Universidade do Estado do Rio de Janeiro

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Controle da eutrofização e de florações de cianobactérias em corpos d'agua salobras: avaliação da eficácia e aplicabilidade da combinação de coagulantes e adsorventes de fósforo em fase sólida

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Tese apresentada como parte integrante dos requisitos para obtenção do título de Doutor, ao Programa de Pós-graduação em Biologia Vegetal, Universidade do Estado do Rio de Janeiro. Área de concentração: Conservação e utilização da biodiversidade.

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Autor desconhecido

RESUMO

MAGALHÃES, Leonardo de. *Controle da eutrofização e de florações de cianobactérias em corpos d'agua salobras: avaliação da eficácia e aplicabilidade da combinação de coagulantes e adsorventes de fósforo em fase sólida*. 2018. 196f. Tese (Doutorado em Biologia Vegetal). Instituto de Biologia Roberto Alcantara Gomes, Universidade do Estado do Rio de Janeiro, Rio de Janeiro, 2018.

A eutrofização é considerada o problema de qualidade de água mais importante em todo o mundo, resultando em florações nocivas de cianobactérias. O controle de fósforo (P) é crucial para mitigação da eutrofização e deve focar tanto na redução dos aportes externos quanto no estoque interno, uma vez que a ciclagem interna pode retardar a restauração do lago por décadas. A Lagoa de Jacarepaguá (RJ), outrora importante berço para a biodiversidade e fonte de recursos pesqueiros, se encontra em estado de eutrofização avançado devido ao inadequado tratamento de esgotos levando a intensas florações de cianobactérias. Esta Tese visa avaliar a eficácia e aplicabilidade de combinações de coagulantes e adsorventes de P em fase sólida no controle da eutrofização e de florações de cianobactérias para a melhoria da qualidade da água da Lagoa de Jacarepaguá. O estudo realizado monitorando as condições ambientais da lagoa entre nov/2014 e dez/2017 mostrou elevadas concentrações médias de fósforo (1,3±0,9 mg L^{-1}) e nitrogênio total (4,4±1,9 mg L^{-1}). No fitoplâncton, dominou o grupo funcional M, com florações de *Microcystis aerugionosa* na maior parte do ano, controladas, principalmente, pela temperatura da água. Nos períodos mais frios o incremento na salinidade e transparência favoreceram uma maior contribuição dos grupos X1, J, F, X2, Y, C, MP, e P. Experimentos em laboratório demonstraram que: i) cloreto de polialumínio (PAC) em baixas doses (≤ 8mg Al L^{-1}) combinado com lastro (solo vermelho, sedimento da lagoa ou bentonita modificada com lantânio - BML) foi eficiente na remoção de cianobactérias; ii) BML (400g m^2) reduziu significativamente a liberação de P do sedimento para água deionizada ou água da lagoa com e sem cianobactérias; iii) em testemunhos de sedimento, PAC+BML reduziu o fluxo de P de 9,9 (±3,3) para 4,6 (±0,3) mg P m^{-2} d^{-1} durante o período experimental de 3 meses. Em sintese, a temperatura da água se mostrou a principal reguladora da dinâmica de florações de *M. aeruginosa*. O uso combinado de coagulante e lastro parece ser uma medida curativa eficiente, barata, rápida e segura para mitigar o efeito nocivo da floração das cianobactérias. Além disso, o tratamento combinado LMB+PAC parece ser uma intervenção promissora na lagoa para diminuir a carga interna de P. Tal intervenção é capaz de acelerar a recuperação da lagoa, uma vez que os aportes externos tenham sido reduzidos ou eliminados.

Palavras-chave: Mitigação. *Microcystis aerugionosa*. Phoslock. PAC. Quisotana.

ABSTRACT

MAGALHÃES , Leonardo de. *Controlling eutrophication and cyanobacterial blooms in brackish water bodies: evaluating the efficacy and applicability of coagulants and solid phase adsorbent for phosphorus removal*. 2018. 196f. Tese (Doutorado em Biologia Vegetal). Instituto de Biologia Roberto Alcantara Gomes, Universidade do Estado do Rio de Janeiro, Rio de Janeiro, 2018.

The control upon eutrophication and cyanobacterial bloom can be achieved reducing the phosphourus (P) availability in the water. Eutrophication is considered the major problem on water quality world wide resulting in proliferation of harmful cyanobacterial blooms. Controling phosphorus is crucial to mitigate eutrophication and should focusing on both reduction of external and internal loading once phosphorus in the sediment can delay water quality recovery for decades. Jacarapaguá lagoon, once crandle for biodiversity and source of fishing resource, is highly eutrophicated due the lack of sewage treatments leading to intese cyanobacterial blooms. This thesys aims to evaluate the efficacy and applicability of the combination between coagulants and phosphate adsorbants on the control of eutrophication and cyanobacterial blooms in Jacarepaguá Lagoon. The monitoring during the period between nov/2014 and dez/2017 showed high mean concentrations of phosphorus (1,3±0,9 mg L^{-1}) and total nitrogen (4,4±1,9 mg L^{-1}). The phytoplankton was mainly composed by function group M in most part of the year and represented by *Microcystis aeruginosa.* The temperature was the main driver of this dominance observed in the Redundance analyse (RDA). In the coldest periods the increasing in salinity and water transparence facilitated the higher contribution of groups X1, J, F, X2, Y, C, MP and P. Experiments conducted in the lab evidenced: i) low doses (≤ 8mg Al L^{-1}) of polyaluminium chloride (PAC) combined with ballast (Red soil, lagoon sediment or Lanthanum modified bentonite – LMB) was efficient to remove cyanobacteria; ii) BML (400g m^2) reduced significantly the phosphorus release from sediment in deonized water or lagoon water with and without cyanobacteria; iii) in sediment cores, PAC + LMB reduced the P flux from 9.9 (±3.3) to 4.6 (±0,3) mg P m^{-2} d^{-1} over the experimental period of 3 months. In summary, the water temperature was the main driver of *M. aeruginosa* bloom. Combining coagulante and ballast is a fast, cheap and safe curative techinique to mitigate harmful cyanobacterial bloom effects. The combination of LMB + PAC is a promissing techinique to diminish the internal P loading speeding up lagoon recovery once external loading is also reduced.

Keyword: Mitigation. *Microcystis aerugionosa*. Phoslock. PAC. Chisotan.

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LISTA DE ABREVIATURAS E SIGLAS

Al	Alumínio
BD	Bicarbonato/Ditionito
CART	Árvore de classificação e regressão
Chl-*a*,	Chlorophyll-*a*
COD	Carbono orgânico dissolvido
FSR	Fósforo solúvel reativo
FT	Fósforo total
La	Lantânio
LMB	Bentonita modificada com lantânio
NID	Nitrogênio inorgânico dissolvido
NT	Nitrogênio Total
P	Phosphorus
PAC	Cloreto de polialumínio
ppt	Parte por trilhão
RDA	Análise de redundância (RDA)
RS	Solo vermelho
SRP	Fósforo solúvel reativo
Temp.	Temperatura
TP	Fósforo Total
Z_{eu}	Zona eufótica

LISTA DE SÍMBOLOS

A^{+3}	Alumínio
$Al\ (OH)_3$	Hidróxido de alumínio
$Al\ (OH)_4$	Tetrahidroxialuminato
$AlPO_4$	Tetraoxidofosfato de aluminio
°C	Grau Celsius
cm	Centímetro
CO_2	Ácido carbônico
Fe	Ferro
HCO_3	Bicarbonato
H_2SO_4	Ácido sulfúrico
Km^2	Quilômetro quadrado
L^{-1}	Litro
Mn	Manganês
mg	miligrama
ml	mililitro
m^2	Metro quadrado
m^3	Metro cúbico
mm^3	milimetro cúbico
mEq	miliequivalente
N_2	Gás nitrogênio
NO_2^-	Íon Nitrito
NO_3^-	Íon Nitrato

NH_4^+	Íon amônio
$NaHCO_3$	Bicarbonato de sódio
NaOH	Hidróxido de sódio
$Na_2S_2O_4$	Ditionito de sódio
O_2	Gás oxigênio
PSII	Fotossistema II
S	Escala prática de salinidade
µg	micrograma

SUMÁRIO

INTRODUÇÃO

1 EUTROFIZAÇÃO E FLORAÇÕES DE CIANOBACTÉRIAS

A eutrofização é considerada o problema mais importante para a qualidade da água em ambientes de águas doce e costeiras em todo o mundo (SMITH & SCHINDLER, 2009). A entrada excessiva de nutrientes é a principal responsável pelas florações de espécies fitoplanctônicas, principalmente de cianobactérias em ambientes de água doce e salobros. Estas podem crescer em grandes densidades, formando densas camadas e espumas na superfície da água (CHORUS et al., 2000). Como consequência, as florações causam uma substancial queda da qualidade da água, tornando-a túrbida e em muitos casos malcheirosa. Além disso, eventos de depleção noturna de oxigênio levam a mortandade de peixes (SMITH et al., 1999, PAERL e HUISMAN, 2008), causando um significante impacto econômico.

As florações de cianobactérias podem ocorrer em diversas partes do globo sendo favorecidas sobre diversas condições ambientais. A temperatura é um importante fator e seu aumento em escala global tem favorecido o surgimento das florações de cianobactérias (PAERL e HUISMAN, 2009). As elevadas temperaturas promovem a estratificação témica da coluna da água, favorecendo o crescimento de organismos capazes de se manter na parte iluminada da coluna da água, como é o caso das cianobactérias portadoras de aerótopos. Em elevadas biomassas, essas algas são capazes de sombrear outras espécies, prejudicando as que não são boas competidoras em condições de pouca luz (SCHEFFER et al., 1997; REYNOLDS, 2002). Além disso, em escala global, as temperaturas elevadas intensificam o período de chuva e tornam o período seco mais prolongado, uma vez que, a longo prazo o aumento da vazão no período de chuvas trará mais nutrientes, fazendo com que o período seco se torne cada vez mais rico em nutrientes, aumentando a incidência das florações (PAERL e HUISMAN, 2008).

A elevação do pH é outro fator importante para as cianobactérias. O mecanismo no qual as cianobactérias são favorecidas pelo aumento do pH se deve

à capacidade de algumas espécies em capturar e utilizar de forma eficiente o CO_2 e bicarbonato como fontes inorgânicas de carbono (SANDRINI et al., 2016). Mas também, pode estar relacionado à interferência direta no transporte de membrana entre os organismos e o meio externo, afetando suas taxas de crescimento (SHAPIRO, 1997; CARACO e MILLER, 1998). A capacidade de fixar nitrogênio é uma outra estratégia adaptativa que algumas cianobactérias desenvolveram ao longo do processo evolutivo que consiste em converter nitrogênio atmosférico (N_2) para a forma de nitrogênio biodisponível, amônia (NH_3), e utilizá-lo quando este se encontra excasso na coluna da água (SMITH, 1983).

As cianobactérias apresentam diferentes estratégias adaptativas quanto ao aproveitamento de recursos limitantes, como luz e nutrientes, bem como mecanismos contra perdas por sedimentação e predação (LITCHMAN e KLAUSMEIER, 2008). Alguns organismos são boas antenas de luz devido à sua alta razão entre superfíce e volume, como as cianobactérias filamentosas. Outras são unicelulares pequenas, e apresentam rápido crescimento, dominando principalmente em estágios transicionais, enquanto que outras formam grandes colônias mucilaginosas que podem sombrear outras espécies e também evitar a herbivoria do zooplâncton.

Outra estratégia adaptativa das cianobactérias é a capacidade de produzir substâncias alelopáticas que podem inibir o crescimento de outras espécies (GANTAR et al., 2008). Dentre as substâncias alelopáticas consideradas, muitas espécies de cianobactérias podem produzir compostos tóxicos (cianotoxinas), sendo prejudiciais para invertebrados, vertebrados aquáticos e para o próprio homem, tornando-se um grave problema de saúde pública. Casos de intoxicação por cianotoxinas já foram reportados tanto em animais (FAASSEN et al., 2012; LÜRLING & FAASSEN, 2013) quanto em seres humanos (JOCHIMSEN et al., 1998). Os casos mais graves de intoxicação humana foram registrados no Brasil, devido à utilização de águas contaminadas em clínica de hemodiálise (JOCHIMSEN et al., 1998; AZEVEDO et al., 2002). Lesões hepáticas por microcistinas também foram registradas na Austrália e relacionadas ao período em que a água de abastecimento foi tratada com adição de sulfato de cobre, substância capaz de provocar lise nas células de cianobactérias, permitindo a liberação de toxinas (FALCONER et al.,

1983). Além dos acasos registrados de óbito, irritações na pele e mucosa ocular podem ocorrer simplesmente ao contato da água contaminada, e a ingestão acidental pode levar à sintomas como a febre do feno, vertigem, fadiga e gastroenterite aguda. As cianotoxinas até o momento conhecidas são: Microcistinas, saxitoxinas, cilindrospermopsinas, nodularina, anatoxina-a, anatoxina (s), lyngbiatoxina, aplysiatoxina e LPS. Dentre estas, a microcistina, nodularina e cylindrospermopsina são hepatotoxinas, sendo capazes de provocar danos nas células do fígado, causando até a necrose dos tecidos. Já as saxitoxinas, anatoxina-a e anatoxina-a (s) são consideradas neurotóxicas, afetando principalmente o sistema nervoso (NIAMIEN-EBROTTIE et al., 2015). Segundo registros na literatura, dentre as cianotoxinas, a microcistina é a de maior ocorrência em todo o globo, sendo produzinda por diversos gêneros de cinobactérias como *Microcystis, Anabaena, Oscillatoria, Nostoc, Anabaenopsis*, além de outros (NIAMIEN-EBROTTIE et al., 2015).

Assim, as cianobactérias apresentam uma gama de estratégias adaptativas que permitem que sobrevivam e proliferem em diferentes condições ambientais e, quando em elevadas densidades, as florações são um grande problema de saúde pública, sendo necessárias medidas de prevenção e remoção. Dentre essas medidas, diversas são as técnicas capazes de remover e/ou prevenir o crescimento de algas potencialmente tóxicas, podendo ser classificadas como controles físicos, químicos ou biológicos.

1.1 **Técnicas de mitigação de florações**

Diversas técnicas têm sido propostas para mitigar as florações de cianobactérias, desde a remoção direta até controle biológico ou químico. Dentre as técnicas de remoção, a aspiração pela remoção física foi descrita por SHIROTA (1989), que utilizou para ambiente marinho um separador por pressão de flotação que, através da produção de bolhas, visava promover a aglomeração das algas na superfície, possibilitando assim sua sucção. Entretanto, os testes realizados naquela

época não foram bem-sucedidos, uma vez que nem sempre as bolhas conseguiram aglomerar a biomassa algal e, mesmo após a adição de coagulante, a filtragem foi prejudicada devido à elevada biomassa (SHIROTA, 1989). Apesar disso, mais recentemente, redes de plâncton foram testadas em sua capacidade de concentrar algas em ambientes marinhos para sua posterior utilização para produção de biodiesel e metabólitos secundários e são passiveis de serem utilizadas para recolher algas em lagos (KUO, 2011).

Uma outra técnica física que vem sendo recentemente estudada é a utilização do ultrassom. Essa técnica baseia-se na produção de ondas por equipamentos de alta potência, formando bolhas que ao colapsarem geram radicais e peróxido de hidrogênio, os quais afetam as taxas de crescimento, atividade fotossintética e aerótopos das cianobactérias (WU et al., 2011; RAJASEKHAR et al., 2012a). Apesar de não utilizar substâncias químicas e de ter funcionado em experimentos de laboratório (WU et al., 2011; RAJASEKHAR et al., 2012a), essa técnica apresenta dificuldade em ser aplicada em lagos pois o elevado volume de água presente é capaz de enfraquecer a tramitação das ondas e, consequentemente, o efeito nas cianobactérias (LEE et al., 2002; AHN et al., 2007; RAJASEKHAR et al., 2012a). Além disso, um efeito negativo na população de zooplâncton pode ser observado (RAJASEKHAR et al., 2012a).

O controle biológico de florações de cianobactérias, pode ser realizado através de interações de predação e parasitismo ou até mesmo pela ação de metabólicos secundários, que inibam o crescimento celular. Nesse sentido, diversos estudos têm tentado descobrir e aprimorar controladores biológicos. Um deles é a descoberta e o estudo do vírus LPP-1 que ataca células de cianobactérias dos gêneros *Lyngbya, Plectonema, Phormidium* (OHKI e FUJITA, 1996; PADAN et al., 1967). Apesar da capacidade em promover lise celular, ainda são importantes a realização de estudos sobre a possível formação de cepas que podem se proteger ou se tornar resistentes à ação do vírus (PADAN et al., 1967). Além disso, a morte célular das cianobactérias potencialmente tóxicas pode provocar a liberação das toxinas que deve ser monitorada. Outra dificuldade dessa técnica são as condições ambientais e a dificuldade em produzir os inóculos em massa.

Um outro exemplo de controle biológico é a utilização de microrganismos eficientes, técnica que consiste em lançar “bolas de lama” contendo microrganismos que, através da exclusão competitiva, pode mudar a comunidade bacteriana, excluindo bactérias indesejadas (ZAKARIA et al., 2010). Apesar de ser proclamada como uma solução para o problema da qualidade da água (ZAKARIA et al., 2010), poucos testes científicos que comprovem a sua eficácia já foram realizados, e os efeitos positivos da aplicação não são claros (JÓZWIAKOWSKI et al., 2009; CHEN et al., 2013). Em experimentos controlados em laboratório, a utilização da dose recomendada não mostrou efeito sobre a taxa de crescimento de *Microcystis aeroginosa*; e concentrações mais altas só mostraram efeito quando a turbidez da água se tornou elevada, sugerindo, na verdade, um efeito indireto proveniente da limitação por luz (LÜRLING et al., 2009; 2010).

