm events, directly enhance run-off, leading to unpredictable pulses of T&O metabolites and increased pressure on water companies to instigate treatment.

A number of different treatment methods are currently utilised within the water industry as a means of minimising the impact of HABs and T&O events, for example coagulation, sedimentation, filtration, chlorination, activated carbon or oxidation such as ozone (Bruce et al., 2002; Srinivasan and Sorial, 2011). An in-reservoir intervention method that is also utilised (where there is a permitted license to do so) is the application of copper sulphate treatment to the reservoir surface. Chemical treatments have been widely utilised over the past century to control phytoplankton and Cyanobacterial blooms in reservoirs (Haughey et al., 2000). Copper sulphate inhibits electron transport and modifies vital enzymatic activities becoming toxic to phytoplankton and Cyanobacterial communities (Pinto et al., 2003). However, the broad-spectrum toxicity of copper sulphate may lead to unwanted additional effects regarding community structure and ecosystem functioning of affected environments (Le Jeune et al., 2006). As an oxidizing agent, copper sulphate is corrosive to mucous membranes, resulting in cell damage and ultimately cell death (Saravu et al., 2007), meaning it has the potential to affect an array of non-target species simultaneously. For example, copper sulphate has been linked to detrimental health defects and mortality in freshwater snails and fish (Kamble and Kamble, 2014; Kirici et al., 2017; Otludil and Ayaz, 2020; Singh et al., 2008). However, the same toxicity renders copper sulphate treatment a common and seemingly effective method in reducing Cyanobacterial and algal biomass in freshwater reservoirs.

A number of previous studies have investigated the impact of copper sulphate treatment on Cyanobacterial and algal communities (Albay et al., 2009; García-Villada et al., 2004; Le Jeune et al., 2006; Liu et al., 2023). Previously, copper sulphate treatment has been linked to a considerable shift in reservoir water quality and a decrease in *Microcystis aeruginosa* biomass (Albay et al., 2009; Liu et al., 2023; Wu et al., 2017), alongside a decrease in total phosphorous (TP) (Albay et al., 2009). Hanson and Stefan (1984) reported that although the application of copper sulphate to shallow lakes successfully eradicated target problem algae, the decomposition of those dead algae led to the depletion of dissolved oxygen within the system as well as the death of fish and macroinvertebrates. Large-scale die off across any taxa, whether higher taxonomic species like fish or simply the target algae, can lead to an influx of nutrients, such as phosphorous, from decaying matter in to the water column (Paytan and McLaughlin, 2007; White et al., 2008). Bacterial and algal communities are then supplied with the necessary nutrient availability to persist or recover, potentially extending or exasperating T&O event duration. In excess, phosphorous further precipitates and binds to reservoir sediments, increasing the potential for internal loading in the future and therefore establishing a less predictable environment in which to manage bloom events (Dittrich et al., 2013; Søndergaard et al., 2003). Hanson and Stefan (1984) found that algal populations not only recovered again within 21 days of the copper sulphate application but that certain species of algae became more tolerant of high copper sulphate dosages. Current literature suggests that although there are short-term gains to copper sulphate application, by means of eradication of problem taxa, there may be long-term or accumulative effects of copper sulphate spraying to consider. One of the benefits of copper sulphate is that it does not last long in solution but instead precipitates as particulate forms – this can, however, lead to significant accumulation of copper within sediments (Gunnarsdóttir et al., 2013; Han et al., 2001; Hanson and Stefan, 1984) which can potentially persist in bioavailable forms (Han et al., 2001).

Water industry continues to monitor and assess the effectiveness of their treatment regimes as a means of safeguarding drinking water supplies and reservoir health. Most previous studies to investigate the impacts of copper sulphate treatment on freshwater communities have used methods such as cell counts and microscopy to categorise changes in abundance, and molecular methods are not currently commonly utilised by water industry within the British Isles for quality monitoring. However, amplicon-targeted sequencing provides a far more accurate alternative for capturing the total diversity (and therefore shifts in diversity) of freshwater systems. Due to its rapid, high-throughput approach, amplicon sequencing has become an integral and widely utilised method for inferring the presence of taxonomic groups (Lundberg et al., 2013).

In this study, we used an amplicon-targeted sequencing approach to assess the diversity and abundance of Cyanobacterial communities before and after a single copper sulphate treatment event in a drinking water supply reservoir in 2022. Further, we investigated associated shifts in levels of dissolved organic nutrients orthophosphate (OP) and total phosphate (TP) in both the water column and the reservoir sediments, before and following copper sulphate treatment as a means of investigating the conversion of fractions and associated release of bioavailable phosphate.

2. Materials and methods

2.1. Sample collection

A total of 41 eDNA samples were collected from three different sampling locations in a British Isles drinking water supply reservoir between June 2022 and February 2023. Using a Smith-Root Citizen Science eDNA Sampler (Smith-Root, Inc.©, USA), 500 mL of reservoir water was filtered across a 0.45 μm self-preserving flat filter (Thomas et al., 2019), which, in accordance with manufacturer instructions, were then preserved via desiccation and stored inside their sampler casing at room temperature until later use at Cardiff University (Thomas et al., 2019). Samples did not require storage longer than two weeks prior to processing despite being viable for up to six months according to Smith-Root recommendations. A paired 500 mL water sample was additionally collected from each sampling site and refrigerated at 4 °C for water chemistry analysis. Samples were collected pre- and post-copper sulphate treatment, which was applied to the reservoir surface once a day between 6th July and July 8, 2022, at a dosage of 0.6 g/m^2.

