Water Research xxx (2015) 1–13

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

# Controlling cyanobacterial blooms through effective flocculation and sedimentation with combined use of flocculants and phosphorus adsorbing natural soil and modified clay

Natalia Pessoa Noyma [a, *], Leonardo de Magalhães [a], Luciana Lima Furtado [a], Maíra Mucci [b], Frank van Oosterhout [b], Vera L.M. Huszar [c], Marcelo Manzi Marinho [a], Miquel Lürling [b, d]

[a] Laboratory of Ecology and Physiology of Phytoplankton, Department of Plant Biology, University of Rio de Janeiro State, Rua São Francisco Xavier 524-PHLC Sala 511a, 20550-900, Rio de Janeiro, Brazil

[b] Aquatic Ecology & Water Quality Management Group, Department of Environmental Sciences, Wageningen University, P.O. Box 47, 6700 AA, Wageningen, The Netherlands

[c] Museu Nacional, Federal University of Rio de Janeiro, 20940-040, Rio de Janeiro, Brazil

[d] Department of Aquatic Ecology, Netherlands Institute of Ecology (NIOO-KNAW), P.O. Box 50, 6700 AB, Wageningen, The Netherlands

ARTICLE INFO

*Article history:*
Received 3 April 2015
Received in revised form
18 November 2015
Accepted 24 November 2015
Available online xxx

*Keywords:*
Cyanobacteria bloom
Eutrophication control
Geo-engineering in lakes
Lake restoration
Local red soil
Phosphorus mitigation

ABSTRACT

Eutrophication often results in blooms of toxic cyanobacteria that hamper the use of lakes and reservoirs. In this paper, we experimentally evaluated the efficacy of a metal salt (poly-aluminium chloride, PAC) and chitosan, alone and combined with different doses of the lanthanum modified bentonite Phoslock® (LMB) or local red soil (LRS) to sediment positively buoyant cyanobacteria from Funil Reservoir, Brazil, (22°30′S, 44°45′W). We also tested the effect of calcium peroxide ($CaO_2$) on suspended and settled cyanobacterial photosystem efficiency, and evaluated the soluble reactive P (SRP) adsorbing capacity of both LMB and LRS under oxic and anoxic conditions. Our data showed that buoyant cyanobacteria could be flocked and effectively precipitated using a combination of PAC or chitosan with LMB or LRS. The SRP sorption capacity of LMB was higher than that of LRS. The maximum P adsorption was lowered under anoxic conditions especially for LRS ballast. $CaO_2$ addition impaired photosystem efficiency at 1 mg $L^{-1}$ or higher and killed precipitated cyanobacteria at 4 mg $L^{-1}$ or higher. A drawback was that oxygen production from the peroxide gave positive buoyancy again to the settled flocs. Therefore, further experimentations with slow release pellets are recommended.



## 1. Introduction

Eutrophication is considered the most important water quality problem in freshwaters and coastal waters worldwide (Smith and Schindler, 2009). One of the key consequences of eutrophication is the occurrence of blooms of potentially toxic cyanobacteria that represent a serious threat to the environment and public health (Chorus et al., 2000). Thus, controlling eutrophication and mitigating cyanobacteria nuisance is considered a key challenge to water quality managers and a prerequisite to improve conditions such that ecosystem services are no longer hampered.

Phosphorous control is critical to mitigate eutrophication (Carpenter, 2008) and should focus on both, strong reduction of its external inputs as well as reduction of internal loading of P released from a sediment pool (Cooke et al., 2005; Mehner et al., 2008). The most straightforward action in tackling the internally stored P is the removal (dredging) of nutrient rich sediments, but targeting the sediment P-release with a P-fixative is a much cheaper option and dredging technique has not being always successful (Annadotter et al., 1999; Cooke et al., 2005). In addition to aluminium-, calcium- and iron salts (e.g. Cooke et al., 1993, 2005; Huser et al., 2015) more recently solid-phase P sorbents (SPB) have gained interest (Spears et al., 2013a). These are mainly clays enriched with aluminium (Al) (Gibbs et al., 2011), iron (Fe) (Zamparas et al., 2012) or lanthanum (La) (Haghseresht et al., 2009), but also industrial-