Dentre os controladores químicos, durante décadas, o sulfato de cobre foi utilizado como o principal algicida para o controle das florações de algas em mananciais, lagos de recreação e reservatórios (EFFLER et al., 1980). Entretanto, vários são os efeitos negativos relacionados ao seu uso. Sua aplicação leva a rápida morte das algas o que pode resultar na diminuição das concentrações de oxigênio dissolvido. No sedimento essa redução pode provocar o aumento da liberação do fósforo, gerando um efeito contrário e intensificando a eutrofização. Além disso, sua aplicação é paliativa e não acaba com a causa do problema, sendo que o uso contínuo promove rápida acumulação de cobre no sedimento. Em concentrações elevadas, o cobre é tóxico para organismos bentônicos, extinguindo-os e inviabilizando seu habitat (HASLER, 1947; HANSON e STEFAN, 1984; LEALE, 1998).

A floculação é outra técnica química que promove a formação de flocos densos que irão precipitar sobre o sedimento. Dentre os compostos com propriedades coagulantes, os que possuem alumínio são os mais amplamente utilizados devido a sua eficiência, baixo preço e fácil utilização (GEBBIE, 2001). O mais utilizado atualmente é o cloreto de polialumínio (PAC) que possui vantagens sobre a utilização de sulfato de alumínio, uma vez que libera menos resíduos, necessita de doses mais baixas e possui certa alcalinidade, diminuindo sua influência sobre o pH (GEBBIE, 2001). Além disso, tem mostrado eficiência em

remover cianobactérias quando combinado a lastro em água doce (LÜRLING e OOSTERHOUT, 2013b) e possui capacidade de remover fósforo (DRÁBKOVA´, 2007; LOPATA e GAWRORÍSKA, 2008). As possíveis desvantagens da utilização de compostos com alumínio são sua afinidade com o carbono orgânico dissolvido fazendo com que, em águas ricas em compostos orgânicos, o processo de floculação seja prejudicado (GEBBIE, 2001). Além disso, o alumínio pode apresentar efeitos tóxicos em pH ácido.

Uma alternativa à utilização de compostos de alumínio é a utilização de quitosana, um polímero biodegradável, não tóxico e de alto peso molecular (RENAULT et al., 2009). Este produto é derivado da desacetilação da quitina, segundo biopolímero mais abundante no mundo, que é extraído da casca de camarões e caranguejos (BRATBY, 2006; RENAULT et al., 2009). A utilização da quitosana para o tratamento de água tem se mostrado eficiente em baixas doses para a redução da tubidez inorgânica (DIVAKARAN e SIVASANKARA PILLAI, 2002) e para a remoção de cianobactéria *Microcystis aeroginosa* em água doce (AHMADI et al., 2011; NOYMA et al., 2016a). A alta eficiência na remoção de cianobactérias e o fato de ser biodegradável e não tóxico torna os floculantes a base de quitosana uma alternativa à utilização de compostos com alumínio (DIVAKARAN & SIVASANKARA PILLAI, 2002). Entretanto, em ambientes marinhos onde a salinidade é elevada, estudos têm demostrado que uma maior dose de sua apliacação é necessária (PEREZ et al., 2016), o que pode tornar sua utilização mais cara. Já em águas salobras sua utilização é escassa ou até mesmo inexistente na literatura.

A aplicação conjunta de coagulante e lastro, pode ser utilizada com o objetivo de melhorar a eficiência do processo de floculação. A técnica “flock and sink”, utilizando um coagulante combinado com lastro natural, torna possível a sedimentação de flocos menos densos e flutuantes. Além disso, faz com que menores doses de floculantes e lastro sejam necessárias. A utilização conjunta de PAC com argila, por exemplo, é capaz de reduzir a utilização de lastro em até uma ordem de grandeza (NOYMA et al., 2017) tornando a técnica mais viável logisticamente e econômicamente. Essa técnica se mostrou eficiente em experimentos de laboratório sendo capaz de flocular espécies marinhas (PAN et al.,

2011a) e de água doce (NOYMA et al., 2016). Entretanto a eficiência na remoção varia de acordo com a espécie alvo, sua concentração no ambiente e a argila utilizada (SENGCO, 2001; SENGCO et al., 2004), fazendo com que testes sejam necessários, visando a otimização e sucesso da técnica.

A maioria das técnicas apresentadas anteriormente, visa a remoção das cianobactérias de forma pontual, já que acabariam com a floração momentaneamente. Para que essas medidas apresentem resultados prolongados é necessária também a remoção dos nutrientes contido na água. Em lagos e reservatórios os nutrientes chegam por fontes externas difusas, pontuais e internas, principalmente por liberação do sedimento. Assim, o primeiro passo para mitigar a eutrofização é a redução direta das entradas de fósforo no ambiente (COOKE et al., 2005). A redução do aporte externo de fósforo é capaz de provocar significativas melhorias na qualidade da água (SAS, 1989). Entretanto, após essa primeira redução, muitas vezes os lagos mostram quase nenhum sinal de recuperação em resposta à redução da carga externa de nutrientes (JEPPESEN et al., 1991; VAN DER MOLEN e BOERS, 1994). Essa lenta resposta pode ser explicada pela elevada carga que permanece no sedimento (SØNDERGAARD et al., 1990; COOKE et al., 2005). A liberação do fósforo pelo sedimento é capaz de atrasar por décadas a recuperação do sistema (SØNDERGAARD et al., 1999; COOKE et al., 2005). Portanto, em sistemas enriquecidos é necessário não somente a redução do aporte externo de fósforo, mas também a redução da carga interna, liberada pelo sedimento. Dentre as técnicas existentes que visam mitigar a liberação do fósforo no sedimento, pode-se destacar a dragagem, utilização de sais de ferro e alumínio e o uso de argilas modificadas.

A dragagem de sedimento consiste na remoção física das camadas mais enriquecidas, e tem sido aplicada em diversas regiões do globo (VAN DER DOES et al., 1992; REDDY et al., 2007). Em alguns casos, grandes esforços são necessários para a remoção (REDDY et al., 2007) e o sucesso parece depender da profundidade da camada a ser extraída (REDDY et al., 2007), tornando o custo elevado em comparação à outras técnicas (LÜRLING e FAASSEN, 2012). Mesmo com o elevado custo, a restauração utilizando apenas a dragagem como método de

remoção do fósforo nem sempre é bem-sucedida (SØNDERGAARD et al., 2007), sugerindo que seu uso combinado com outras técnicas deve ser considerado.

Os sais de ferro e alumínio vêm sendo utilizados à décadas como agentes floculantes, mas também como adsorventes de fósforo (KENNEDY et al., 1987; BOERS, 1991a; COOKE at al., 1993). O ferro inorgânico pode ser encontrado livre na água, principalmente nas formas de F_3^+ ou F_2^+, dependendo do pH e do potencial redox. Já o hidróxido de ferro [Fe $(OH)_3$], possuí elevada capacidade de adsorção de fósforo, mas é fortemente dependente do pH e do potencial redox. Em períodos de estratificação térmica, quando ocorre a diminuição da concentração de oxigênio e do potêncial redox, o ferro pode sofrer redução $F_3^+ \rightarrow F_2^+$ e liberar o fósforo novamente (LIJKLEMA, 1977; BOERS, 1991a; COOKE at al., 1993). Outro ponto negativo da utilização de ferro é a ineficiência em ambientes com elevadas concentração de carbono orgânico dissolvido (COD), uma vez que sua afinidade com o COD promove sua complexação, diminuindo a eficiência do tratamento (COOKE et al., 1993). No caso dos sais de ferro, apesar das concentrações utilizadas não mostrarem letalidade sobre macrófitas aquáticas, por exemplo, vale ressaltar que testes em laboratório demonstraram que concentrações maiores que 40 $gFe.m^{-2}$ podem reduzir a taxa de crescimento de algumas espécies e favorecer outras, podendo então modificar a estrutura das comunidades de macrófitas (SNOWDEN e WHEELER, 1995; IMMERS, 2014).

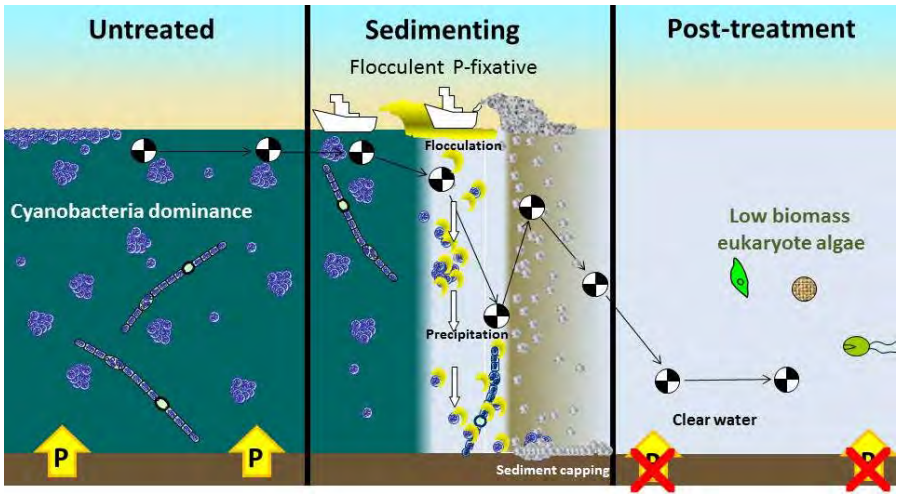
Em ambientes naturais, a adição de sais de alumínio em vez de ferro vem sendo preferível, uma vez que a sua ligação ao fósforo é menos sensível ao potencial redox (LIJKLEMA, 1977; COOKE et al., 1993). Quando o sulfato de alumínio é adicionado na água as formas iônicas são liberadas e, através de uma série de hidrólises, ocorre a formação do $Al(OH)_3$ com alta capacidade de adsorção de fósforo. No caso do alumínio o pH é o principal fator que regula a formação dos $Al(OH)_3$, onde o ótimo se encontra em um potencial hidrogeniônico entre 6-8; porém formas tóxicas como o Al^{+3} podem se tornar a espécie química predominante em pH < 4 (COOKE et al., 2003). Apesar da utilização de sal de alumínio apresentar rápidas respostas, a longevidade do tratamento é questionada uma vez que em alguns casos dura apenas alguns meses (KENNEDY et al., 1987; RYDIN e WELCH, 1999).

Recentemente, argilas modificadas vêm ganhando espaço, sendo mais utilizadas em projetos de restauração. A bentonita modificada com lantânio, por exemplo, vêm mostrando ser promissora devido ao baixo custo e longevidade do tratamento (LÜRLING & OOSTERHOUT, 2013b; SPEARS et al., 2016), já tendo sido utilizada com sucesso em lagos holandeses (ROBB et al., 2003; HAGHSERESHT et al., 2009). Porém, em alguns casos (LÜRLING & OOSTERHOUT, 2013a) a remoção de fósforo, utilizando apenas argilas modificadas não alcançou os resultados esperados. Diversos são os fatores que podem interferir na ligação entre o fósforo e o adsorvente, sendo consideradas mais importantes as mudanças no pH (ROSS et al., 2008), as concentrações de oxigênio dissolvido (CORREL, 1998) e substâncias húmicas (LÜRLING et al., 2014). O aumento do pH provoca a formação de espécies hidroxiladas, diminuindo o número de sítios de ligação entre o adsorvente e o fósforo (DIBTSEVA et al., 2001). Além disso, provoca o aumento da repulsão eletrostática, diminuindo a capacidade de adsorção (NIRIELLA e CARNAHAN, 2006). Já a variação nas concentrações de oxigênio é importante principalmente quando ocorrem mudanças de condições óxicas para anóxicas. A anoxia é capaz de reduzir significativamente a capacidade de adsorção e provocar a liberação do fósforo já adsorvido, mas sua influência varia de acordo com as diferentes substâncias empregadas (CORREL, 1998). Apesar disso, no caso da argila modificada com lantânio, estudos demonstraram escassa liberação de fósforo em condições de anoxia, o que torna sua utilização indicada para ambientes que apresentam estratificação térmica com constantes mudanças nas concentrações de oxigênio dissolvido (ROSS et al., 2008). Todavia, as substâncias húmicas vêm sendo apontadas como a principal razão para o desempenho inferior apresentado pela bentonita modificada com lantânio (LÜRLING e OOSTERHOUT, 2013a) e essa interferência deve-se a sua capacidade de quelar a argila e o lantânio, formando complexos que impedem a precipitação do fósforo (TOMBÁCZ et al., 2004; LÜRLING et al., 2014).

Nesse contexto, a técnica “Flock and Lock” que combina pequena dose de floculante com uma argila modificada parece ser mais adequado em águas com elevadas concentrações de compostos húmicos (Figura 1). Este método, além de remover as formas dissolvidas e particuladas de fósforo (células de cianobactérias),

reduzem a influência de substâncias húmicas e compostos oxiônicos que interferem no processo de adsorção (LIU et al., 2009, LÜRLING & VAN OOSTERHOUT, 2013a). Essa técnica já foi utilizada com sucesso promovendo o clareamento da coluna d'água em um pequeno lago, o que possibilitou o crescimento de macrófitas submersas (LÜRLING et al., 2013b). Uma vez restabelecida, a comunidade de macrófitas, através da absorção de nutrientes (MOSS, 1990) e compostos alelopáticos (XIAN et al., 2005), são capazes de prolongar o estado claro da água. Em função dessa remoção de fósforo e consequentemente do clareamento da coluna de água, são esperadas também mudanças na comunidade microbiana do sedimento, mudanças nas condições redutoras e anóxicas para condições oxidantes e aeróbicas, maior diversidade da flora e da fauna, tudo isso junto criando uma retroalimentação positiva através da estabilização e oxigenação do sedimento, melhorando significativamente a qualidade da água.

Figura 1 - Esquematização do tratamento "flock and lock" em um lago raso hipotético utilizando a combinação de floculante e adsorvente de fósforo.



Legenda: Tratamento combinado de floculante e adsorvente (combinação de baixa dose de floculante e areia ou argila local) em um lago raso com elevada entrada de fósforo externo. É esperado que a remoção das cianobactérias e das partículas em suspensão, assim como o aprisionamento do fósforo no sedimento, promova a redução da turbidez e abra uma janela para o estabelecimento de macrófitas aquáticas submersas, prolongando a fase de águas claras.

Fonte: Cortesia Miquel Lurling, 2017.

Dentre os sistemas que apresentam problemas de florações de cianobactérias, as lagoas costeiras possuem grande importância econômica quando em boas condições, gerando produção pesqueira, uso de suas águas para aquicultura, recreação e paisagismo (SPAULDING, 1994). Além disso, esses sistemas são frequentemente apontados como os mais produtivos do mundo devido as altas taxas de produção primária e secundária (KNOPPERS, 1994).

A Lagoa de Jacarepaguá, localizada na região Oeste do município do Rio de Janeiro, é uma lagoa costeira rasa e de águas salobras. É a terceira lagoa do complexo lagunar de Jacarepaguá que compreende as lagoas de Jacarepaguá, Camorim, Marapendi e Tijuca, desembocando no canal do Joátinga, que as liga na praia da Barra da Tijuca. Nas últimas décadas seu entorno (Baixada de Jacarepaguá) sofreu com um alto crescimento de ocupação antrópica sem infra-estrutura adequada, o que fez com que a lagoa servisse basicamente para receber o descarte de efluentes domésticos e industriais. Relatórios da FEEMA sobre os problemas ambientais da Lagoa de Jacarepaguá dão atenção ao processo acelerado de eutrofização devido à grande descarga de matéria orgânica e nutrientes (esgoto sanitário) e de altas concentrações de compostos tóxicos de fontes industriais e ao assoreamento causado pela deposição de sedimentos e lixo, todos estes vinculados aos rios contribuintes (REBELO, 2016). A rápida eutrofização trouxe consigo a queda da qualidade da água que levou à prolongada dominância de cianobactérias e que vêm se intensificando ao longo do tempo (SAIEG-FILHO, 1986; FERNANDES, 1993; DOMINGOS, 2001). Devido às condições em que a lagoa se encontra e ao período prolongado e contínuo de aporte de nutrientes é esperado que, mesmo havendo uma redução das entradas de fósforo, o processo de melhoria da qualidade da água demore anos. Sendo assim, para uma melhoria eficaz e duradoura da qualidade da água de Jacarepaguá, medidas que removam ou inviabilizem o fósforo contido no sistema se fazem necessárias.

Nesse sentido, considerando a importância social, econômica e ambiental da Lagoa de Jacarepaguá e o fato de possuir águas salobras com elevadas cargas de nutrientes de fontes antrópicas, se justifica a avaliação da eficácia e aplicabilidade da combinação de coagulante e adsorvente de fósforo no controle da floração de

cianobactérias e da carga de nutriente interno, presente na Lagoa de Jacarepaguá. Além disso, este trabalho visa contribuir para o desenvolvimento do campo de restauração de ecossistemas aquáticos no Brasil, uma vez que a experiência no controle e mitigação da eutrofização e das florações de cianobactérias em águas superficiais brasileiras é ainda limitada.