Additionally, sediment samples (1 kg each) were collected from the same reservoir in May 2023 using a UWITEC sediment corer. Sediment samples were stored at 4 °C while in transit, whereby a sub-sample of 2–20 g was shipped to Cardiff University and stored at −20 °C until analysis, and the remaining sample volume was shipped to Envirolab (Hattersley, UK).

2.2. DNA extraction, amplification and sequencing

Methods for DNA extraction and sequencing are outlined in Watson et al. (2024). In brief, one half of each filter was stored in a 50 mL falcon tube for later use and the other half was cut into small pieces and transferred to a sterile 15 mL falcon tube. ATL Buffer (Qiagen, UK) and Proteinase K were added to each sample, before being subjected to a vigorous free-thaw process and subsequent bead beating and lysis. The remaining DNA extraction steps followed those outlined in the DNeasy Blood and Tissue Kit Protocol for Purification of Total DNA from Animal Blood or Cells (Spin-Column Protocol) (Qiagen; following manufacturer instructions), starting from Step 4. Extraction controls were run alongside each extraction set.

Targeted amplification of the 16 S rRNA gene was conducted using the bacteria-specific primer set; 515 F (forward) 5′-GTGCCAGCMGCCGCGGTAA -3′ and 806 R (reverse) 5′- GGACTACHVGGGTWTCTAAT -3′, on an Applied Biosystems SimpliAmp thermocycler and the following steps; 95 °C for 2 min (one cycle), 95 °C for 5 s, 55 °C for 15 s, 72 °C for 10 s (30 cycles), 72 °C for 5 min (one cycle). Amplification was conducted in triplicate and included a negative PCR control. Amplified products were pooled and purified using a Zymo Research DNA Clean-up Kit™. Illumina® Nextera XT indices (Illumina®) were incorporated via a secondary PCR using the following steps; 95 °C for 3 min (one cycle), 95 °C for 30 s, 55 °C for 30 s, 72 °C for 30 s (8 cycles), 72 °C for 5 min (one cycle). Samples were normalised to equimolar concentrations using a SequalPrep™ Normalization Plate Kit (Invitrogen, USA) and sequenced on a Illumina® MiSeq (2 × 300 bp reads) at Cardiff School of Biosciences Genome Research Hub.

2.3. Bioinformatic analysis of sequencing data

Bioinformatic pipelines follow methods outlined in Watson et al. (2024) and were conducted using QIIME2 2021.8 (Bolyen et al., 2018) supported by the High Performance Computer facilities provided by the Cardiff School of Biosciences Biocompute Research Hub. The data presented in this study are available on request from the corresponding author. The raw sequencing data can be found at the National Centre for Biotechnology Information (NCBI) Sequence Read Archive (SRA) [Accession number: PRJNA1044064].

2.4. Statistical analysis of sequencing data

All analyses were carried out using R statistical software package, (version 4.2.2) (R Core Team, 2022). The package ‘Phyloseq’ (McMurdie and Holmes, 2013) was used to combine the taxonomy, abundance and metadata into an R object. Singletons were removed along with any samples containing less than 2000 reads, in accordance with rarefaction plots. Samples were rarefied to an equal depth within 90% of the minimum observed sample size (specifically 2145 reads per sample). After filtering, a total of 60,088 reads remained across the samples, constituting 3398 different taxa.

2.5. Water chemistry analysis

Water chemistry analysis was conducted on 75 samples provided by the water industry partner involved in this study, as well as from samples belonging to three other anonymous UK water partners (sample collection and analysis were identical across partners and are used here to provide a comparison in baseline nutrient levels). Water samples were stored at 4 °C while being transferred to Cardiff University for analysis. Dissolved inorganic nutrients (orthophosphate (OP) and total phosphorus (TP)) within water samples were determined using colorimetric methods (Rice et al., 2012).

2.6. Sediment analysis

Iron content analysis was performed by Envirolab using ICP-OES. Extraction of iron-bound (Fe–P), calcium-bound (Ca–P) and labile phosphorous fractions were conducted at Cardiff University in May 2023. Sediment samples were thawed at 4 °C in the dark overnight and homogenised prior to analysis. Triplicate 0.5–2 g subsamples of each sediment were dried at 85 °C for 24 h and water content was determined as mass lost as a percentage of the initial weight. Sediment was then incubated with 0.1 M sodium hydroxide, 0.5 M hydrochloric acid, or 1 M ammonium chloride respectively (Perkins and Underwood, 2001). Samples were mixed with 20 mL of extractant and incubated at room temperature, with slight agitation. Fe–P samples were incubated with hydrochloric acid for 24 h, Ca–P samples were incubated for 17 h with sodium hydroxide. Labile phosphate was extracted with ammonium chloride, incubating for 2 h. At the end of the incubation, the sodium hydroxide samples were neutralised with 4 mL 0.5 M hydrochloric acid and the hydrochloric acid samples were neutralised with 3 mL of 3 M sodium hydroxide. Samples were then centrifuged for 10 min at 4000 rpm.

The supernatant was analysed for orthophosphate (OP) using the ascorbic acid method (Rice et al., 2012), adapted to a 96-well plate and read using a BMG SPECTROstar NANO plate reader. A neutralised blank of each of the incubation solutions was used to prepare the standards (with KH2PO4) and dilute samples where required. Each sample was analysed with these methods three times. The amount of phosphate per dry sediment (mg P-PO4/g sediment) was calculated for each individual analysis.

Phosphate Absorption Capacity (PAC) was assessed by incubating sediment samples exposed to a range of phosphate concentrations and determining the amount absorbed at equilibrium (Perkins and Underwood, 2001). Wet sediment equivalent to a known dry weight of 0.1–0.2 g dry weight was weighed into five 50 mL plastic centrifuge tubes. Phosphate (KH_2PO_4) solutions of 0, 0.05, 0.5, 1 and 5 mg/L P-PO_4 were prepared and 20 mL of each of the concentrations was added to a tube. Tubes were agitated and incubated over the course of 24 h. At 1, 2, 4, 6, and 24 h, the samples were mixed by inversion and a 1 mL aliquot was taken. The aliquots were centrifuged for 10 min at 4000 rpm and then analysed for OP (see above), using phosphate standards prepared with KH_2PO_4 in ultrapure water for the calibration curve.