* Corresponding author. Laboratory of Ecology and Physiology of Phytoplankton, Department of Plant Biology, University of Rio de Janeiro State, Rua São Francisco Xavier 524-PHLC Sala 511a, CEP 20550-900, Rio de Janeiro, Brazil.
*E-mail address:* np.noyma@gmail.com (N.P. Noyma).

http://dx.doi.org/10.1016/j.watres.2015.11.057
0043-1354/© 2015 Published by Elsevier Ltd.

and building practices waste-products (Spears et al., 2013a) or soils such as natural red soil or enriched with La (Dai and Pan, 2014), that settle on the sediment where they act as active barrier.

These SPB's are expected to bind water column soluble reactive P (SRP) as well as reduce the SRP-efflux from sediments. However, during a bloom we can have concentrations of tens of thousands to millions of cells $mL^{-1}$, and P stored in cyanobacteria cells in the water column can go up to hundreds of $\mu g\ L^{-1}$, while water column SRP will be far below the level of detection. In this situation a SPB will have little to no effect on the P present in the water column, because they can neither bind particulate P, nor precipitate the cyanobacteria out of the water column (Lürling and van Oosterhout, 2013). A low ionic strength of fresh waters impairs clay flocculation of cyanobacteria (Han and Kim, 2001; Pan et al., 2006a). This implies that the application of a SPB will not remove an established bloom, which in turn may be a sufficient P reservoir to maintain high risk for ongoing cyanobacterial blooms.

As cyanobacterial blooms present a high risk to the uses of the infested waters, immediate reduction of the hazard is most desirable. Applying a SPB when most of the water column P is present as SRP could be an option. However, this means that water managers have to wait for this situation to occur and hence may be impossible in waters suffering from perennial blooms (e.g., Yéprémian et al., 2007). To overcome this problem, Lürling and van Oosterhout (2013) developed a “Flock and Lock” treatment that combines a low-dose flocculent with a SPB. This treatment first strips the water column from cyanobacteria including TP using the flocculent and a clay as sinking weight. Here after the internal P loading is blocked by applying the SPB (Lürling and van Oosterhout, 2013). This technique can be applied whole year round and has been implemented successfully in Lake Rauwbraken (Van Oosterhout and Lürling, 2011; Lürling and van Oosterhout, 2013) and Lake De Kuil (Waajen et al., 2015), two isolated and stratifying lakes in The Netherlands. In Lake Rauwbraken poly-aluminium chloride (PAC) was used as a flocculent, in Lake De Kuil iron (III) chloride was used. In both lakes the La modified bentonite (LMB) Phoslock® (Douglas, 2002; Copetti et al., 2015) was used as ballast and solid-phase P sorbent.

The use of metal-based flocculants and modified clays can meet some critics. Hence, non-toxic and biodegradable flocculants, such as chitosan and local soils, could be a welcome addition. Chitosan is a biopolymer derived from marine shrimps and crabs. It is widely used in water and wastewater treatment and is non-toxic, biodegradable with good coagulation/flocculation properties (Renault et al., 2009). Chitosan has been reported as an effective flocculent that in combination with clays and soils may successfully control cyanobacterial blooms by settling the biomass (Zou et al., 2006).

Although advocated as prerequisite for successful mitigation, it is not always economically feasible to reduce external P-loading. In this situation effect oriented measures may provide the most suited nuisance control. Effect oriented or curative measures mostly have shortly lived effects and probably will need to be repeated regularly. However, if such applications are fast, easy, cheap and safe, the may be a feasible alternative to the more elaborate methods that require high investments. Here, the combination of a flocculent and ballast (not necessarily a P-sorbent) seems best suited above other measures, such as algaecides that would kill the cyanobacteria in the water column and bring immediately nutrients and toxins in the water or have other constraints (Jančula and Maršálek, 2011). The combination of PAC and chitosan with sand or local soil achieved a high removal efficiency of marine harmful algae (Pan et al., 2011a). Likewise, strong removal of cyanobacteria using chitosan mixed with natural soils and clays has been reported (Pan et al., 2006a,b; 2012; Zou et al., 2006).