1.2 Hipóteses

Devido ao avançado estágio de eutrofização da Lagoa de Jacarepaguá e ao fato de ser uma lagoa rasa, nossa hipótese é que os nutrientes estarão sempre disponíveis na coluna da água propiciando a ocorrência de florações de cianobactérias frequentes e intensas. Considerando essas condições e devido ao histórico de floração de *Microcystis aeruginosa*, capaz de formar grandes colônias, nossa hipótese é que a dinâmica das populações de cianobactérias é controlada por controladores ascendentes, como as concentrações de nutrientes, o pH, temperatura da água, e por ser uma lagoa costeira, também pela salinidade (capítulo 1).

Em relação as técnicas de mitigação, devido a capacidade de flocular biomassa de cianobactéria demonstrada em outros estudos, nossa hipótese é que PAC e quitosana sejam capazes de flocular a floração de cianobactéria da Lagoa de Jacarepaguá e que a precipitação seja otimizada com a utilização combinada de foculante e lastro (capítulo 2). Além disso, a utilização combinada de PAC com bentonita modificada com lantânio é capaz de bloquear a liberação do fósforo do sedimento da Lagoa de Jacarepaguá (capítulo 3).

1.3 **Objetivo geral**

O objetivo deste estudo é avaliar a eficácia e aplicabilidade de combinações dos coagulantes PAC e quitosana com lastro e argila modificada com lantânio no controle da eutrofização e de florações de cianobactérias para a melhoria da qualidade da água da Lagoa de Jacarepaguá.

1.3.1 Objetivos específicos

- Elucidar os principais fatores ambientais direcionadores da dinâmica da floração de cianobactérias na Lagoa de Jacarepaguá (Cap.1).

- Testar experimentalmente em laboratório a eficácia de dois tipos de coagulantes, cloreto de polialumínio (PAC) e quitosana (produzida com cascas de camarão), isoladamente ou combinado com dois tipos de lastro (solo vermelho e sedimento da própria laguna) para remover populações naturais de cianobactérias da Lagoa de Jacarepaguá (Cap. 2).

- Avaliar a eficiência da combinação de PAC com a argila bentonita modificada com lantânio (BML) (Flock & Lock) na remoção de cianobactérias da coluna da água e bloqueio da liberação de P do sedimento de um sistema de águas salobras (Cap. 3).

2 FATORES AMBIENTAIS DIRECIONADORES DA DINÂMICA DAS FLORAÇÕES DE CIANOBACTÉRIAS DA LAGOA DE JACAREPAGUÁ (RIO DE JANEIRO, BRASIL).

2.1 Introdução

As cianobactérias são organismos procariotos que podem ser encontradas em diferentes habitats em todo o globo sendo importantes produtores primários. Apesar da sua importância como produtores primários as florações de espécies potencialmente tóxicas são um problema para a saúde publica que inviabiliza os sistemas para seus múltiplos usos. O cenário atual de mudanças globais, aquecimento e aumento populacional, tem favorecido o crescimento dessas espécies de cianobactérias em todo o mundo, onde as lagoas de águas doces e salobras estão entre os sistemas mais afetados (PAERL e HUISMAN, 2008). As cianobactérias potencialmente produtoras de toxinas apresentam comumente dominância em condições de boa disponibilidade de nutrientes, em ambientes meso ou eutróficos (PAERL e HUISMAN, 2009). Além disso, florações de algas ocorrem quando há nutrientes em excesso, sendo capazes de degradar a qualidade da água gerando mau odor, depleção de oxigênio e mortandade de peixes, ocasionando prejuízos econômicos e sociais.

Apesar da importância dos nutrientes para a ocorrência das florações, nenhum fator ambiental sozinho, ou apenas a influência antrópica, tem sido considerado o causador das florações. Assim, perturbações ecológicas de larga escala como urbanização, agricultura e introdução de espécies invasoras (BYKOVA et al., 2006), combinados com mudanças climáticas, são comumente os principais fatores que influenciam a intensidade e frequência da ocorrência de florações de cianobactérias tóxicas (PAERL e PAUL, 2012; VISSER et al., 2016).

As lagoas costeiras são sistemas lênticos com entradas de água doce e, em muitos casos, com conexões com a água do mar, sofrendo influências de ambos sobre sua composição física, química e biológica. Possuem comumente rica

diversidade biológica, proporcionando ampla variedade de serviços como pesca, lazer e turismo que agregam alto valor econômico à região (GÖNENÇ e WOLFLIN, 2005; PÉREZ-RUZAFA et al., 2005). Esses sistemas, por se localizarem muitas vezes próximos a áreas urbanas, são fortemente influenciadas por estressores naturais e antropológicos. Apesar da influência que sofrem gerando mudanças nas comunidades biológicas, principalmente quando ocorre alternância entre períodos de chuva e seca, a eutrofização artificial é a principal força que vem impactando esse sistema (SMITH e SHINDLER, 2009).

A Lagoa de Jacarepaguá, situada na zona oeste da cidade do Rio de Janeiro (Brasil), tem sofrido com a elevada entrada de resíduos domésticos e industriais que tornam o ambiente propício a eventos de florações de cianobactérias (GOMES et al., 2009), as quais vêm sendo registradas desde 1986 (SAIEG-FILHO, 1986). Nesse sistema o processo de eutrofização é agravado pela escassa troca de água com o mar, fazendo com que as florações permaneçam na lagoa. Atualmente as florações de cianobactérias são representadas principalmente por *Microcystis aeruginosa,* que provoca intensa coloração verde às águas da lagoa. Esse problema se agrava uma vez que as florações de *Microcystis aeruginosa* da lagoa já se mostraram capazes de produzir toxinas que se acumulam no zooplâncton e no pescado da região (FERRÃO-FILHO et al., 2002b; MAGALHÃES et al., 2001).

As cianobactérias do gênero *Microcystis* são importantes formadoras de florações. Registros de florações de *Microcystis* já foram documentados em todos os continentes do globo, com exceção do continente antártico (ZURAWELL et al., 2005). Sua elevada afinidade por nutrientes a torna boa competidora, principalmente em lagos rasos onde períodos de mistura fazem com que o nutriente localizado no fundo retorne à coluna de água (BALDIA et al., 2007; SAXTON et al., 2012). Em períodos em que a coluna de água se encontra estratificada, são capazes de migrar para as camadas mais profundas em busca de nutrientes e de retornarem para as camadas mais iluminadas graças à presença dos aerótopos, evitando assim perdas por sedimentação. Além dos nutrientes, as florações de *Microcystis* também apresentam relação com a temperatura da água, podendo ocorrer quando esta excede 15 °C (REYNOLDS et al., 1981; JACOBY et al., 2000). Enquanto os nutrientes em excesso são capazes de sustentar elevadas biomassas, a

temperatura funciona como um catalizador para seu crescimento. As florações potencialmente tóxicas de *Microcystis* representam um risco a saúde (AZEVEDO et al., 2002; LÜRLING e FAASSEN, 2013) e trazem prejuízo econômico para a utilização de sistemas de água doce e costeiros (SANVERINO et al., 2016).

Este estudo visa elucidar quais fatores influenciam a dinâmica das florações de cianobactérias, aumentando o conhecimento sobre as florações em sistemas salobros e indicando quais medidas são necessárias para a melhoria da qualidade da água da Lagoa de Jacarepaguá.

2.2 **Material e Métodos**

2.2.1 Coleta, preservação e análise das amostras

Foram realizadas coletas durante um período de três anos (novembro de 2014 à dezembro de 2017), em dois pontos da Lagoa de Jacarepaguá, JAC 18 (S 22° 58′ 36.8″, W43° 22′ 48.5″) e JAC 20 (S 22° 59′ 14.1″, W 43° 24′ 9.6″), a fim de monitorar a ocorrência de florações de cianobactérias e variações da qualidade de suas águas. Em campo, foram medidas na sub superfície, 0,5 metros e no fundo: temperatura da água, salinidade, concentrações de oxigênio dissolvido, pH e potencial redox, através de sonda multiparamétrica (YSI modelo 600 QS); a profundidade nos pontos de coleta foram medidos utilizando um profundimetro; a transparência da água foi medida através da profunidade de desaparecimento do disco de Secchi e a zona eufótica estimada como 2,7 vezes a profundidade de Secchi (COLE, 1994). Amostras integradas da coluna d'água de cada ponto de coleta foram obtidas com um tubo coletor de PVC de 1,0 m e 4,2 cm de diâmetro para a medição dos outros parêmetros. Amostras para quantificação das populações fitoplanctônicas foram fixadas imediatamente com solução de lugol. Amostras para análises de clorofila, nutrientes e alcalinidade foram acondicionadas em frascos plásticos, resfriadas e levadas ao laboratório. No laboratório, amostras filtradas

(filtros GF-3 - Macherey-Nagel) e não filtradas (totais) foram congeladas até o momento da análise de nutrientes dissolvidos e totais. A determinação da concentração de clorofila-*a* foi realizada através de analisador de fitoplâncton (PHYTOPAM, Walz-Alemanha). A alcalinidade foi determinada através do método volumétrico por titulação. As concentrações dos nutrientes dissolvidos (fósforo solúvel reativo, nitrito, nitrato e amônia) e totais (fósforo e nitrogênio totais) foram determinadas utilizando sistema automático de análise por injeção de fluxo - FIA (FIAlab, modelo 2500), segundo os protocolos do fabricante. O nitrogênio inorgânico dissolvido (NID) considerou o somatório das concentrações de nitrito, nitrato e amônia.

As populações fitoplanctônicas foram enumeradas de acordo com método de sedimentação (UTERMÖHL, 1958) e quantificado em campos aleatórios (UHELINGHER, 1964) usando a microscópio invertido (OLUMPUS, CKX41). O biovolume fitoplanctônico ($mm^3.L^{-1}$) foi estimado através de formas geométricas aproximadas (HILLEBRAND et al., 1999). O biovolume de diatomáceas foi considerado subtraindo o valor correspondente ao vacúolo, sendo 35% nas espécies penadas e 65%, nas cêntricas (ROUND et al., 1990). Para a determinação dos grandes grupos taxonômicos de algas foram adotados os critérios de VAN DEN HOECK et al*.,* (1997), ROUND et al., *(*1990) e KOMÁREK e ANAGNOSTIDIS (1999, 2005). Para a inclusão dos táxons nos diferentes grupos funcionais do fitoplâncton, foram selecionadas as espécies que contribuíram com no mínimo 5% para o biovolume total em ao menos uma amostra. As espécies foram classificadas de acordo com os grupos funcionais de Reynolds (GFR, REYNOLDS et al., 2002; PADISÁK et al., 2009).

2.2.2 Análises estatísticas

As diferenças entre os dois pontos de coleta e entre os dois períodos climatológicos, considerando juntos todos os três anos de coleta, foram avaliadas pelo teste *t*-Student. Quando não normais, os dados foram transformados em Log10

(X+1) para atender ao critério da análise, quando não alcançada a normalidade o teste Mann-Whitney foi realizado. Em todos os testes as diferenças foram consideradas significativas quando P<0,05. Foram avaliados nesse estudo dois períodos climatológicos, um quente-chuvoso que incluiu os meses de novembro a março, e um período frio-seco que compreendeu os meses de abril a outubro. Correlações múltiplas entre o fitoplâncton e as variáveis ambientais foram testadas através da correlação de Spearman para evidenciar a relação entre os descritores ambientais e o biovolume dos principais grupos funcionais fitoplanctônicos observados na lagoa. Estas análises foram realizadas com auxílio do pacote de ferramentas estatístiscas do software SigmaPlot 12.5.

Inicialmente a análise de correspondência sem tendência (DCA) foi realizada com os descritores ambientais (temperatura da água, pH, salinidade, alcalinidade, $Z_{eu,}$ NO_2^-, NO_3^-, NH_4^+, FSR, PT e NT) e o biovolume dos grupos fitoplantônicos, e evidenciou um gradiente ambiental curto (<3,0), indicando a utilização de um método de ordenação linear como o mais recomendado (TER BRAAK e SMILAUER, 1998). Desse modo, a análise de redundância canônica (RDA) foi então realizada para evidenciar quais fatores foram responsáveis pela dinâmica da floração de cianobactérias e das algas eucarióticas na Lagoa de Jacarepaguá (TER BRAAK, 1986). Na RDA foram consideradas apenas variáveis não colineares: temperatura da água, pH, salinidade, alcalinidade, $Z_{eu,}$ NO_2^-, NO_3^-, NH_4^+, FSR, PT e NT. A seleção a *posteriori* (forward selection), realizada através do teste de Monte Carlo com 999 permutações, foi aplicada para determinar quais variáveis ambientais apresentam relação significativa com a dinâmica dos grupos funcionais (p<0.05). Os dados foram transformados em Log10 (X+1) antes das análises e executados utilizando software CANOCO 5.0 (TER BRAAK e SMILAUER, 1998).

Com o objetivo de evidenciar as variáveis ambientais relacionadas à períodos de ausência das florações de cianobactérias, aumento, e elevado biovolume fitoplanctônico, foi realizada a árvore de classificação e regressão (CART). Assim, as amostras foram classificadas em três grupos de acordo com o biovolume fitoplanctônico encontrado: 1 (com biovolume $\leq$ 3 mm^3 L^{-1}); 2 (com biovolume > 3 e < 50 mm^3 L^{-1}); e 3 (biovolume $\geq$ 50 mm^3 L^{-1}). A árvore de classificação foi construída através de partições binárias de amostras, buscando a

constituição de subamostras internamente homogêneas. Nesse processo, a variável preditora é selecionada através de optimizações considerando a soma do quadrado dos erros (BREIMAN, 2001). A análise foi realizada através da função “rpart” do pacote “mvpart” no software R.

2.3 **Área de estudo**

A Lagoa de Jacarepaguá está localizada na baixada de Jacarepaguá ao sul da costa no município do Rio de Janeiro, entre os paralelos S’22’58’ e 23’00’ e meridianos O’43°21’ e 43°25’. É limitada ao norte pelo maciço da Pedra Branca, ao Sul pelo Oceano Atlântico e a Oeste pelo maciço da Tijuca (CALHEIROS, 2006). As lagoas do Camorim, Tijuca e Marapendi formam o complexo de lagoas da baixada de Jacarepaguá (DOMINGOS, 2001) (Figura 2). A lagoa de Jacarepaguá é a mais interiorizada do complexo e possui conecção direta com a lagoa do Camorim que, na verdade, funciona como um canal ligando-a à lagoa da Tijuca, através desta se conecta com o mar pelo canal da Joatinga. A Lagoa de Jacarepaguá é um sistema oligohialino, raso, com profundidade média de 3,3 m, com 3,7 km^2 de espelho d’água e volume de 12.276.000 m^3 (SANTOS, 2014). Devido as elevadas concentrações de nutrientes vem sendo classificada como hipereutrófica onde florações de cianobactérias são constantes, e contaminação do pescado por microcistinas tem sido observada (MAGALHÃES et al., 2001; GOMES et al., 2009).

Figura 2 - Complexo Lagunar de Jacarepaguá

Legenda: Imagem do complexo lagunar de Jacarepaguá evidenciando os pontos de coleta (JAC 20 e JAC 18) e as principais paisagens ao redor da Lagoa de Jacarepaguá.
Fonte: https://earth.google.com/web/, 2018.

2.4 **Resultados**

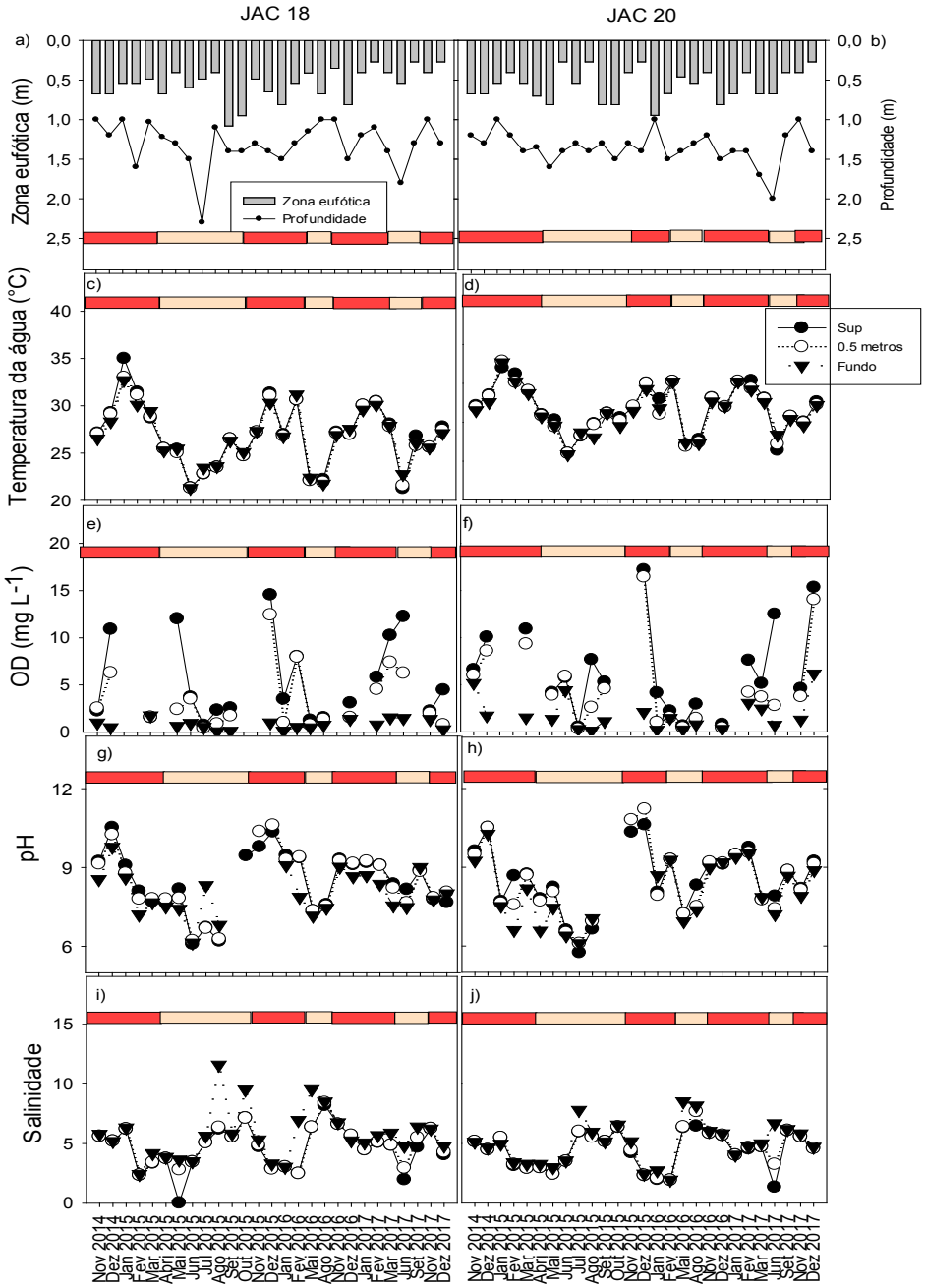
2.4.1 Regime físico e químico

A Lagoa de Jacarepaguá é um sistema raso onde a profundidade máxima chegou até 2,3 metros no ponto JAC 18 e 2,0 metros no JAC 20. A zona eufótica em nenhum momento atingiu a profundidade máxima iluminando sempre parte da coluna da água, 0,6% em média. No ponto JAC 18 a profundidade da zona eufótica variou entre 0,27 m no mês de setembro de 2017 e 1,1 m no mês de setembro de 2015 (figura. 3a). Já em JAC 20 a profundidade da zona eufótica variou de 0,3 m no mês de agosto de 2015 à 0,9 m no mês de janeiro de 2006 (figura 3b).