The Equilibrium Phosphorous Capacity (EPC) is calculated by plotting the final phosphate concentration, mg/L P-PO_4 (C) and the amount of phosphate absorbed per gram of dry sediment at equilibrium, mg/g P-PO_4 (E). The logarithmic trend was calculated in R (R Core Team, 2023). The standard error for the EPC was calculated by adding the standard errors from the output to the above equation for c and m and determining the difference between the two. Data were fitted to the Freundlich equations. The Freundlich equation expresses the rate and capacity of the absorption.

3. Results

3.1. Shifts in community structure and diversity

In June 2022, pre-copper sulphate treatment, 11 different phyla of bacteria were detected within water samples, with the dominant phylum being Cyanobacteria (present at a total abundance of 9129 reads across the two sampling dates) (Fig. 1a). During this time, the predominant genera contributing to Cyanobacteria abundance were; *Aphanizomenon* sp. (read abundance: 6881) and *Microcystis* sp. (read abundance: 2231), with only one other genus present but at a much lower read abundance (*Cyanobium* sp. - read abundance: 4) (Fig. 1b and 2). Samples taken on the July 12, 2022, post-copper sulphate treatment, showed a decrease in the abundance of Cyanobacteria with a total of just 589 reads, with this reduction persisting with a total of just 36 reads in September 2022 (Fig. 2). As the abundance of Cyanobacteria decreased, an increase in the abundance of the phyla Planctomycetota was seen during this time, again up until the end of September 2022. The predominant genera contributing to the abundance of *Planctomycetota* were; *Roseimaritima* sp. (13,787 reads), an uncultured sp. (3735 reads) and *Pirellula* sp. (3290 reads); the other 17 genera present made up a total of 2025 reads combined (ranging from 541 reads to 1 read). Between the end of September and the end of October 2022, another shift in phyla dominance was detected whereby a decrease in the abundance of Planctomycetota (to just 187 reads) was replaced by an increased abundance of the phylum Actinobacteriota (4657 reads) and, to a lesser extent, Verrucomicrobiota (3643 reads) (Fig. 1a). After this time, between mid-November and January, the Shannon diversity within water samples increased from between 2.3 and 4.8 (mean: 3.8, SD: 0.69) to between 4.3 and 5.5 (mean: 5.1, SD = 0.32) (Fig. 3). This change in diversity can also