The nine million people in metropolitan Rio de Janeiro region (Brazil) depend on the Guandu River as main source of water. However this river is fed by Funil Reservoir (Rio de Janeiro State, Brazil) which has undergone drastic eutrophication, with long-standing perennial dominance of cyanobacteria (Soares et al., 2009). Despite ongoing external load, measures that reduce cyanobacteria blooms are needed. Thus, Funil Reservoir also qualifies for curative measures in the short run where the surrounding red soil might be a compound of potential interest. One important aspect of mitigating eutrophication or its symptoms is the uniqueness of lakes which implies that mitigation methods are tailor made (Björk, 1972). Part of this uniqueness may be the availability of local soils with natural P binding capacities, e.g. red soils (Rout et al., 2014). This would not only reduce transportation and material costs (Pan et al., 2012), but also offer a more natural additive to the cyanobacteria infested lake than modified clays or products collected/manufactured elsewhere. For instance, local soil collected from the lakeside and mixed with chitosan successfully settled a cyanobacteria bloom in a whole bay (0.1 $km^2$) experiment conducted in the northern Taihu Lake, China (Pan et al., 2011b).

Therefore, in this study we evaluated the efficacy of both PAC and chitosan alone and combined with different dosages of the LMB or local red soil (LRS) in sedimenting positively buoyant cyanobacteria— predominantly *Microcystis aeruginosa* (Kützing) Kützing, from Funil Reservoir. In addition, we evaluated the SRP adsorbing capacity of both LMB and LRS.

After it has been precipitated using a flocculent with ballast, *M. aeruginosa* may survive for prolonged time (Brunberg and Boström, 1992) and potentially be liberated from flocks. To minimize the biomass that may recolonize the water column, permanent removal of the precipitated cyanobacteria is desirable. A possibility could be to kill these settled cyanobacteria using calcium peroxide (Cho and Lee, 2002). Calcium peroxide could produce hydrogen peroxide, which is a potent oxidizing agent that acts via the formation of hydroxyl radicals (•OH) (Russell, 2003). As compared to hydrogen peroxide to control cyanobacteria (Drábková et al., 2007a), the calcium peroxide releases hydrogen peroxide over a far longer period (Li et al., 2014) and can be far easier brought as pellets on the sediment where their activity is needed.

We hypothesize that both PAC and chitosan will be effective flocculants, whereas ballast in the form of either LMB or LRS will be needed to settle the cyanobacteria. In addition, we expect that because of the La modification, the SRP removal capacity of LMB will be larger than the LRS, but that LRS will also be able to bind SRP. We hypothesize that the SRP sorption of the LMB will not be affected under anoxia (cf. Ross et al., 2008), while we expect less SRP sorption by LRS under anoxic conditions due to the expected portion of reductive labile Fe in the red soil. Finally, we tested the effect of calcium peroxide on suspended and settled cyanobacteria from Funil, where we hypothesize that adding calcium peroxide will kill the precipitated cells.

## 2. Materials and methods

### 2.1. Study site

Funil Reservoir (Fig. 1) is located in the southern part of Rio de Janeiro State, Brazil (22°30′S, 44°45′W, altitude 440 m). The climate conditions are a wet-warm summer and dry-mild cold winter (Cwa in the Köppen system). The reservoir receives water from the Paraíba do Sul River, it has a catchment area of 16,800 $km^2$, a surface area of 40 $km^2$, a mean and maximum depth of 22 and 70 m, respectively, a mean total water volume of 890 × $10^6$ $m^3$, which may vary considerably depending on climate conditions, and a

Please cite this article in press as: Noyma, N.P., et al., Controlling cyanobacterial blooms through effective flocculation and sedimentation with combined use of flocculants and phosphorus adsorbing natural soil and modified clay, Water Research (2015), http://dx.doi.org/10.1016/j.watres.2015.11.057