Médias significativamente mais elevadas ($P \leq 0{,}001$) de temperaturas da água foram observadas no período que abrange o verão (novembro a março) em ambos os pontos de coleta sem apresentar diferença significativa entre os pontos. Durante esse período a temperatura média foi de 28,9 ± 2,1 °C com

máxima de 35 °C observada no mês de janeiro de 2015 (figura. 3 c,d). Durante o período mais frio que compreendeu os meses de abril a outubro a temperatura média foi de 23,9 ± 1,9 °C alcançando uma temperatura mínima de 21,0 °C em junho de 2015 (figura 3C). Em relação ao perfil vertical pouca variação pode ser observada entre as diferentes profundidades, entretanto as maiores temperaturas foram observadas na superfície na maior parte do tempo.

Figura 3 - Variação espacial e temporal das principais variáveis limnológicas na Lagoa de Jacarepaguá.



Legenda: Produndidade da zona eufótica e profundidade do ponto de coleta (a, b), perfis de temperatura da água (c, d), oxigênio dissolvido (e, f), pH (g, h) e salinidade (I, j) na Lagoa de Jacarepaguá abrangendo o período de novembro de 2014 a dezembro de 2017 em dois diferentes pontos de amostragem: JAC 18 e JAC 20. O período quente-chuvoso estão evidenciados em vermelho e os meses referentes ao período frio-seco estão representados em bege.

Fonte: O autor, 2018

A coluna da água esteve estratificada em relação às concentrações de oxigênio dissolvido com maiores concentrações na superfície. Ao longo dos meses a média de oxigênio na superfície variou de 5,97 ± 4,59 mg L^{-1}, sem haver diferença significativa entre os períodos e os pontos amostrados. No fundo da lagoa condições hipoxicas < 1 mg L^{-1} foram observadas na maioria dos meses (figura 3 e, f).

Os valores de pH obtidos no monitoramento variaram de levemente ácidos a alcalinos em ambos os pontos. Em relação ao perfil vertical pouca variação foi observada, entretanto maiores valores de pH foram registrados na superfície durante a maior parte do tempo. Em relação aos meses de coleta os períodos mais quentes apresentaram pH significativamente mais elevados ($P<0,001$) com valores médios de 9,1 ± 0,9 enquanto o período mais frio apresentou valores médios de 8,5 ± 1,2 (figura. 3 g, h).

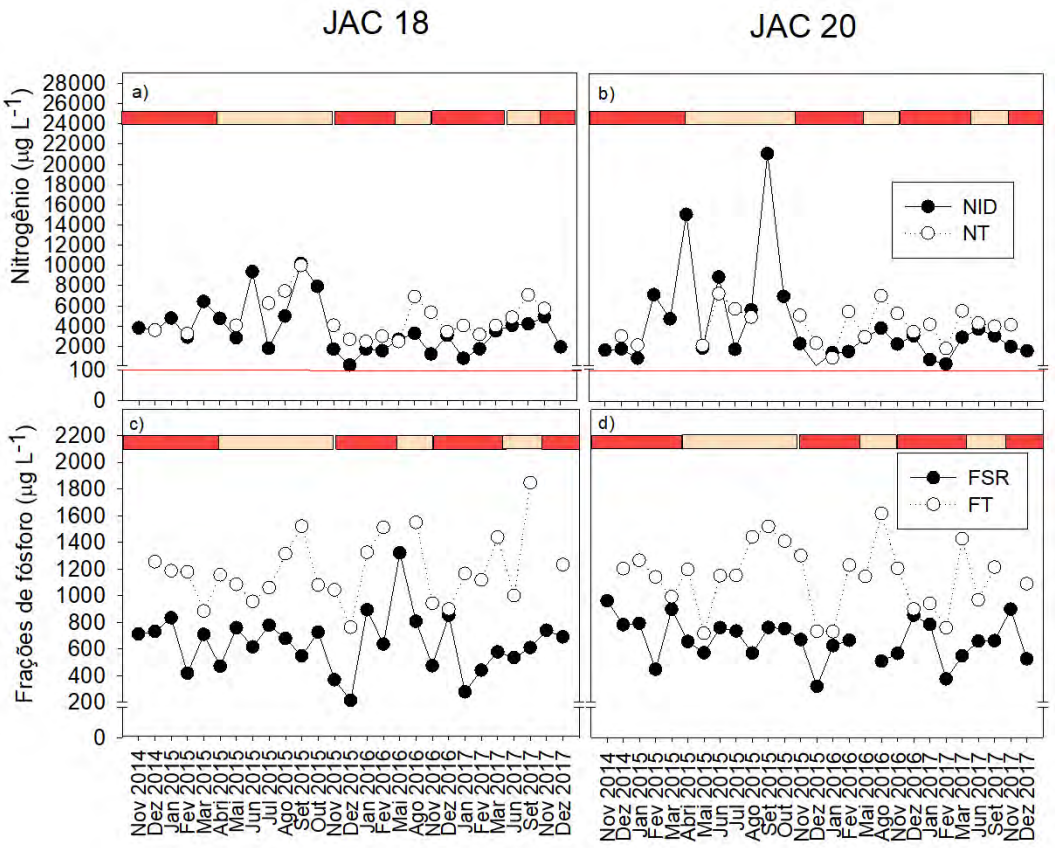
A lagoa de Jacarepaguá apresentou características oligohalinas com salinidade não ultrapassando 8,2 S na superfície e 11,59 S no fundo. Considerando as médias de salinidade na superfície, esta não variou significativamente entre os pontos e os períodos. Entre os meses de coleta, a superfície da água apresentou valores médio de 4,52 ± 1,67 S, onde a maior salinidade de 8,2 S foi observada no mês de agosto de 2016 (figura 3 I, j).

As concentrações de nitrogênio total (NT) e inorgânico dissolvido (NID) não variaram significativamente entre os pontos de coleta porém foram significativamente mais elevadas no período mais quente ($P<0,05$) com média de NT de 2156,1 ± 1544,7 µg L^{-1} enquanto que o NID foi significativamente maior ($P<0,01$) no período mais frio, apresentando valores médios de 5943,85 ± 4745,6 µg L^{-1}. O íon amônio foi a fração do nitrogênio inorgânico dissolvido mais importante em todo o período representando 87 ± 13 % do NID com exceção apenas do mês de fevereiro de 2015 onde o nitrato representou 43 ± 40% (figura 4 a e b).

O fósforo total apresentou valores médios significativamente menores de 1092,8 ± 233,3 µg L^{-1} no período mais quente e valores de 1247,7 ± 274,5 µg L^{-1} no período mais frio sem apresentar diferença significativa entre os pontos de coleta. Já a fração inorgânica dissolvida (FSR) não apresentou diferença significativa entre os

pontos de coleta e nem entre os perídos, estando sempre elevadas, com média de 675,1 ± 260,1 µg L^{-1} considerando todo o perído de estudo (figura 4 c,d).

Figura 4 - Variação espacial e temporal das concentrações de nitrogênio e fósforo na Lagoa de Jacarepaguá.



Legenda: Concentrações de NID (nitrogênio inorgânico dissolvido) e NT (nitrogênio total - a,b), e concentrações de FRS (fósforo solúvel reativo) e fósforo total (FT – c,d), na lagoa de Jacarepaguá no período de novembro de 2014 a dezembro de 2017 em dois diferentes pontos de amostragem: a) JAC 18; e b) JAC 20. A linha vermelha assinalada a concentração de NID=100 µg L^{-1} considerada limitante ao crescimento fitoplanctônico (Reynolds 1997). Os meses referentes ao período quente-chuvoso estão evidenciados em vermelho e os meses referentes ao período frio-seco estão representados em bege.

Fonte: O autor, 2018

2.4.2 Comunidade fitoplanctônica

2.4.2.1 Composição taxonômica

A comunidade fitoplanctônica na Lagoa de Jacarepaguá ao longo do período estudado foi composta por um total de 58 táxons, sendo eles distribuídos dentre as classes: Cyanobacteria (14), Bacillariophyceae (11), Cryptophyceae (10), Chlorophyceae (23).

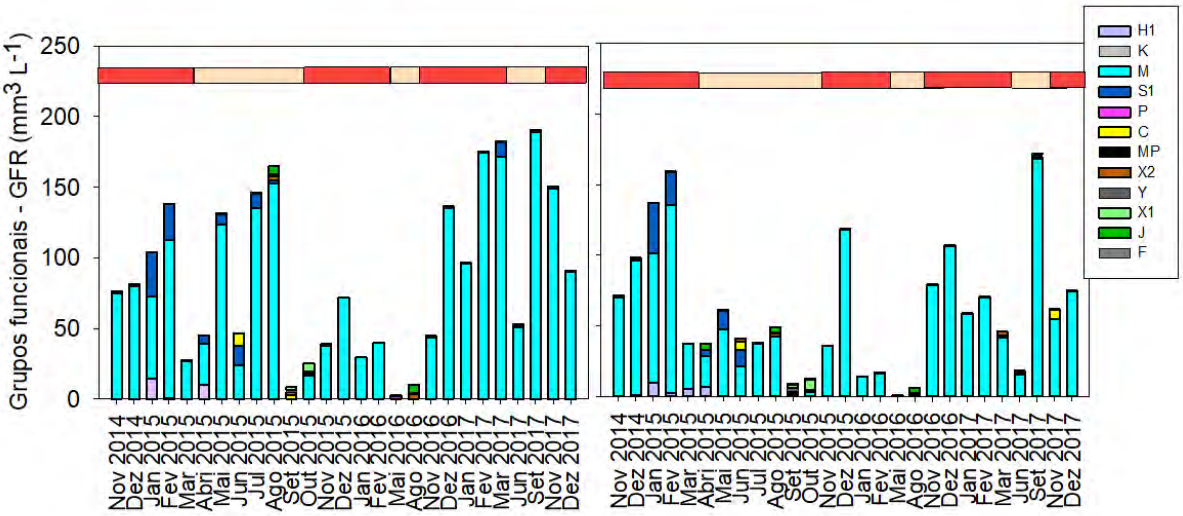
2.4.2.2 Biovolume fitoplanctônico

O biovolume fitoplanctônico na Lagoa de Jacarepaguá foi marcado por dominância da espécie de cianobactéria *Microcystis aeruginosa* em quase todos os meses estudados. Os pontos de coleta não apresentaram diferenças significativas e maiores biovolumes fitoplanctônicos foram observados no período mais quente ($P<0,05$), quando foi observado valor médio de 83,7 ± 46,7 $mm^3 L^{-1}$ e dominância de *M. aeruginosa* que contribuiu com 88,7 ± 2,76 % do biovolume total nesse período.

Considerando os grupos funcionais de Reynolds, os 58 taxons foram agrupados em 12 grupos funcionais (figura 5). Dentre estes podemos destacar os grupos M, H1, S1, C, MP, X2, Y, X1, J, F com espécies que contribuíram com 5% do biovolume total em pelo menos uma amostra. O grupo M composto por *M. aeruginosa* apresentou dominância elevada em quase todo o período estudado. Durante as florações de M. aeroginosa, um aumento na contribuição dos grupos S1 e H1 ocorreu nos meses de janeiro e fevereiro de 2015 contribuindo respectivamente com 22 ± 6,9 e 5,7 ± 6,2% do biovolume fitoplanctônico. A exeção da dominância do grupo M foi observada apenas nos períodos mais frios durante os

meses de setembro e outubro de 2015 e maio e agosto de 2016 quando o biovolume fitoplanctônico se encontrou reduzido e marcado pelo aumento na contribuição dos grupos X1, X2, Y, J, F e C.

Figura 5 - Biovolume do fitoplâncton representado por grupos funcionais na Lagoa de Jacarepaguá.



Legenda: Biovolume dos grupos funcionais fitoplanctônicos na superfície da Lagoa de Jacarepaguá no período de novembro de 2014 a dezembro de 2017 em dois diferentes pontos de amostragem: a) JAC 18; e b) JAC 20. Os meses referentes ao período quente-chuvoso estão evidenciados em vermelho e os meses referentes ao período frio-seco estão representados em bege.

Fonte: O autor, 2018

2.4.3 Relações entre os grupos funcionais e as variáveis limnológicas

Em relação aos grupos funcionais com maior contribuição, o grupo M apresentou correlação significativamente positiva com a temperatura da água, assim como o grupo H1, enquanto que correlações negativas de M foram observadas com Z_{eu} e N-NH_4 (Tabela 1). A Zeu e o N-NH4 também foram importantes para o grupo F, enquanto que a temperatura da água apresentou correlação negativa com os grupos X1, X2 e J. O grupo H1 apresentou correlação

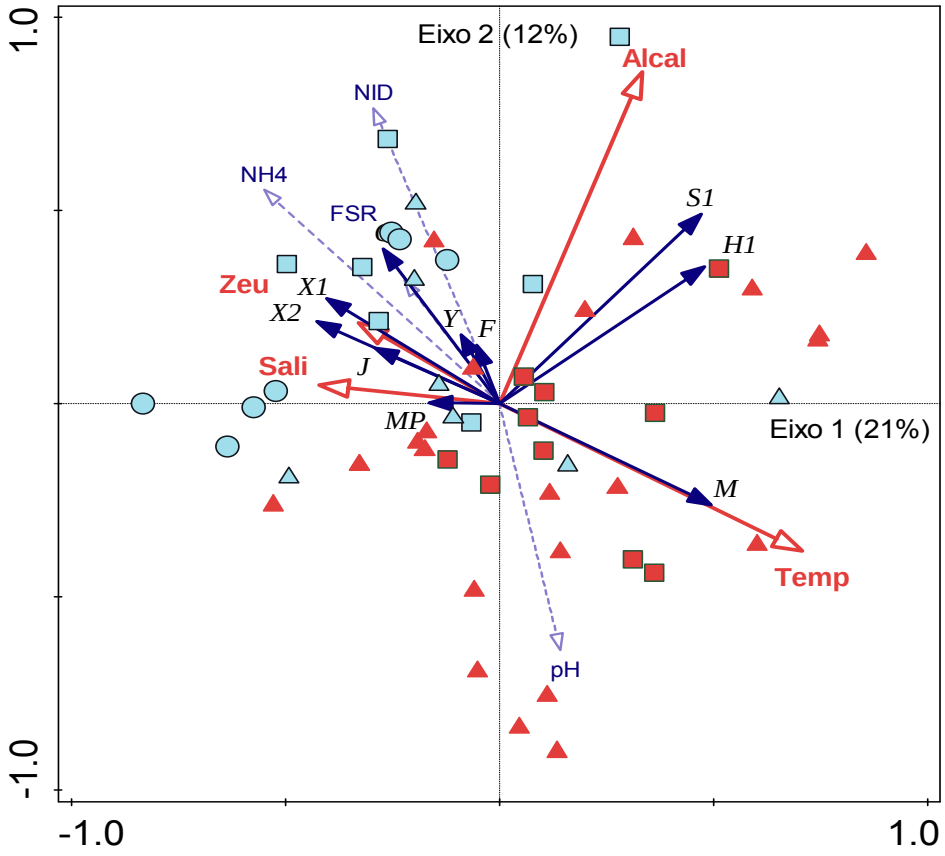
positiva com a temperatura da água e negativa com o nitrogênio total. Em comum com os grupos S1 e C, o grupo H1 também apresentou correlações positivas com nitrato e alcalinidade. A salinidade da água também se mostrou importante e esteve correlacionada positivamente com os grupos X1, X2, MP (Tabela 1).

Tabela 1 - Correlação de Sperman entre os principais grupos funcionais fitoplanctônicos e as principais variáveis limnológicas (apenas valores significativos P<0,05 estão apresentados).