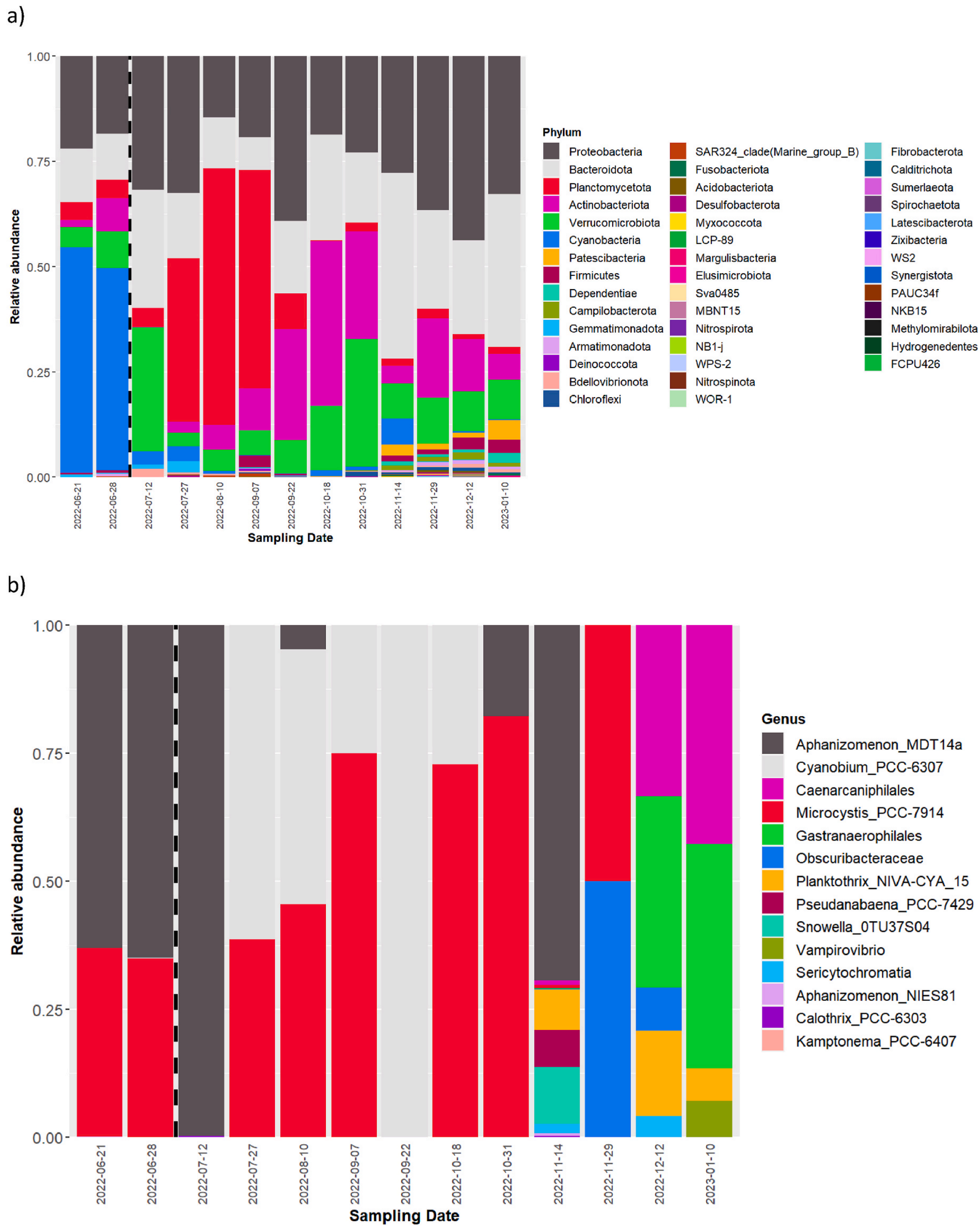

Fig. 1. 1a. Stacked bar chart of the relative abundance of bacterial phyla present in water samples taken between June 2022 and January 2023. Dashed black line marks the point at which copper sulphate treatment was applied. **1b.** Stacked bar chart of the relative abundance of genera belonging to the phyla Cyanobacteria detected within water samples taken between June 2022 and January 2023. Dashed black line marks the point at which copper sulphate treatment was applied.

be seen within the Cyanobacteria present: the number of Cyanobacterial genera increased from a maximum of four genera between June and October 2022, to 11 genera between November 2022 and January 2023 (Fig. 1b and 3). A number of these detected genera are known T&O producers, including *Aphanizomenon, Microcystis, Planktothrix* and *Pseudoanabaena,* and notably also cyanotoxin producers, alongside *Snowella*. The diversity and abundance of these Cyanobacterial genera fluctuated between the bi-monthly sampling dates (Fig. 1b).

3.2. Shifts in water chemistry

Phosphorous fraction analysis demonstrates that OP levels prior to copper sulphate application ranged from 178 μg/L to 252 μg/L (Mean: 213.7 μg/L, SD: 23 μg/L) and that OP as a percentage of TP ranged from 17 to 37% (Mean: 26.8%, SD: 6%). After copper sulphate application OP levels increased to between 228 μg/L and 673 μg/L (Mean: 425.6, SD: 160 μg/L) between July and the end of August 2022, with OP as a

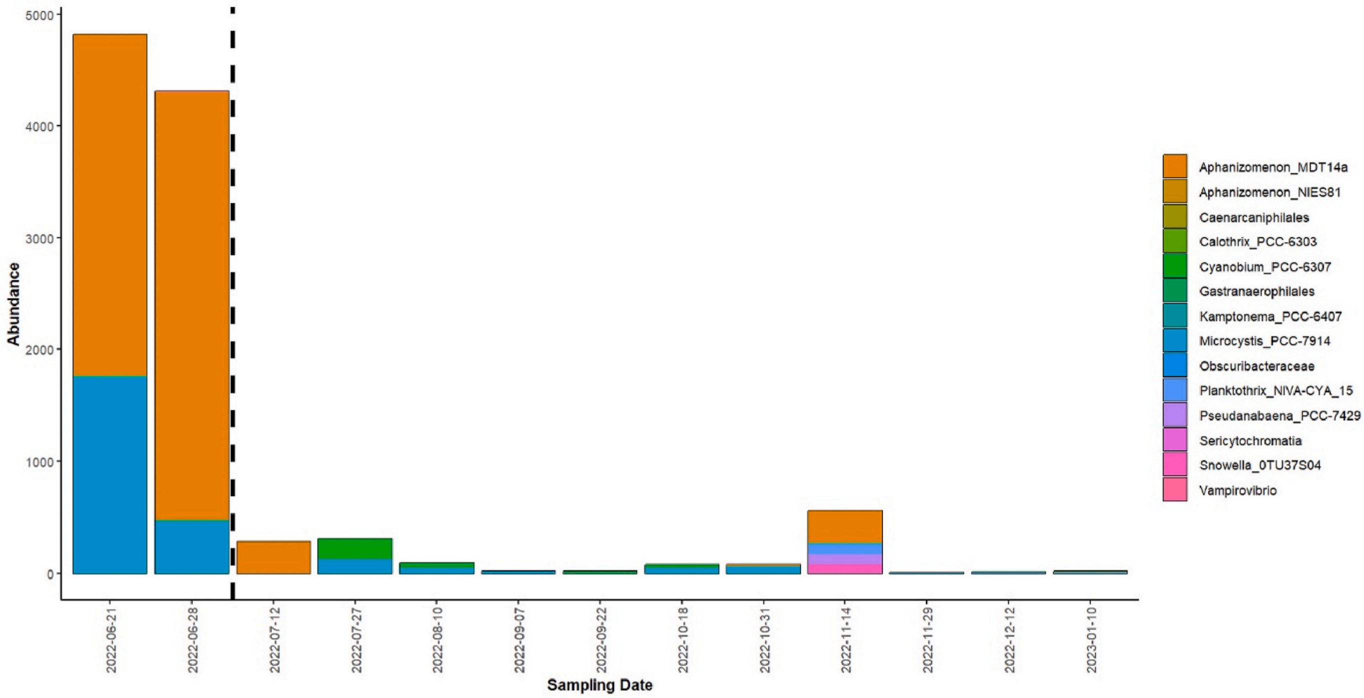

Fig. 2. Stacked barchart showing the absolute read abundance of Cyanobacteria (plotted at genus level) within water samples taken between June 2022 and January 2023. Dashed black line marks the point at which copper sulphate treatment was applied.