Variáveis/Classes	M	H1	S1	C	MP	X2	X1	J	Y	F
Temp	0,38	0,38				-0,64	-0,31	-0,32		
Z_{eu}	-0,44									0,28
pH						-0,50				
Alcalinidade		0,55	0,61	0,34	0,41					
Condutividade					0,27	0,35	0,46			
Salinidade					0,27	0,36	0,46			
N-NH_4	-0,34				0,30	0,48				0,32
NO_2			0,39							
NO_3		0,41	0,48	0,28						
FSR										
NT		-0,41				0,45			0,28	
PT					0,33					

A análise de redundância apresentou a relação entre as principais variáveis limnológicas e a sazonalidade das florações de cianobactérias. A RDA, utilizando os grupos funcionais de Reynolds, explicou significativamente 35% da distribuição das amostras onde o eixo I contribui com 61% e eixo II com 34% dessa explicação. A temperatura da água (F= 7,6; P=0,001) esteve positivamente relacionada com o eixo I e relacionada positivamente com o maior biovolume do grupo M. A alcalinidade da água (F= 7,6; P=0,002) foi importante para o eixo II e esteve relacionada positivamente com os grupos H1 e S1, enquanto que o restante dos grupos, X1, F, J, X2, Y, C, MP e P foram relacionados positivamente com os maiores valores de salinidade da água (F=3,5; P=0,018) e o aumento da zona eufótica (F=4,4 ; P=0,01; Figura 6).

Figura 6 - Análise de redundância (RDA) entre as principais variáveis limnológicas e a dinâmica do biovolume dos grupos funcionais fitoplanctônicos na Lagoa de Jacarepaguá.

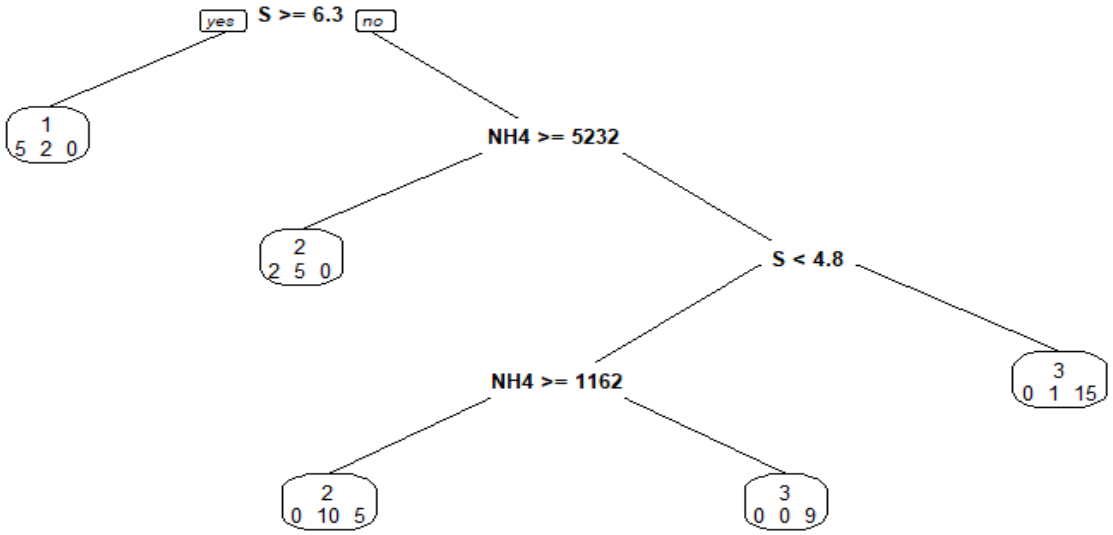


Legenda: Diagrama de ordenação da RDA utilizando as amostras dos pontos JAC 18 e 20, compreendendo o período de novembro de 2014 a dezembro de 2017. Destacados em azul claro, estão os meses referentes ao período frio-seco. Em vermelho, estão destacados os meses referentes ao período quente-chuvoso. Os triângulos representam o período em que foram observados os maiores valores de biovolume fitoplanctônico (≥ 50 mm^3 L^{-1}), enquanto que os quadrados representam os valores intermediários (> 3 e < 50 mm^3 L^{-1}) e os círculos correspondem aos períodos caracterizados pela ausência de floração de M. *aeruginosa* e baixo biovolume fitoplanctônico (≤ 3 mm^3 L^{-1}). Os vetores vermelhos correspondem às variáveis limnológicas significativas (P<0,05) para a ordenação das amostras: temperatura da água (Temp), limite da zona eufótica (Z_{eu}), salinidade (sali) e alcalinidade (alcal). Os vetores pontilhados correspondem a variáveis utilizadas como suplementares. Os vetores cinzas correspondem aos grupos funcionais observados na lagoa de Jacarepaguá: M, S1, H1, C, MP, P, X2, Y, X1, J, F.

Fonte: O autor, 2018

A árvore de classificação e regressão evidenciou que a salinidade e a concentração de NH_4 estiveram relacionadas a variação da biomassa fitoplanctônica e aos períodos em que foram observadas ou não florações de cianobactérias. Nos períodos de maior salinidade (≥ 6,3 S) não foram observadas florações de cianobactérias e as biomassas fitoplanctônicas foram baixas, resultando na separação do grupo 1 (Figura 7). Nos períodos em que a salinidade foi mais baixa, porém a concentração de NH_4 foi elevada, foram observadas elevadas biomassas fitoplanctônicas (grupo 2) especialmente de cianobactérias. Os períodos do estudo caracterizados por florações de cianobactérias com biomassas > 50 mm^3 L^{-1}, apresentaram, em geral, concentrações de NH_4 mais baixas e salinidades baixas (<4,8) ou moderadas (4.8 a 6.3). O íon Amônia também foi um importante fator onde os maiores biovolumes de *M. aeruginosa* que foram observados entre as concentrações de 1162 e 5232 µg L^{-1}.

Figura 7 - Árvore de classificação e regressão (CART) relacionando e os períodos sem floração (1), de floração menos intensa (2) e mais intensa (3), com as principais variáveis ambientais.



Legenda: Árvore de classificação e regressão (CART) utilizando as variáveis ambientais e o biovolume de cyanobacteria agrupados em três grupos de acordo com o biovolume de cyanobacteria observado: Grupo I (≤ 3 mm^3 L^{-1}), Grupo II (> 3 e <50 mm^3 L^{-1}), Grupo III (≥50 mm^3 L^{-1}). Cada nódulo da ramificação corresponde a uma condição determinante para a ocorrência do grupo. Os números na região inferior das caixas representam o número de casos observados. Originalmente o grupo 1 possuí 7 casos, o grupo 2 possuí 18 casos e o grupo 3 possuí 29 casos no total.

Fonte: O autor, 2018

2.5 **Discussão**

A Lagoa de Jacarepaguá, durante o período estudado, foi caracterizada pelo elevado estágio de eutrofização com intenso acúmulo de nutrientes e presença constante de florações de cianobactérias, como também observado em estudos anteriores (FERRÃO FILHO et al., 2002a; GOMES et al., 2009). As elevadas concentrações de fósforo e nitrogênio totais, somadas à baixa transparência da água e concentrações de clorofila-*a* acima de 25 μg L^{-1} (NÜRNBERG, 1996) classificam a lagoa como hipereutrófica na maior parte do ano.

A estrutura da comunidade fitoplanctônica na Lagoa de Jacarepaguá foi caracterizada pelos maiores biovolumes do grupo funcional M, composto integralmente pela espécie *Microcystis aeruginosa*, dominante em quase todos os meses do estudo. A dominância de cianobactérias ocorre geralmente devido a abundância na disponibilidade de nutrientes que somada à elevada temperatura torna o problema ainda mais agravado (REYNOLDS et al., 2002). Em elevadas concentrações de nutrientes, como as observadas na Lagoa de Jacarepaguá, as cianobactérias encontram um ambiente propício para seu crescimento dominando no ambiente devido a diversas vantagem competitivas, como preferência por águas com pH elevado, capacidade de algumas espécies em regular seu posicionamento na coluna de água, possuir alta taxas de crescimento em temperaturas elevadas e formar colônias que dificultam o seu consumo pelo zooplâncton.

Devido a capacidade de utilizar, com menor custo energético, fontes alternativas de carbono as cianobactérias são favorecidas em águas alcalinas. Esta vantagem pode ter somado para a o aumento da contribuição do grupo S1 e H1 no período de maior alcalinidade da água e para a dominância do grupo M, quando o pH esteve elevado a maior parte do tempo. Os grupos S1 e H1 são compostos por cianobactérias filamentosas, onde os indivíduos do grupo H1 são capazes de fixar nitrogênio. O grupo M é formado por cianobactérias coloniais portadoras de aerótopos, que conseguem usar diretamente o HCO_3, abundante em pH alcalino, para a produção primária (TALLING, 1976). Mais dispendiosamente, outras algas,

como as algas verdes, precisam da utilização de enzimas como a anidrase carbônica para absorverem HCO_3 fazendo com que esta atividade seja mais lenta e custosa. Essa condição faz com que as cianobactérias apresentem uma taxa de crescimento mais elevada quando comparada às algas eucarióticas (SHAPIRO, 1984, 1997). Em experimento de laboratório, YANG et al., (2018) demonstraram a preferência de *Microcystis aeruginosa* por águas neutras a levemente alcalinas onde a vantagem competitiva só é perdida quando a temperatura da água se encontra mais baixa, o que desfavorece o seu crescimento.

A temperatura da água foi o principal fator modulador da dinâmica de *Microcystis aeruginosa* na Lagoa de Jacarepaguá, apontada pela correlação múltipla e pela RDA. A espécie *Microcystis aeruginosa* é uma forte competidora em temperaturas elevadas possuindo um ótimo crescimento entre 30 e 35°C (KRÜGER e ELOFF, 1978; VAN DER WESTHUIZEN e ELOFF, 1985; WATANABE e OISHI, 1985) e em temperaturas elevadas é capaz inibir o crescimento de outras algas através da síntese de exsudados, produzidos mais intensamente nessa condição ambiental (GOMES et al., 2015). A redução da população de *M. aeruginosa*, assim como a quebra de dominância desse grupo, foi observada nos meses de maio e agosto de 2016, onde temperatura da água esteve mais fria (~ 22°C), e em setembro onde a queda da população aconteceu em temperaturas mais amenas (26,13 °C). Nesses meses a estrutura da comunidade fitoplanctônica mudou, apresentando co-dominância de algas dos grupos funcionais X1, X2, C, Y, F e J. A queda da biomassa de *Microcystis aeruginosa* em períodos mais frios foi observada também por OHKUBO et al., (1993) no lago Kasumigaura, onde a temperatura esteve fortemente correlacionada com a alternância entre espécies de cianobactérias durante o início e o fim do verão. Em estudo anterior na Lagoa de Jacarepaguá, GOMES et al., (2009), avaliando a dinâmica das florações de cianobactérias durante o período de 1996, 1997, 1999 e 2007, também observaram queda da dominância de cianobactérias coincidente com os períodos mais frios, sendo substituídas principalmente por algas verdes e diatomáceas. Em experimento de competição entre *Microcystis aeruginosa* e *Scenedesmus obliqus,* a exclusão de *Microcystis aeruginosa* foi observada quando a temperatura da água se encontrava em torno de

20 °C demonstrando que essa temperatura é prejudicial ao seu crescimento (YANG et al., 2018).

Logo após o declínio da floração de *Microcystis aeruginosa* a comunidade fitoplanctônica foi composta por organismo de diversos grupos funcionais. O grupo X1 apresentou maiores biovolumes nos meses de setembro e outubro de 2015, no período em que ocorreu o desaparecimento da floração de *M. aeroginosa*. As algas pertencentes a esse grupo são pequenos r-estrategistas (PIANKA, 1970), apresentando crescimento rápido em boas condições de iluminação e disponibilidade de nutrientes, o que as tornam boas competidores em estágios transicionais (RAVEN, 1998; CALLIERI & STOCKNER, 2002; REYNOLDS, 2006; KRUK et al., 2010).

Outros grupos importantes no período de ausência da floração foram o J e F. O grupo J é composto principalmente por algas verdes de médio porte e sem traços especializados. Essas algas são sensíveis a condições de pouca disponibilidade de luz (REYNOLDS, 2002) e foram favorecidas pelo aumento da camada iluminada como evidenciado pela RDA. O grupo F é composto por algas verdes formadoras de colônias com mucilagem e sensíveis a depleção de CO_2 (REYNOLDS, 2002). A depleção de CO_2 é esperada em períodos de floração de cianobactérias em condições de pH >8,9. Entretanto, com a queda do pH após períodos de floração as condições novamente se tornam favoráveis ao seu crescimento.

Os grupos X2 e Y são compostos por organismos flagelados de pequeno e de médio a grande porte, respectivamente. Os organismos do grupo X2 apresentam crescimento rápido em condições similares ao grupo X1. Por outro lado, os integrantes do grupo Y podem ter sido favorecidos também pela condição eutrofizada da lagoa, uma vez que além da abundância de fósforo e nitrogênio, esses organismos são mixotróficos podendo utilizar também fontes orgânicas de nutrientes (TITTEL et al., 2003). Devido a constante entrada de despejos orgânicos vindo dos rios contribuintes é esperada que a concentração de carbono orgânico seja elevada durante todo o ano. Assim, a redução da biomassa com consequente aumento da disponibilidade de luz pode ter facilitado o crescimento de espécies do grupo Y. A capacidade de utilizar fonte de nutriente orgânico é também apresentada pelos grupos C e MP, compostos por diatomáceas. Os integrantes desses grupos

são sensíveis a estratificação térmica, porém, em ambientes rasos onde a mistura da água acontece frequentemente, são observados no plâncton onde podem se desenvolver (REYNOLDS, 2002; PADISAK, 2009). No geral, o aumento da disponibilidade de luz tornou possível uma comunidade fitoplanctônica mais diversa. Além da melhor disponibilidade de luz a RDA também apontou o efeito da salinidade como importante fator sobre a dinâmica desses grupos e o desaparecimento da floração.

Apesar da influência da água do mar, *M. aeruginosa* (grupo M) se desenvolveu muito bem, na maior parte do tempo, nas condições de salinidade da Lagoa de Jacarepaguá. DOMINGOS 2001, através de experimentos com uma cepa de *M. aeruginosa* da Lagoa de Jacarepaguá, observou que a salinidade até 5 S não é prejudicial ao seu crescimento. A presença *M. aeruginosa* conhecida principalmente em ambientes de água doce também já foi observada em outros ambientes costeiros, evidenciando sua capacidade de crescer nesse tipo de sistema (ROBSON e HAMILTON, 2003; LEHMAN et al., 2005). Entretanto os limites de tolerância de *M aeruginosa* a variações de salinidade é controverso na literatura e pode estar relacionado tanto a fatores ambientais quanto a características intrínsecas das cepas. Em experimentos de laboratório, por exemplo, avaliando o efeito da salinidade sobre o crescimento de *M. aeruginosa*, TONK et al., (2007) demonstraram que essa espécie apresenta elevada resistência às variações de salinidade, podendo resistir até uma salinidade de 17,5 S. Em outro experimento, ROBSON e HAMILTON (2013) observaram um ótimo de crescimento de *Microcystis aeruginosa* em salinidades até 4 S e declínio gradativo das taxas de crescimento chegando a zero em salinidade ~25 S. Em geral, a literatura aponta a tolerância de *M. aeruginosa* a valores < 10 S, porém essa tolerância está entre outros fatores, relacionada a capacidade de aclimatação da espécie (TOLAR, 2012), indicando que uma rápida elevação da salinidade pode provocar morte das células. A salinidade observada na Lagoa de Jacarepaguá, sempre menor que 8 S, parece não ter sido prejudicial ao crescimento de *M. aeroginosa* na maior parte do tempo, porém a análise de CART mostrou que valores de salinidade acima de 6,3 S estão relacionados ao desaparecimento da floração em pelo menos 5 dos 7 casos e junto com a RDA sugerem um possivel efeito combinado da salinidade com a temperatura

da água. Entretanto a possibilidade de um rápido aumento da salinidade ter provocado a queda da população de *M. aeruginosa* não deve ser descartada.

Apesar do zooplâncton não ter sido considerado nesse estudo, é razoável considerar que os organismos zooplanctônicos não exerçam eficiente pressão de herbívoria sobre a elevada biomassa de *M. aeruginosa* observada em quase todos os meses de estudo. É proposto que devido ao menor tamanho dos cladoceros em ambientes tropicais, estes não consigam exercer um controle descendente efetivo sobre as florações de cianobactérias (ARCIFA et al., 1996; DECLERK et al., 1997). O zooplâncton na lagoa de Jacarepaguá, durante os períodos de floração de cianobactérias compreendendo os meses de estudo dessa tese, foi composto principalmente por copépodos (cont. pessoal). Esse padrão foi observado também por GOMES et al., (2009) na mesma lagoa onde dominância de copépodos e rotíferos foram associados ao período de floração de *M. aeruginosa*. Entretanto, naquele estudo, mesmo em abundânica, os copépodos foram representados por poucas espécies o que mostra o efeito negativo da floração sobre a biodiversidade de outras comunidades (GOMES et al., 2009). Devido a constante eventos de floração, podem ocorrer a seleção de espécies resistentes que passam a apresentar uma abundância elevada (NANDINI e RAO, 1998; FERRAO-FILHO et al., 2002a).

A dominância de copépodos em ambientes dominados por cianobactérias em detrimento a outros grupos se deve principalmente à sua capacidade em escolher formas alternativas de nutrientes, como ciliados e flagelados heterotróficos (SOMMER e SOMMER, 2006). Uma vez que algumas cianobactérias apresentam baixo valor nutricional, como a deficiência de ácidos graxos poli-insaturados essenciais (COUTTEAU e SORGELOOS, 1997, DEMOTT e MÜLLER-NAVARRA, 1997), os organismos que conseguem selecionar seu alimento possuem vantagem na obtenção de recursos. No caso dos cladóceros, por serem filtradores generalistas, acabam sofrendo mais com a deficiência de nutrientes tendo seu crescimento desfavorecido. Além disso, *M. aeruginosa* é uma espécie potencialmente produtora de toxina e, possivelmente de outros metabólicos, os quais podem prejudicar o crescimento do zooplâncton (LÜRLING, 2003).

Nossos resultados evidenciam o elevado processo de eutrofização e a constante ocorrência de florações da cianobactérais na Lagoa de Jacarepaguá. A

espécie *M. aeruginosa* que possui diversas estratégias adaptativas favoráveis à sua dominância em ambiente com elevada concentração de nutrientes, parece estar sendo favorecida, principalmente pelas temperaturas elevadas, pela capacidade de sombrear outras espécies e pela baixa salinidade durante a maior parte do ano. O estado de degradação em que a lagoa se encontra nos mostra, sem dúvida, a importância de uma urbanização estruturada com sistemas de esgoto conectados às estações de tratamento, reduzindo significativamente as fontes alóctones de nutrientes. Apesar da positiva correlação com temperatura, é esperado que *M. aeruginosa* não consiga desenvolver bem em ambientes com baixas concentrações de nutrientes. Devido ao estado em que a lagoa se encontra é factível que medidas que reduzam a entrada de nutrientes e inviabilizem o que já se encontra na lagoa devem ser tomadas para que atividades como pesca, lazer e turismo possam ser retomadas e a lagoa volte a ser um berço para a biodiversidade.

2.6 **Referências bibliográficas**

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3 EFFICACY OF COAGULANTE AND BALLAST COMPOUNDS IN REMOVAL OF CYANOBACTERI (*MICROCYSTIS*) FROM WATER OF TROPICAL LAGOON JACAREPAGUÁ (RIO DE JANEIRO, BRAZIL).

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Abstract

Eutrophication is considered the most important water quality problem in freshwaters and coastal waters worldwide promoting frequent occurrence of blooms of potentially toxic cyanobacteria. Removal of cyanobacteria from the water column using a combination of coagulant and ballast is a promising technique for mitigation and an alternative to the use of algaecides. In laboratory we tested experimentally the efficiency of two coagulants, polyaluminium chloride (PAC) and chitosan (made of shrimp shells), alone and combined with two ballasts: red soil (RS) and the own lagoon sediment, to remove natural populations of cyanobacteria, from an urban brackish coastal lagoon. PAC was a very effective coagulant when applied at low doses (≤ 8 mg Al L^{-1}) and settled the cyanobacteria, while at high doses (≥ 16 mg Al L^{-1}) large flocks aggregated in the top of test tubes. In contrast, chitosan was not able to form flocks, even in high doses (> 16 mg L^{-1}) and did not efficiently settle down cyanobacteria when combined with ballast. The RS itself removed 33-47% of the cyanobacteria. This removal was strongly enhanced when combined with PAC in a dose dependent matter; 8 mg Al L^{-1} was considered the best dose to be applied. The lagoon sediment alone did not promote any settling of cyanobacteria but removal was high when combined with PAC. Combined coagulant and ballast seems a very efficient, cheap, fast and safe curative measure to lessen the harmful cyanobacteria bloom nuisance in periods when particularly needed.

Keywords: Bloom control, chitosan, cyanobacteria, eutrophication, mitigation, PAC.

3.1 Introduction

Anthropogenic activities have led to major degradation of coastal waters worldwide (KENNISH, 2002), where eutrophication is one of the main stressors having a severe impact on water quality (SMITH and SCHINDLER, 2009; KENNISH et al., 2014; PAERL et al., 2014). One of the key symptoms of eutrophication is the development of harmful algal blooms (HEISLER et al., 2008). There is broad scientific consensus that harmful algal blooms in coastal areas have increased worldwide over the last decades (ANDERSON et al., 2012; PAERL et al., 2014). Such blooms may have large consequences for ecosystem functioning and ecosystem services. Particularly coastal lagoons with relative long water residence time are vulnerable to nutrient enrichment (KENNISH et al., 2014) that may lead to such harmful algal blooms (HEISLER et al., 2008). Augmented human population growth, urbanization and industrialization of the coastal area are considered the most important driver of eutrophication (KENNISH, 2002; KENNISH et al., 2014). Cultural eutrophication is also viewed as the most common problem affecting Neotropical coastal lagoons (ESTEVES et al., 2008).

A severely impacted coastal lagoon is Jacarepaguá in the western part of Rio de Janeiro (Brazil), where water and sewage treatment are inadequate leading to heavy blooms of cyanobacteria, especially *Microcystis aeruginosa*, of which the toxins even accumulate in fish used for consumption (MAGALHÃES et al., 2001). It is straightforward that restricting or complete stopping of the excessive external nutrient input is the first step to manage eutrophication (COOKE et al., 2005). In Jacarepaguá Lagoon also the accumulated nutrients in the organic rich sediments are expected to delay recovery when external load reductions have been done (JEPPESEN et al., 1991; SØNDERGAARD et al., 1999; COOKE et al., 2005). Since Jacarepaguá Lagoon is located adjacent to the 2016 Olympic Park, authorities are discussing dredging as a measure to mitigate the cyanobacterial nuisance. However, this seems shutting the stable door after the horse has bolted as external nutrient inputs have not been reduced and the water will keep rich in nutrients and infested cyanobacteria. Nowadays, cyanobacteria in Jacarepaguá Lagoon are present

perennially and build more frequent and longer lasting perennial blooms that without additional measures will maintain a high risk for ongoing cyanobacterial blooms even after dredging. Therefore, we explored the possibility for efficient, cheap, fast and safe curative measures to lessen the cyanobacteria nuisance in periods when particularly needed, such as around the 2016 Olympics.

Algaecides are among the commonly used curative measures, but their application may come with shortcomings such as toxins and nutrient release or unwanted ecotoxicological side-effects (JANČULA and MARŠÁLEK, 2011; MEREL et al., 2013). Likewise, although found effective against *Plankthotrix agardhii* (MATTHIJS et al., 2012), diluted hydrogen peroxide is not considered the intervention of first choice against *Microcystis aeruginosa* – the dominant cyanobacterium in Jacarepaguá Lagoon – as toxins may be liberated (LÜRLING et al., 2014), extracellular polymeric substances may protect *Microcystis* against peroxide making higher doses necessary (GAO et al., 2015), and positively buoyant cyanobacteria biomass may accumulate at the surface (WANG et al., 2012; BARRINGTON et al., 2013) aggravating nuisance. Instead, we explored the stripping of the water column from cyanobacteria with a coagulant and ballast (e.g., LI and PAN, 2013; LÜRLING and VAN OOSTERHOUT, 2013; NOYMA et al., 2016) as a promising alternative to the use of algaecides.

In this technique, cyanobacteria in the water column are flocked and the aggregates of intact cells/colonies are settled to the sediment with entrapped ballast. As ballast, natural soils and clays are commonly used (PAN et al., 2006 a,b; 2011 a,b; ZOU et al., 2006). In stratifying inland waters with much lower external phosphorus (P) load than internal loading, cyanobacteria removal with flocculants and a lanthanum-modified clay as ballast - to chemically inactivated phosphorus released from the sediment- has also yielded very promising results (LÜRLING and VAN OOSTERHOUT, 2013b; WAAJEN et al., 2016). Recently, NOYMA et al., (2016) showed that buoyant cyanobacteria (primarily M. aeruginosa) from the freshwater Funil Reservoir (Rio de Janeiro, Brazil) could be flocked and effectively precipitated using a combination of poly-aluminium chloride (PAC) or chitosan (made of shrimp shells) with a local red soil (collected from the banks of the reservoir, consisting mainly of kaolinite clay) as ballast. Based on those results, we hypothesized that the

cyanobacteria flourishing in Jacarepaguá Lagoon could also be effectively removed from the water column using a combination of PAC or chitosan with red soil as ballast. To test this hypothesis, we ran several controlled experiments in laboratory with cyanobacteria and water from Jacarepaguá Lagoon that were exposed to different concentrations of PAC and chitosan alone and in presence of red soil. In addition, we tested the local sediment as potential ballast compound.

3.2. Material and Methods

3.2.1 Jacarepaguá Lagoon

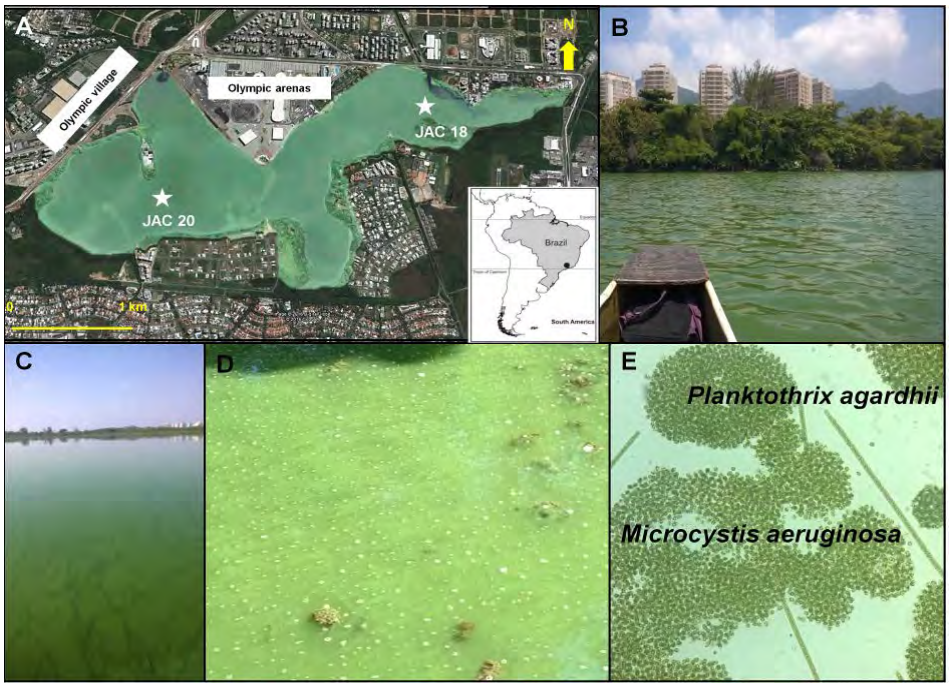
The Jacarepaguá Lagoon (43º17' - 43º30'W, 22º55' - 23º00'S) is part of a lagoon complex located in the coastal plain of at the southern coast of Rio de Janeiro, Brazil (Fig. 9). This complex consists of four main elongated lakes: Jacarepaguá, Camorim, Tijuca and Marapendi (GOMES et al., 2009). The Jacarepaguá Lagoon has a surface area of 3.7 km^2, an average depth of 3.3 m and little water exchange with the sea since it communicates with the sea through the Camorim and Tijuca lagoons. Jacarepaguá complex has the largest drainage area of the region (103 km^2) and a water inflow from rivers of about 0.8 m^3 s^{-1} (GOMES et al., 2009). The main tributaries of Jacarepaguá Lagoon flow through urban settlements surrounding the lagoon transporting not only sediment, but also industrial and household sewage (GOMES et al., 2009).

3.2.2 Sampling

On 18th November, 16th December 2014 and 19th January 2015 samples were taken at two stations in Jacarepaguá Lagoon (JAC 18 – 22º58’36.8’’S 43º22’48.5”W,

depth 1.2 m and JAC 20 - 22º59'14.1''S 43º24'9.6''W, depth 1.3m; Fig. 1A). Water transparency in each sampling station was measured using a Secchi disk. In situ, water temperature, conductivity, salinity, redox, pH, dissolved oxygen concentrations and saturation were measured with a multiparameter sonde (YSI model 600R) at three depths: top, 0.5 m and bottom. Dissolved and total nitrogen and phosphorus, chlorophyll-*a* and quantitative phytoplankton samples were collected with an integration tube (4.5 cm diameter) integrating 1 m of water column. Phytoplankton samples were fixed with Lugol's solution and nutrients samples were kept frozen until analysis.

Figure 8 - Localization and eutrophication condition of Jacarepaguá Lagoon (RJ)



Legend: Panel shows the close vicinity of some of the 2016 Olympic arenas, the Olympic park of Jacarepaguá lagoon and the two sampling stations (JAC 18, JAC 20). Panel B shows some of the Olympic park buildings as seen from the lagoon. Panels C and D show the green water of the lagoon (January 19th 2015) and panel E, the main phytoplankton species (*Microcystis aeruginosa* colonies and *Planktothrix agardhii* filaments).

Source: Author, 2018.

3.2.3 Sample analysis

The soluble reactive phosphate (SRP), ammonium ($N\text{-}NH_4^+$), nitrate ($N\text{-}NO_3^-$), nitrite ($N\text{-}NO_2^-$) and total phosphorus (TP) were measured using flow injection analysis according to manufacturer instructions (FIAlab 2500, FIALab Instruments Inc., Seattle, Washington). Chlorophyll-*a* concentrations were measured using a PHYTO-PAM phytoplankton analyser (Heinz Walz GmbH, Effeltrich, Germany). Phytoplankton populations were enumerated according to the settling technique (UTERMÖHL, 1958) in random fields (UHELINGER, 1964) using an inverted microscope (Olympus, CKX41).

3.2.4 Chemicals and materials

At station JAC 20, 10 L of surface water were collected for experiments with flocculants and ballasts. The dominant species was *Microcystis aeruginosa* (Kützing) Kützing with some undergrowth of *Planktothrix agardhii* (Gomont) Anagnostidis & Komárek. Jacarepaguá sediment was collected with a plastic core sampler on January 19th 2015. Red soil (RS) used as ballast was collected from the banks of the Funil Reservoir (22°30'S, 44°45'W, Rio de Janeiro, Brazil). Prior to use, RS was dried and grinded using pestle and sieved over 0.5 mm. This soil has been characterized according to particle size and mineralogical composition, and consisted of 99% fine earth (< 2 mm) comprised mainly of clay (≅ 50 %). Kaolinite was most abundant, followed by goethite and mica. (details see Noyma et al. 2016). The coagulant PAC-AP (polyalumnium chloride; $Al_n(OH)_mCl_{3n-m}$, $\rho \approx 1.37$ kg L^{-1}, 8.9% Al, 21.0% Cl) was obtained from Pan-Americana (Rio de Janeiro, Brazil), whereas chitosan made of shrimp shells was obtained from Polymar Ciência e Nutrição S/A (Ceará, Brazil). The chitosan was acidified with a 1% hydrochloric acid as the protonation of amino

groups makes chitosan positively charged that allows flocculation (PAN et al., 2006b). PAC was diluted 100 times in demineralised water prior to use.

3.2.5 Experiments

Aliquots of 60 mL cyanobacteria suspensions from Jacarepaguá Lagoon were transferred to 75 mL glass tubes (25x200 mm). The initial cyanobacterial chlorophyll-*a* (µg L^{-1}) as well as the Photosystem II (PSII) efficiency was determined using a PHYTO-PAM phytoplankton analyser (Heinz Walz GmbH, Effeltrich, Germany). Cyanobacteria suspensions were treated with the designated compound(s) (treatment) or left untreated (controls). Suspensions were mixed at start and placed in the laboratory at 25°C under stagnant conditions. After one hour 5 mL samples were taken from both the top and the bottom of the tubes in which chlorophyll-*a* concentrations and PSII efficiencies were measured. The pH was measured in the tubes.

In the first experiment, the effect of the floculants PAC and chitosan on the vertical distribution of the cyanobacteria was studied. The initial cyanobacteria chlorophyll-*a* concentration was 205 (± 8) µg L^{-1}. The cells were in good physiological conditions as shown by the PSII efficiency of 0.40 (± 0.04). PAC was dosed at 0, 1, 2, 4, 8, 16 and 32 mg Al L^{-1} and chitosan at 0, 1, 2, 4, 8, 16 and 32 mg L^{-1}. We tested this range considering that these flocculants are efficient to remove algae at low doses as 2 mg L^{-1} (DIVAKARAN e PILLAI, 2002; NOYMA et al., 2016). Immediately after adding the flocculants from the prepared stocks, the contents in each test tube were mixed briefly using a glass rod. Tubes were left untouched for one hour, then top and bottom samples were taken and analysed as mentioned above. The aluminium species prevailing in the PAC treatments was modelled using the program CHEAQS Next (VERWEIJ, 2015). As the input in the model were served the measured pH, the added Al concentration, a carbonate concentration of 229 mg L^{-1} as calculated from alkalinity and a phosphate concentration of 1 mg L^{-1}.

In the second experiment, the effect of different concentrations of flocculants, PAC or chitosan, on the vertical distribution of the cyanobacteria was studied in presence of a fixed dose of RS (320 mg L^{-1}). The RS dose was applied as a slurry and the dose was based on a previous study in which 320 mg L^{-1} appeared sufficient to sink positively buoyant *M. aeruginosa* out of water from the Funil Reservoir, Brazil (NOYMA et al., 2016). Similar to the first experiment, PAC was dosed from 0 to 32 mg Al L^{-1} and chitosan from 0 to 32 mg L^{-1}chitosan. Both series included a control that received no RS and no coagulant. The cyanobacteria suspension used was the same as for the first experiment. Immediately after adding the RS -by making slurry with some of the water from the test tube - the designated amount of coagulant was added and the content in the test tube mixed briefly using a glass rod. Tubes were then left untouched for one hour, after which top and bottom samples were taken and analysed as mentioned above.