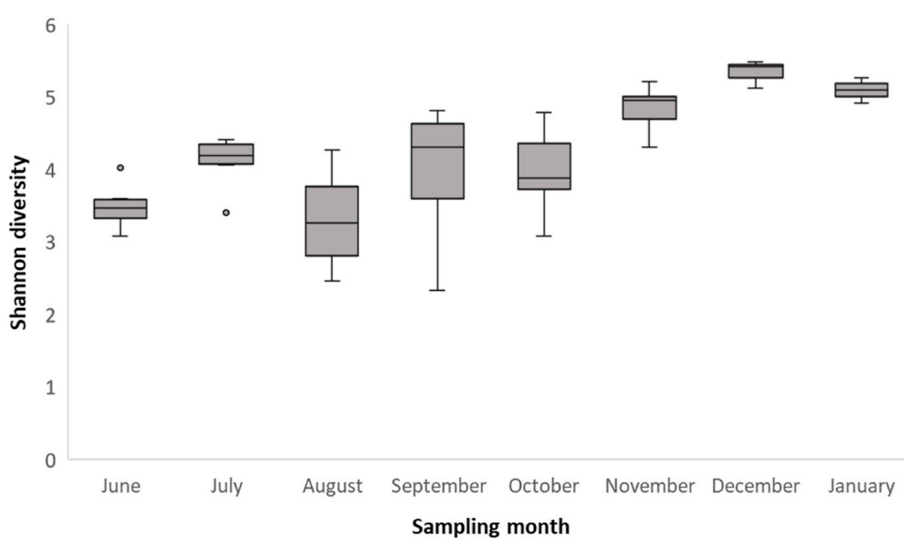

Fig. 3. Shannon diversity within water samples taken between June 2022 and January 2023.

percentage of TP also increasing within this time (range: 27%–90%, Mean: 41.5%, SD: 20%) (Fig. 4a and b). After this time, OP levels (OP as a percentage of TP) persisted at high levels for another two months before gradually decreasing throughout November and December 2022. Compared with baseline data for three other anonymous water companies, OP levels greatly exceeded levels detected in other water partners across the entire sampling period (Fig. 5).

3.3. *Internal loading of nutrients from sediment*

All three sites on the reservoir demonstrated low levels of labile-P (0.01–0.09 mg/g) but had moderate or high levels of Ca–P; 1.49–2.17 mg/g for site B and 0.24–0.32 mg/g for site C. Site A demonstrated high levels of Fe–P (1.59–1.76 mg/g), whilst sites B and C had moderate levels of Fe–P (0.20–0.77 mg/g) (Table 1; Fig. 6). These data indicate a significant storage of P within this reservoir.

The sediment samples demonstrated an Equilibrium Phosphorous Capacity (EPC) of 0.44 mg/L (Freundlich, $E = 0.03C^{0.99}$, $r^2 = 0.67$), with OP levels within the reservoir remaining below the EPC for most of the survey period (Supplementary Figs. 1a and 1b). The only time in which OP exceeded the EPC of 0.44 mg/L was August to October 2022, following copper sulphate treatment (Fig. 7). These data indicate that for the majority of the time, apart from at times of treatment, internal loading of P from the sediment is likely as the overlying water phosphate concentration is below the EPC.

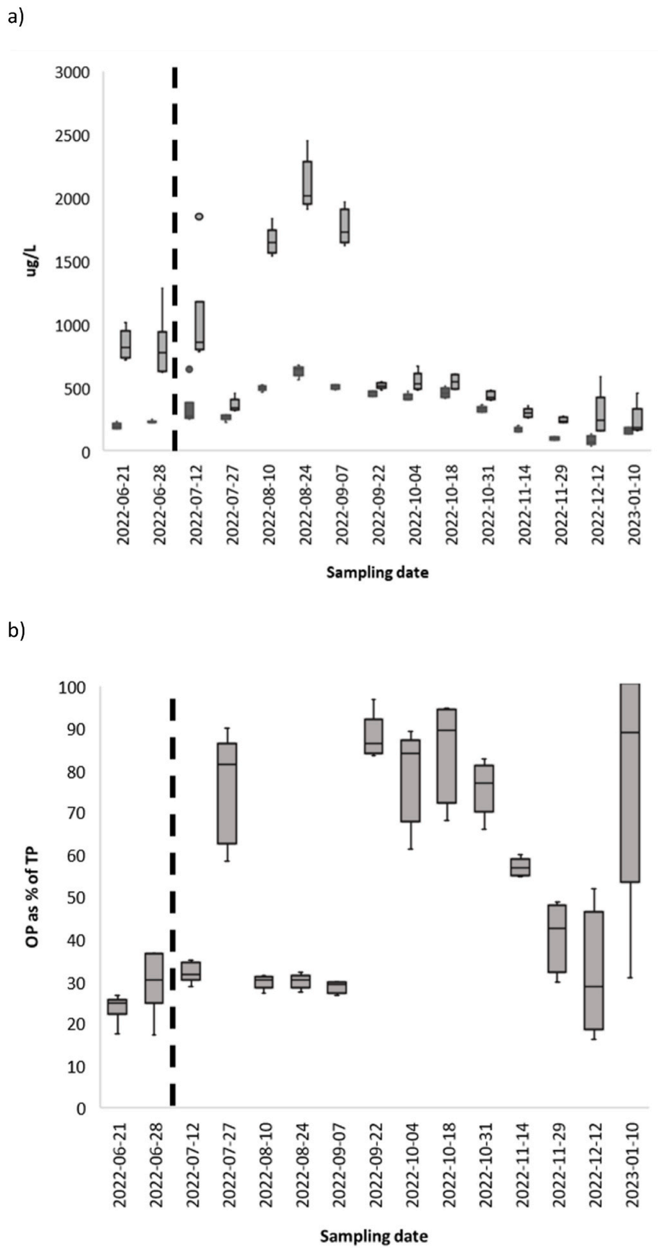

Fig. 4. Box and whisker plots demonstrating levels of a) OP (dark grey) and TP (light grey) and b) OP as a percentage of TP, within water samples taken between June 2022 and January 2023. Dashed black line marks the point at which copper sulphate treatment was applied.