In the third experiment, the effect of different concentrations of RS (0 to 320 mg L^{-1}) in presence of a fixed dose of PAC (8 mg Al L^{-1}) on the vertical distribution of the cyanobacteria was studied. The PAC dose was based on the results from the previous experiments. Based on the outcomes of the previous experiments chitosan was no longer included in this experiment. The initial cyanobacteria chlorophyll-*a* concentration was 222 (± 2) µg L^{-1} with healthy cells as reflected in a PSII efficiency of 0.53 (± 0.03). The experiment included a control without any compound added and was performed with three replicates per treatment. Immediately after adding the designated amount of RS the PAC flocculent was added and the content in the test tube mixed briefly using a glass rod. Tubes were treated as mentioned before.

In the fourth experiment, wet sediment from Jacarepaguá Lagoon was tested on its ability to settle cyanobacteria out of the Jacarepaguá water. To apply the sediment, slurry was made with 10 g L^{-1} wet sediment of which 1.92 mL was pipetted into 60 mL cyanobacteria suspension (dose of 320 mg wet sediment L^{-1}). In another treatment, the flocculent PAC was dosed at 8 mg Al L^{-1} immediately after the sediment. An additional control with only PAC addition was included. Immediately after dosing, the contents in each test tube were mixed briefly using a glass rod. The treatments were run in triplicates as outlined above.

3.2.6 Statistical Analyses

For the third (effect of different concentrations of RS in presence of a fixed dose of PAC) and fourth (ability of wet sediment to settle cyanobacteria out) experiments, the chlorophyll-a concentrations in the top and those measured at the bottom of the test tubes, as well as PSII-efficiencies and pH values were statistically evaluated through a one-way ANOVA. Chlorophyll-a concentrations were log-transformed to meet the requirement of homogeneity in variance (Equal Variance Test; Brown-Forsythe). An all pairwise multiple comparison was performed to distinguish means that were significantly different at the 0.05 level (Holm-Sidak method).

3.3 **Results**

3.3.1 Water quality in Jacarepaguá Lagoon

The water of the tropical lagoon Jacarepaguá was warm, brackish, cyanobacteria-infested, with high pH, and low transparency (Table 2). During the studied period the water temperature was reached 30.5±4.1 °C in the upper water layer and 28.9±3.3 °C near the bottom. Despite these small differences in temperature, dissolved oxygen varied from oxic (top and 0.5 m) to hypoxic in JAC 18 near on the bottom (Table 2). Low salinity (averages < 5.77 ppt) and high conductivity and alkalinity were found. Considering the high concentrations of TP, chlorophyll-*a* and the low water transparency, the lagoon can be classified as hypereutrophic (NÜRNBERG, *1996*). During the sampling period, *Microcystis aeruginosa* and *Planktothrix agardhii* together represented on average more than

90% of total phytoplankton biomass (Table 2). *Microcystis aeruginosa* was always present and comprised 56-99% of total biomass while *Planktothrix agardhii* contributions reached up 25% and 22% in JAC 18 and JAC 20, respectively.

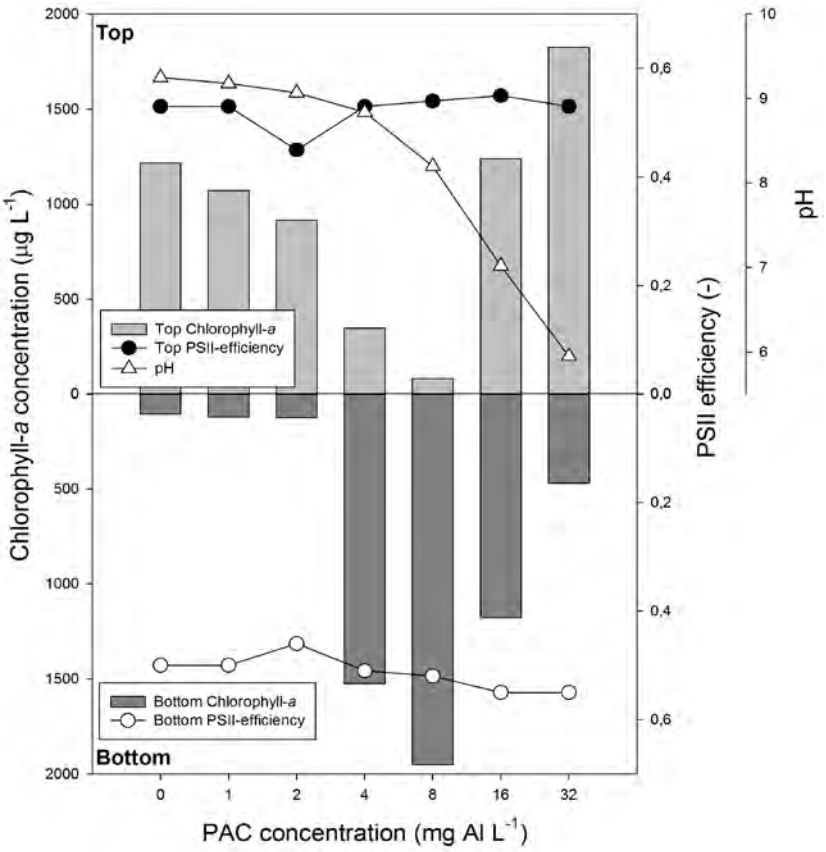
Table 2 - Average values and range of limnological variables, measured in November and December (2014) and January (2015), at two different sites in Jacarepaguá lagoon: JAC 18 and JAC 20. Samples from integration tube (integr.) and three different depths: surface, 0.5 meters and bottom. WT, water temperature; OD, dissolved oxygen; Zeu, euphotic zone; Zmax, Maximum deep; pH; Alkalinity; Salinity; DOC, dissolved organic carbon; Cond, electrical conductivity; N NO_2^-; N NO_3^- and N NH_4^- concentrations; SRP, soluble reactive phosphorus concentration; TP, total phosphorus; Chl-*a*, chlorophyll-*a* concentration; Percentage contribution of *Microcystis aeruginosa* and *Planktothrix agardhii* to total biovolume of phytoplankton.

Limnological variables/Sites	JAC 18				JAC 20			
	Integr.	Surface	0.5 m	Bottom	Integr.	Surface	0.5 m	Bottom
WT (C°)	-	30.46 27.12-35.0	29.71 27.02-33.0	29.18 26.53-32.7	-	29.21 27.13-32.0	29.39 26.93-32.85	28.93 26.53-32.7
OD (mg L^{-1})	-	6.59 2.26-10.91	4.42 2.54-6.29	0.76 0.51-1.0	-	8.33 6.60-10.06	7.29 6.0-8.57	3.43 1.71-5.15
Zeu (m)	-	0.63 0.54-0.68	-	-	-	0.63 0.54-0.68	-	-
Zmax (m)	-	1.07 1.0-1.2	-	-	-	1.17 1.0-1.3	-	-
pH	-	9.61 9.08-10.52	9.39 8.78-10.25	8.98 8.55-9.78	-	9.28 7.70-10.52	9.21 7.63-10.52	9.01 7.52-10.27
Salinity (ppt)	-	5.67 5.21-6.21	5.68 5.21-6.23	5.77 5.19-6.33	-	5.04 4.47-5.49	5.05 4.48-5.50	4.90 4.63-5.12
Cond (mS cm^{-1})	-	10.14 9.35-11.08	10.14 9.35-11.1	10.27 9.31-11.25	-	9.05 8.11-9.81	9.09 8.11-9.88	9.16 8.37-9.93
Alkal (mEq L^{-1})	4.36 4.24-4.48	-	-	-	3.95 3.54-4.35	-	-	-
N NO_2^- (mg L^{-1})	0.09 0.03-0.15	-	-	-	0.04 0.02-0.06	-	-	-
N NO_3^- (mg L^{-1})	0.80 0.34-1.26	-	-	-	0.27 0.16-0.38	-	-	-
N NH_4^- (mg L^{-1})	3.34 2.40-4.39	-	-	-	1.08 0.46-1.58	-	-	-
SRP (mg L^{-1})	0.76 0.71-0.83	-	-	-	0.84 0.78-0.96	-	-	-
TP (mg L^{-1})	1.22 1.19-1.25	-	-	-	1.23 1.20-1.27	-	-	-
Chl-*a* (ug L^{-1})	211.7 203.7 216.3	-	-	-	205.5 165.4-225.6	-	-	-
M .aeruginosa (%)	85 56-99	-	-	-	89 72-98	-	-	-
P. agardhii (%)	8 0-25	-	-	-	7 0-22	-	-	-

Effects of PAC and chitosan on the vertical position of the cyanobacteria

The cyanobacteria collected in Jacarepaguá had a strong positive buoyancy as in the absence of PAC (0 mg Al L^{-1} in Fig. 9) or chitosan (0 mg L^{-1} in Fig. 11); the chlorophyll-*a* concentrations in the top of the test tubes after one hour were, on average, respectively 11 times and 8 times higher than in the bottom. In the PAC series, at 1 and 2 mg Al L^{-1} small flocks were formed that aggregated at the water surface, while at 4 and 8 mg L^{-1} the flocks formed were dense enough to settle the cyanobacteria to the bottom of the tubes reaching a removal efficiency of 71 and 93 % respectively; at higher PAC dose large fluffy aggregates accumulated at the water surface in the tubes (Fig. 9). PSII-efficiency was unaffected at all PAC doses and was on average 0.52 (± 0.01) in the top of the tubes and 0.51 (± 0.01) in the bottom of the tubes. The pH gradually decreased with higher PAC doses; from a pH value of 9.19 (± 0.09) in 0 - 2 mg Al L^{-1}, pH 8.84 in 4 mg Al L^{-1}, pH 8.20 in 8 mg Al L^{-1}, pH 7.02, in 16 mg Al L^{-1} and pH 5.95 in a dose of 32 mg Al L^{-1} (Fig. 9).

Figure 9 - Chlorophyll-a concentrations (µg L^{-1}) in the top and bottom of the test tubes treated with PAC.

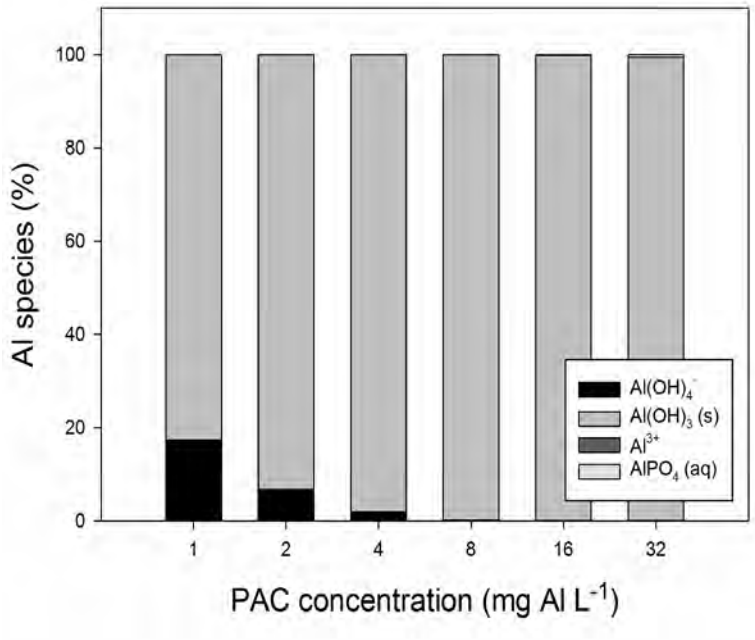


Legend: Chlorophyll-*a* concentrations (µg L^{-1}) in the top 5 mL (top light grey bars) and bottom 5 mL (lower dark grey bars) of 60 mL cyanobacteria suspension from Jacarepaguá Lagoon incubated for one hour in the absence or presence of different concentrations of the flocculent PAC (0 – 32 mg Al L^{-1}). Also included are the Photosystem II efficiencies (PSII) of the cyanobacteria collected at the water surface (filled circles) and at the bottom (open circles) as well as the pH values of the suspensions (open triangles).

Source: Author, 2018.

The most dominant Al species in all treatments was the Al $(OH)_3$ precipitate (Fig. 10), while in the lower PAC doses some aluminate was present as consequence of the higher pH. In none of the PAC treatments occurrence of Al^{3+} was predicted (Fig. 10).

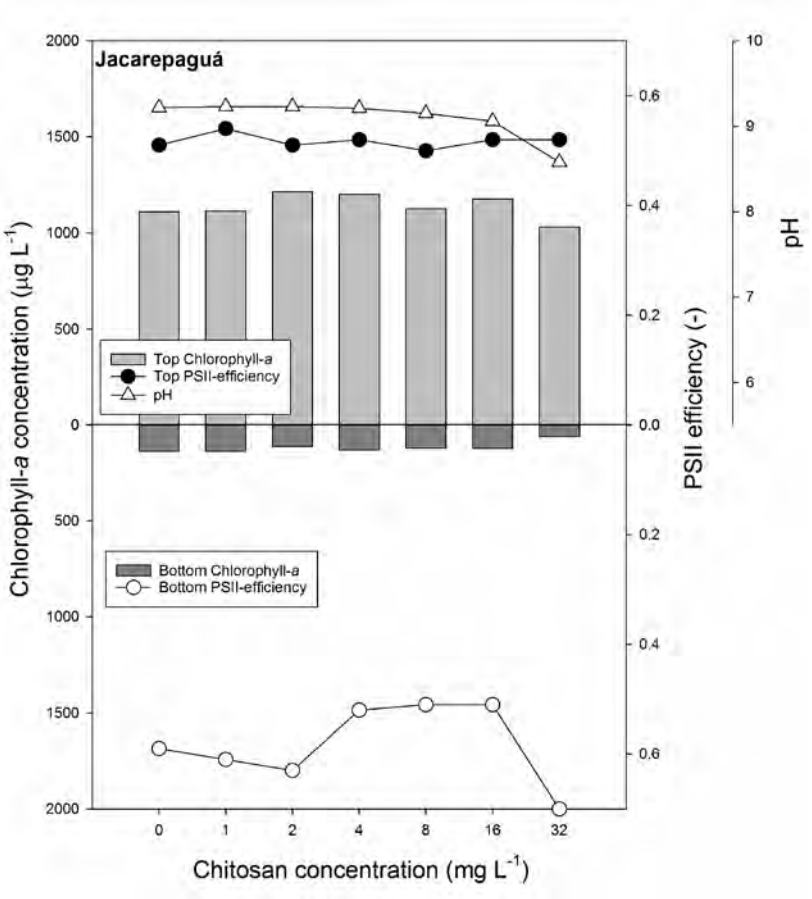
Figure 10 - Aluminum species with different PAC concentrations.



Legend: Proportion of Al species in water from Jacarepaguá Lagoon treated with different PAC concentrations.
Source: Author, 2018.

In the chitosan series, no flocks were formed; not even at the highest dose of 32 mg L^{-1} which settled only 7% of the cyanobacteria. In all treatments, most of the cyanobacteria aggregated at the water surface in the tubes (Fig. 11). PSII-efficiency was unaffected at all chitosan doses and was on average 0.52 (± 0.01) in the top of the tubes and 0.52 (± 0.07) in the bottom of the tubes. The pH remained unaffected in the chitosan range 0 to 8 mg L^{-1} (pH 9.21 ± 0.03), it was slightly lower at 16 mg chitosan L^{-1} (pH 9.06) and pH was 8.58 at the highest chitosan dose (Fig. 11).

Figure 11 - Chlorophyll-a concentrations (µg L^{-1}) in the top and bottom of the test tubes treated with Chitosan.



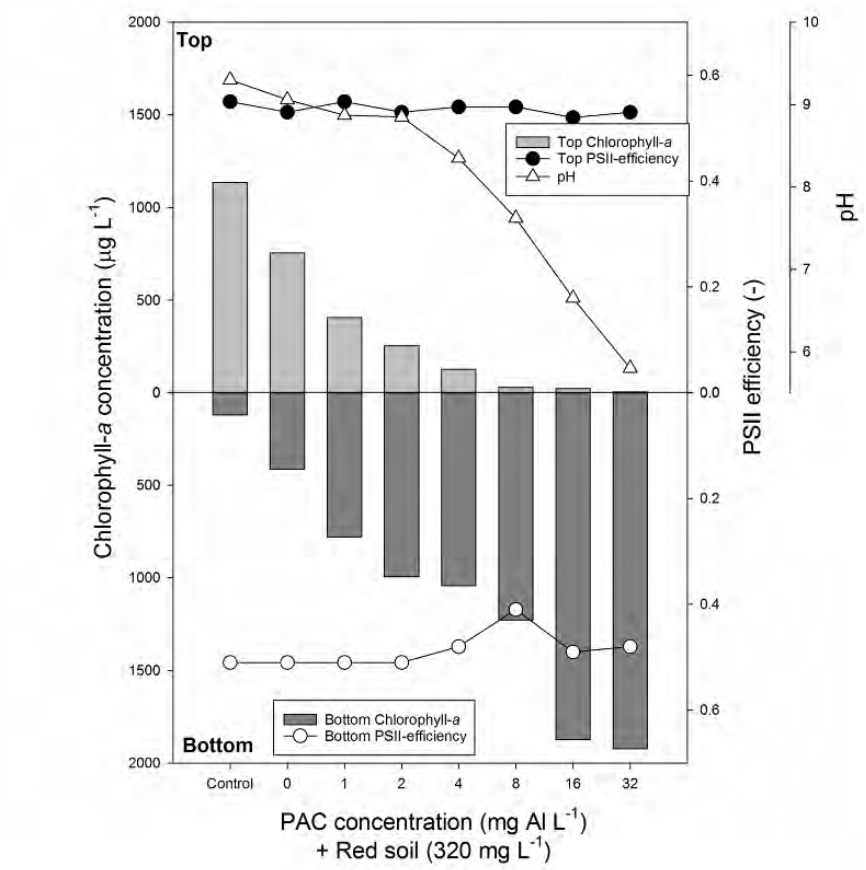
Legend: Chlorophyll-*a* concentrations (µg L^{-1}) in the top 5 mL (top light grey bars) and bottom 5 mL (lower dark grey bars) of 60 mL cyanobacteria suspension from Jacarepaguá Lagoon incubated for one hour in the absence or presence of different concentrations of the coagulant Chitosan (0 – 32 mg L^{-1}). Also included are the Photosystem II efficiencies (PSII) of the cyanobacteria collected at the water surface (filled circles) and at the bottom (open circles) as well as the pH values of the suspensions (open triangles).