4. Discussion

4.1. Summary of findings

This work is novel in that it uses the established methodology of eDNA community analysis to determine unforeseen impacts of a widely used treatment for algal bloom management and highlights the currently unforseen circumstances of copper sulphate use in terms of legacy nutrients and risk of internal loading. The finding that such management approaches may result in an enhanced ability of Cyanobacteria to induce future water quality risks is novel and of high importance for lake and reservoir managers. Here, we demonstrate that the application of copper sulphate to reservoir water is effective in reducing Cyanobacterial abundance in the short-term but may potentially exacerbate factors which may contribute to T&O events in the future. As such, continual monitoring of potential knock-on effects of copper sulphate treatment is encouraged. After copper sulphate treatment, we detected a fundamental shift in the phyla and genera dominating the water samples, as well as a significant shift in the diversity of bacteria present. Elimination of Cyanobacteria resulted in a shift in bacterial dominance favouring Planctomycetota throughout the summer and a combination of Actinobacteriota and, to a lesser extent, Verrucomicrobiota, throughout the autumn months. As Cyanobacterial abundance started to recover again, the returning genera present were far more diverse when compared to a maximum of just three Cyanobacterial genera present across samples pre-treatment – an increased diversity that persisted for 6-months post-treatment. The increased bacterial diversity observed constituted a number of known T&O producers, including *Aphanizomenon, Microcystis, Planktothrix* and *Pseudoanabaena,* and notably during this time, an increase in cyanotoxin producers *Planktothrix NIVA-CYA-15* and *Snowella* were also detected. Additionally, following the initial eradication of Cyanobacteria, subsequent shifts in OP and OP as a fraction of TP were detected in the water column. Additionally, sediment analysis indicated a significant likelihood for internal loading of phosphorus from the sediment, either by diffusiuon or redox mediated release. Overall the phosphorus data for the water column and sediment would indicate an abundant source for algae and Cyanobacteria. It is suggested that the increased range of Cyanobacterial taxa, and the presence of taxa associated with water quality risks, provides a greater plasticity in response to future environmental and biogeochemical variables, hence increasing the range and potentially the magnitude of risk of events such as T&O or toxin producing HABs.

4.2. Community analysis implications

Dramatic shifts in diversity can be a signature of instability within an ecosystem (Pennekamp et al., 2018). Essentially, in the absence of dominance in the community, there is little control to suppress the growth of potential problem taxa. During a time when nutrient shifts are volatile, it becomes difficult to predict which taxa may be selected for, creating an unpredictable environment for water quality management to navigate. Although after copper sulphate application a decrease in *Aphanizominon* (a key T&O metabolite producer) was observed, there was a rapid establishment of a diverse consortium of other T&O producers (*Aphanizomenon, Microcystis, Planktothrix* and *Pseudoanabaena*; Huang et al., 2018; Watson, 2003; Wonorowski, 1992), as well as potential toxin producers (e.g. *Planktothrix* and *Snowella*; Echenique et al., 2014; Pancrace et al., 2017; Watson, 2003). The observed shift from Cyanobacteria to Planctomycetota and Actinobacteriota is notable; Planctomycetota is a phylum that plays a critical role in nitrogen cycling and is associated with harmful algal blooms (Mosley et al., 2022; Suarez et al., 2023), while Actinobacteriota plays an important role in nutrient recycling and include a large portion of taxa that are also known T&O producers (Liu et al., 2023; Zhang et al., 2023). The increased abundance of Verrucomicrobiota is also noteworthy. Verrucomicrobiota specialise in consuming microalgal sugars and their abundance has been coupled with the onset of algal blooms (Cardman et al., 2014; Martinez-Garcia et al., 2012; Orellana et al., 2022; Sichert et al., 2020). This "cocktail" of taxa therefore provides the ideal starting point for a range of water quality risks if environmental variables are favourable, and/or nutrient availability increases (including OP and OP as a fraction of TP, see below). For example, it is important to recognise that there may be an increase in the diversity of species able to respond to T&O event triggers, as well as a range of other water quality risks. Under the right conditions (e.g. elevated temperature, nutrient pulses etc., see Hooper et al., 2023; Perkins et al., 2019), this high diversity of species is positioned opportunistically, ready to exploit whichever conditions favour their requirements. What we now understand from recent literature, is that T&O events are not necessarily biomass-related but rather are linked to a quick succession (or perfect storm) of triggers (Chong et al.,

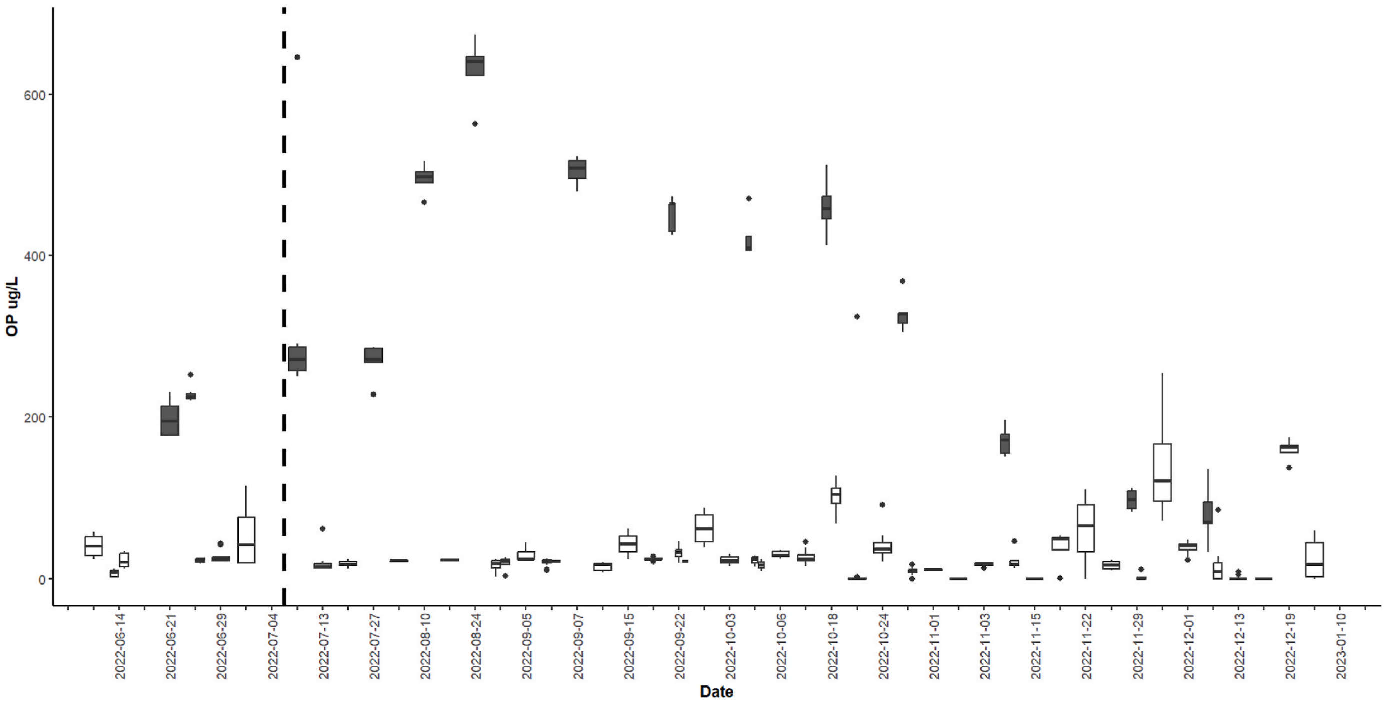

Fig. 5. Orthophophate (OP) measurements from samples provided by the water partner involved in this current study utilising copper sulphate treatment (grey), as well as from samples belonging to three other anonymous UK water partners during the same sampling period, using the same sampling and analysis methods, who do not utilise copper sulphate treatment (unfilled). Dashed black line marks the point at which copper sulphate treatment was applied.

Table 1
Average, minimum and maximum calcium (Ca) bound, Iron (Fe) bound and labile phosphorous in sediment samples taken from three sites along a British Isles drinking reservoir.

Site	Ca bound (mg/g)			Fe/Al bound (mg/g)			Labile (mg/g)		
	Average	Min	Max	Average	Min	Max	Average	Min	Max
A	1.82	1.53	2.17	1.44	1.00	1.76	0.08	0.08	0.09
B	1.70	1.49	2.03	0.55	0.28	0.77	0.04	0.03	0.06
C	0.27	0.24	0.32	0.32	0.20	0.42	0.01	0.01	0.02

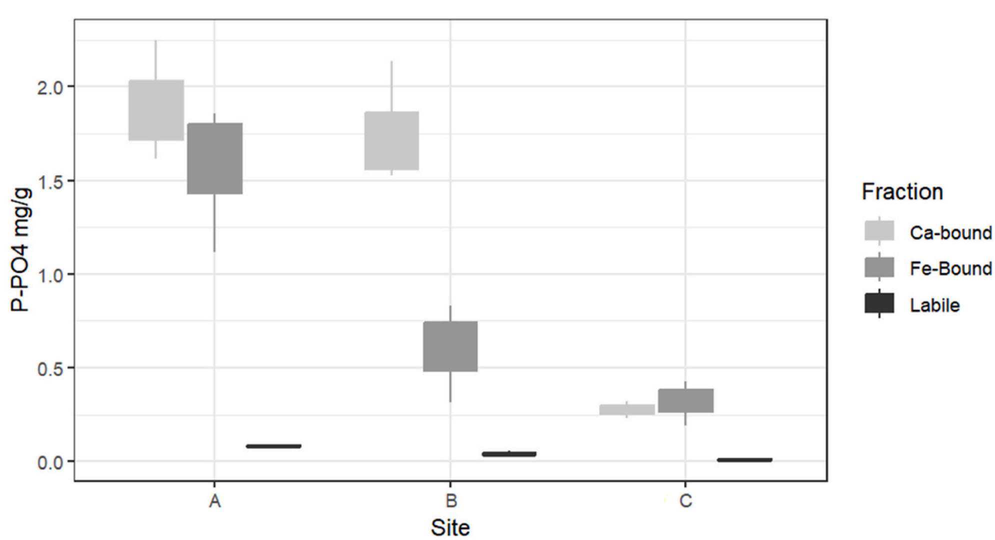

Fig. 6. Calcium (Ca), Iron (Fe) and labile bound phosphorous levels across three sites in a British Isles reservoir.

2018; Graham et al., 2010; Hooper et al., 2023; Perkins et al., 2019; Watson et al., 2008). Even low abundances can stimulate water quality risk events (Watson et al., 2008). Considering Water Companies in the UK and elsewhere now report T&O events often persist late into November–December (personal communication from >10 Water Companies), indicating T&O triggers are still at play during these months,

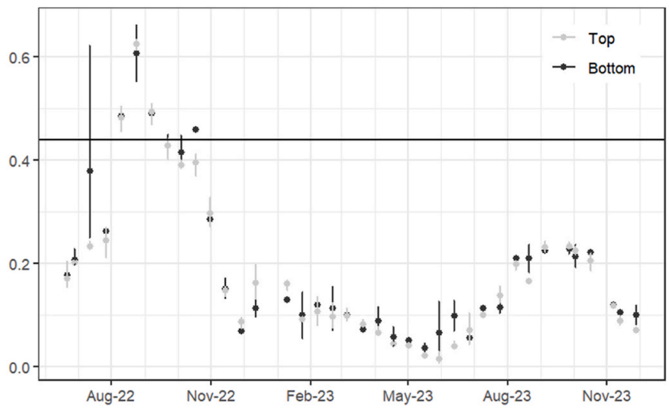

Fig. 7. Orthophosphate concentrations (mg/L) in water samples taken from the top of the water column versus the bottom. Equilibrium Phosphorous Capacity (EPC) is shown with a solid horizontal line.

the diversity shift reported here could increase the risk of a T&O event. It is worth noting that it is becoming increasingly recognised that algal blooms can also occur during low-temperature periods (Cen et al., 2020; Reinl et al., 2023). With a broader population biology perspective in mind, it is well understood that ecosystem function and resilience is dependent upon diversity, which we address within this study, and not a simplistic algal bloom biomass process. As such, what we present here is extremely significant in terms of implications for reservoir management.

It is important to note, however, that in some instances increased diversity is considered beneficial to ecosystem resilience. High bacterial richness and evenness can increase ecosystem stability where there is significant functional overlap between species (i.e. redundancy), meaning there is less impact from the loss of key species during times of perturbation or disturbance (Briones and Raskin, 2003). However, this trend is potentially absent where functional overlap is lacking, i.e. there are still not enough species present to support redundancy. Here, it appears that the species contributing to the increased diversity detected, consist of several potential problem taxa.

4.3. *Implications of nutrient levels and internal loading from sediment*

Alongside the reported shifts in diversity and changes in the abundance of potential problem taxa, changes in phosphorus availability (e.g. OP and OP as a fraction of TP) were observed within the water column and a high risk of internal loading of P was detected from reservoir sediment. The increase in OP as a fraction of TP, and the absolute increase in magnitude of P fractions, indicate an increase in bioavailable phosphate and therefore enhance the risk of enhancing productivity or potential storage of P within the reservoir sediment for future internal loading (Perkins and Underwood, 2001). It should be noted that T&O event risk has been linked with Cyanobacterial productivity rather than absolute biomass (Hooper et al., 2023; Perkins et al., 2019; Watson et al., 2008). Phosphate availability is a key factor associated with the proliferation of Cyanobacterial communities (Redfield, 1960), yet can be a limiting factor in freshwater owing to its low solubility and adsorption on to particulate matter. As well as acting as a sink, excessive phosphorus stored in freshwater sediments provides an internal loading source which, upon liberation into the water column, can prolong the eutrophic status of a lake and exacerbate phytoplankton communities further down the line (Perkins and Underwood, 2001; Wang et al., 2006; Wu et al., 2011; Zhu et al., 2013). The release of this phosphorus in to the water column is determined by a number of factors which are often beyond water management control, including temperature, redox condition, dissolved oxygen, pH, and hydraulic conditions of the given water body (Dittrich et al., 2013). Ultimately, copper sulphate spraying may have led to increased biological availability at a time when there was an increased range of problem Cyanobacterial taxa ready to respond, or may add to the internal storage of P and therefore an overabundance of legacy phosphate within the system.

5. Conclusions

Copper sulphate treatment has been used for more than a hundred years (Goudey, 1936) and is still utilised in a number of countries without a full appreciation of the long-term effects to drinking water supplies. By this, we mean an appreciation of legacy implications in terms of ecosystem change and shifts in nutrient balances over time which can have huge implications for drinking water quality, but importantly also for reservoir management options. Once these issues arise, controlling those nutrient shifts becomes very difficult and treatment options for water quality risks that take advantage of those conditions become limited. This is highly important to the water industry as a whole regarding long term changes of many intervention management solutions for water quality risks. We conclude that copper sulphate spraying is likely an efficient short-term treatment for the mitigation of (Harmful) Algal Blooms, but post-treatment there is likely an increase in phosphorus availability and at the same time, an increase in the range of problematic Cyanobacterial taxa in relation to water quality risk. Therefore, we propose that copper sulphate spraying has the potential to set in to motion a series of events that ultimately lead to a less predictable environment for water quality management to navigate. We further suggest that the longer-term effects of copper sulphate spraying should be considered carefully before the treatment is considered as a potential contender for not just HAB control, but also in prevention of T&O events. Copper sulphate application may not only potentially induce a more diverse community which may be responsive to T&O triggers but also may contribute to the accumulation and storage of bioavailable phosphate in reservoir sediments, which may enable T&O risk to persist subsequently, something which has not previously been considered with copper sulphate treatment. The finding that such management approaches may result in an enhanced ability of Cyanobacteria to induce future water quality risks is novel and of high importance for lake and reservoir managers.

CRediT authorship contribution statement

S.E. Watson: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **C.H. Taylor:** Writing – review & editing, Resources, Methodology. **V. Bell:** Writing – review & editing, Project administration, Methodology, Data curation. **T.R. Bellamy:** Writing – review & editing, Software. **A.S. Hooper:** Writing – review & editing. **H. Taylor:** Writing – review & editing, Project administration, Methodology, Data curation. **M. Jouault:** Writing – review & editing, Resources, Methodology. **P. Kille:** Writing – review & editing, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **R.G. Perkins:** Writing – review & editing, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2024.121828.

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