Source: Author, 2018.

3.3.2 Effect of flocculants and red soil on the vertical position of the cyanobacteria

In the experiment with different concentrations PAC in presence of 320 mg L^{-1} RS, solely the RS (0 mg Al L^{-1} treatment) already caused a 33% decrease in the top chlorophyll-*a* concentration and a 3.4 times increase at the bottom (Fig. 12). Adding PAC strongly improved the cyanobacteria removal from Jacarepaguá water; from 64% removal from the top layer in 1 mg Al L^{-1} to 97% at 8 mg Al L^{-1} or even 99% removal at 32 mg Al L^{-1} (Fig. 12). PSII-efficiency was unaffected at all PAC doses and was on average 0.52 (± 0.01) in the top of the tubes and 0.52 (± 0.03) in the bottom of the tubes. The pH gradually decreased with higher PAC doses; from a pH value of 9.30 in the control to pH 7.62 in the 8 mg Al L^{-1} dose and further down to pH 5.80 in the 32 mg Al L^{-1} dose (Fig. 12).

Figure12 - Chlorophyll-a concentrations (µg L^{-1}) in the top and bottom of the test tubes treated with solely Red Soil and it combination with PAC.

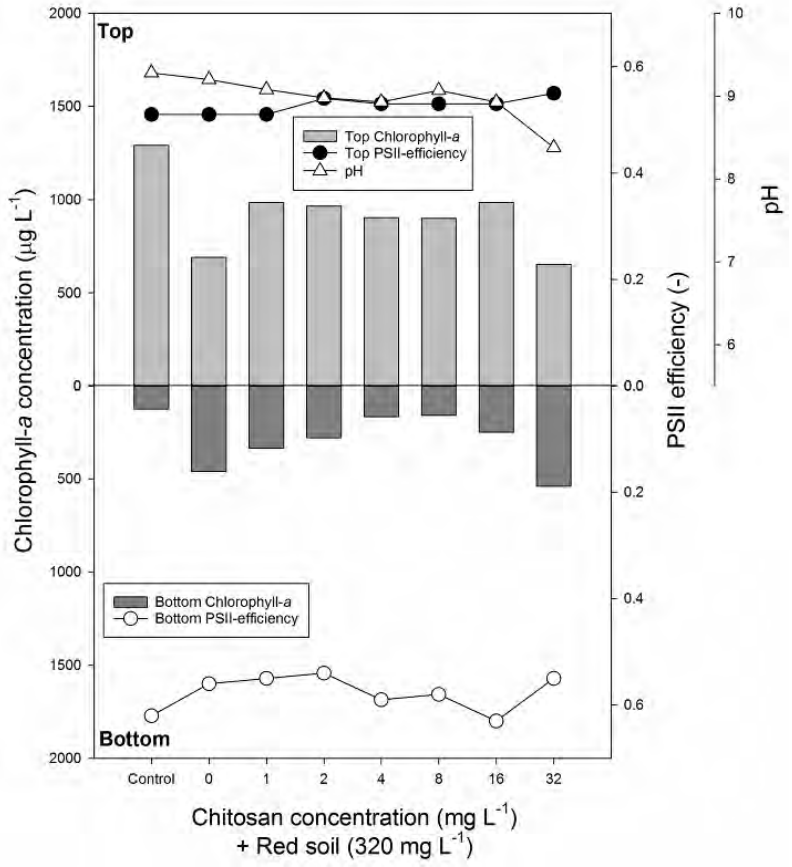


Legend: Chlorophyll-*a* concentrations (µg L^{-1}) in the top 5 mL (top light gray bars) and bottom 5 mL (lower dark gray bars) of 60 mL cyanobacteria suspension from Jacarepaguá Lagoon incubated for one hour in the absence or presence of different concentrations of the coagulant PAC (0 – 32 mg Al L^{-1}) combined with a fixed dose of red soil (320 mg L^{-1}) as ballast. Also included are the Photosystem II efficiencies (PSII) of the cyanobacteria collected at the water surface (filled circles) and at the bottom (open circles) as well as the pH values of the suspensions (open triangles).

Source: Author, 2018.

In the experiment with different concentrations chitosan mixed with a fixed dose of 320 mg L^{-1} RS, solely the RS (0 mg L^{-1} treatment) resulted in a 47% decrease in the top chlorophyll-*a* concentration and a 3.7 times increase at the bottom of the test tube (Fig. 13).

Figure 13 - Chlorophyll-a concentrations (µg L^{-1}) in the top and bottom of the test tubes treated with solely Red Soil and it combination with chitosan.



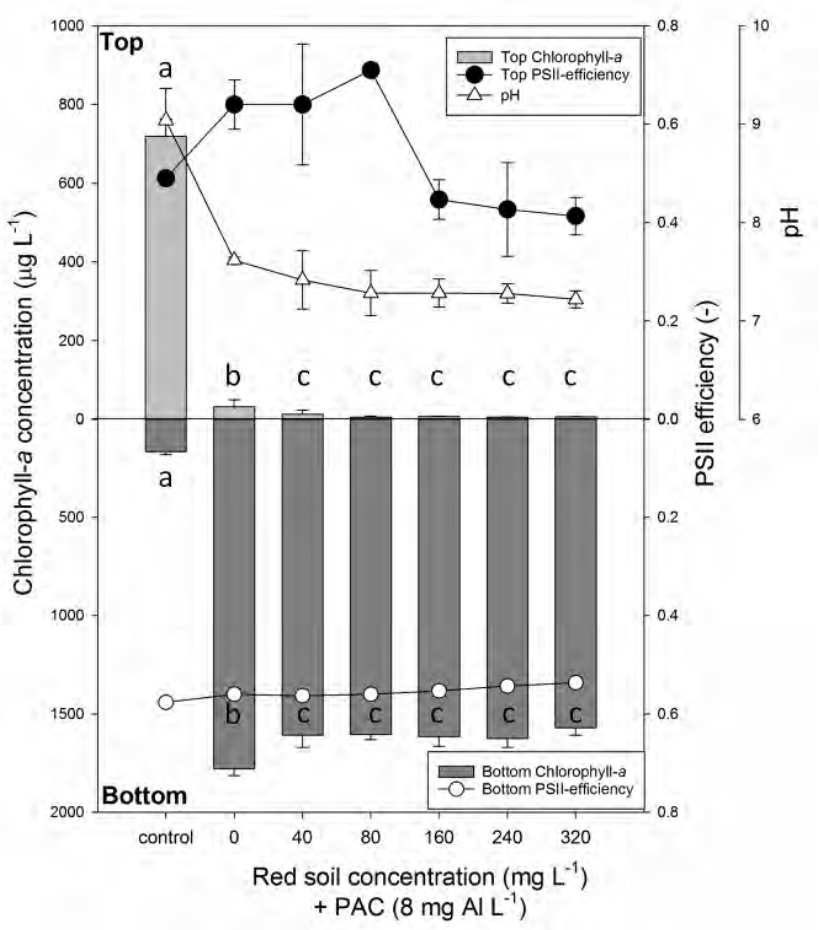
Legend: Chlorophyll-*a* concentrations (µg L^{-1}) in the top 5 mL (top light gray bars) and bottom 5 mL (lower dark grey bars) of 60 mL cyanobacteria suspension from Jacarepaguá Lagoon incubated for one hour in the absence or presence of different concentrations of the coagulant chitosan (0 – 32 mg L^{-1}) combined with a fixed dose of red soil (320 mg L^{-1}) as ballast. Also included are the Photosystem II efficiencies (PSII) of the cyanobacteria collected at the water surface (filled circles) and at the bottom (open circles) as well as the pH values of the suspensions (open triangles).

Source: Author, 2018

However, adding chitosan did not improve this and, actually, in the range 1 to 16 mg L^{-1} chitosan the reduction in the top chlorophyll-*a* concentration was only 26 (± 3) % compared to the control without anything added. Only in 32 mg chitosan L^{-1} the reduction in chlorophyll-*a* concentration in the top of the test tube (49%) was comparable to the solely RS treatment (Fig. 13). The PSII-efficiencies were similar in the top of the tubes 0.52 (± 0.01) regardless RS and RS plus chitosan additions; the same was observed in the bottom of the test tubes with a mean PSII-efficiency of 0.52 (± 0.03) (Fig. 13). The pH was on average 9.07 (± 0.13) in the control and the treatments up to a chitosan concentration of 16 mg L^{-1}; only at 32 mg chitosan L^{-1} the pH was slightly reduced to 8.38 (Fig. 13). Based on the former experiments a fixed PAC dose of 8 mg Al L^{-1} appeared most suitable in terms of removal efficiency through flocculation, influence on the pH and no toxic Al^{3+} formation, but solely the flocculating colloidal-sized $Al(OH)_3$ (s) (Fig 11).

The effect of adding additional ballast (RS) to this fixed PAC dose showed that top chlorophyll-*a* concentrations were even further reduced than the 95% reduction by solely PAC; at 40 mg RS L^{-1} more than 98% was removed and at higher dose more than 99% of the cyanobacteria were removed from the top water layer (Fig. 14). The one-way ANOVA indicated the differences were significant ($F_{6,14}$ = 63.7; p < 0.001), while the *post-hoc* comparison revealed three homogenous groups that were significantly different from each other: 1) the controls, 2) the sole PAC treatment, and 3) all PAC + RS treatments. Also for the chlorophyll-*a* concentrations measured at the bottom of the tubes, an one-way ANOVA indicated significant differences ($F_{6,14}$ = 560.6; p < 0.001), while the *post-hoc* comparison revealed three homogenous groups that were significantly different from each other: 1) the controls with the lowest chlorophyll-*a* concentrations, 2) the sole PAC treatment with the highest chlorophyll-*a*, and 3) all PAC + RS treatments (Fig. 14). The PSII efficiencies showed some variability in the top of the tube but remained fairly high (0.41 – 0.71), while in the bottom they were similar (0.55 ± 0.01). The pH in the controls (9.04 ± 0.01) was significantly higher than the pH values (mean 7.35 ± 0.20) in all other treatments ($F_{6,14}$ = 50.2; p < 0.001), which was confirmed by the *post-hoc* comparison (Fig. 14).

Figure 14 - Chlorophyll-a concentrations (µg L^{-1}) in the top and bottom of the test tubes treated with solely Red Soil and it combination with PAC.



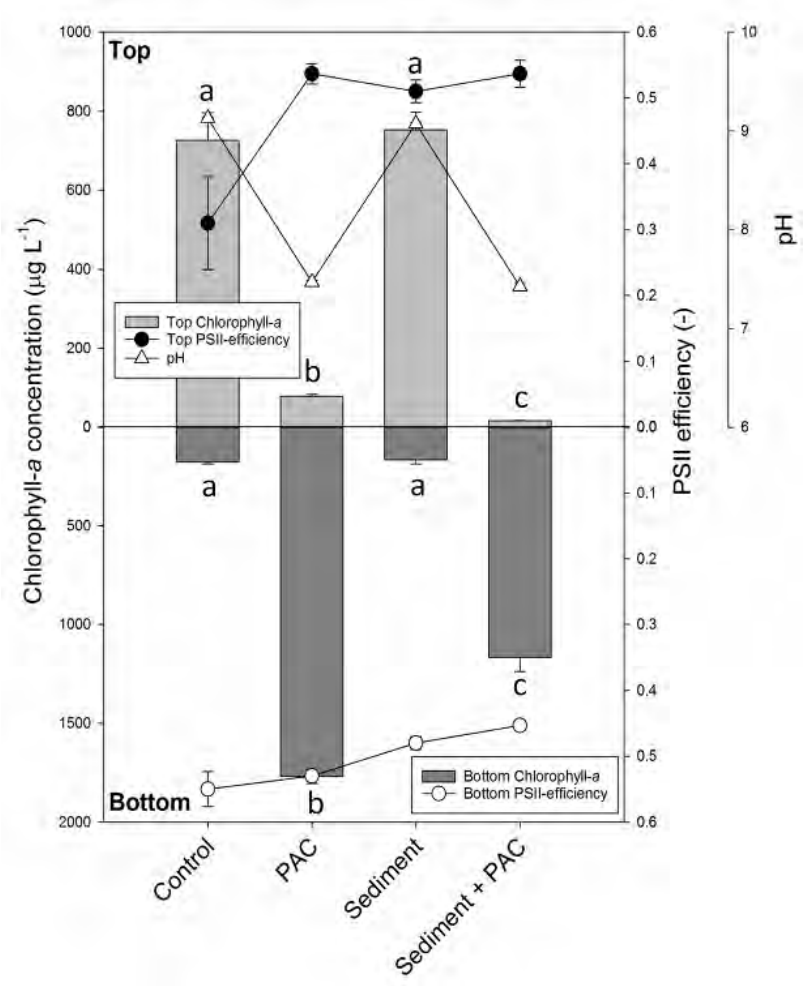
Legend: Chlorophyll-a concentrations (µg L^{-1}) in the top 5 mL (top light grey bars) and bottom 5 mL (lower dark grey bars) of 60 mL cyanobacteria suspension from Jacarepaguá Lagoon incubated for 1 h in the absence and presence of the coagulante PAC (8 mg Al L^{-1}) combined with diferente concentration of red soil (0 – 320 mg L^{-1}) as ballast. Also included are the Photosystem II efficiencies (PSII) of the cyanobacteria collected at the water surface (filled circles) and at the bottom (open circles) as well as the pH values of suspensions (open triangles). Error bars indicate one standard deviation (n = 3). Similar letters indicate homogeneous groups according to the Holm-Sidak method

Source: Author, 2018

3.3.3 Effect of sediment on the vertical position of the cyanobacteria

Adding only sediment did not lead to removal of cyanobacteria from the water column in the test tubes in contrast to adding PAC at a dose of 8 mg Al L^{-1} (Fig. 15). The one-way ANOVA indicated significant differences in both the chlorophyll-*a* concentration in the top of the test tubes ($F_{3,8}$ = 2290; p < 0.001) as in the bottom ($F_{3,8}$ = 853.7; p < 0.001); in both cases the *post-hoc* comparison revealed three homogenous groups that were significantly different from each other: 1) the control and the solely sediment treatment, 2) the sole PAC treatment, and 3) the PAC + sediment treatment. The PSII-efficiency in the top of the control tubes was significantly lower ($F_{3,8}$ = 26.6; p < 0.001) than in the treatments, while in the bottom PSII-efficiency in the control and PAC treatment were significantly higher ($F_{3,8}$ = 28.5; p < 0.001) than in the sediment and sediment+PAC treatments (Fig. 16). Finally, the pH was significantly different ($F_{3,8}$ = 4964; p < 0.001) and clearly reduced in the two treatments with PAC added (pH 7.47 and 7.42) compared to the control (pH 9.13 $\pm$ 0.01) and the only sediment addition (pH 9.07 $\pm$ 0.01) (Fig. 15).

Figure 15 - Chlorophyll-a concentrations (µg L^{-1}) in the top and bottom of the test tubes treated with PAC, Sediment, and sediment + PAC.



Legend**:** Estimated SRP fluxes in the different experiments and treatments performed in this study. Negative values indicate a net SRP removal from over-standing water and thus an accumulation in the sediment, whereas positive values indicate a net release from the sediment (internal loading). The green line represents the estimated critical transition from clear to turbid water, while the grey line represents the critical transition from turbid to clear based on the PCLake Metamodel.

Source: Author, 2018.

3.4 **Discussion**

Our field work confirmed the strong cyanobacterial proliferation of the water in Jacarepaguá Lagoon. Jacarepaguá is an oligo-mesohaline system suffering from strong anthropogenic pressure of which eutrophication is causing massive cyanobacterial blooms (GOMES et al., 2009) that also threaten humans consuming fish from the system which have accumulated cyanobacterial toxins (MAGALHÃES et al., 2001). Hence, there is strong pressure to reduce the harmful cyanobacteria blooms. While nutrient input control may take quite some years, we hypothesized that the cyanobacteria flourishing in Jacarepaguá Lagoon could also be effectively removed from the water column using a combination of PAC or chitosan with a RS or local sediment as ballast. Our experimental data showed an efficient removal when these ballast compounds were joined with PAC, but not for chitosan, which did not form flocks in the Jacarepaguá Lagoon water.

Chitosan is widely used in water and waste water treatment, because it is a non-toxic, non-corrosive natural product, which is efficient in cold water without causing environmental pollution (RENAULT et al., 2009). Deacetylation of chitin - mostly derived from shrimps and crabs- produces chitosan, which is a linear copolymer of D-glucosamine and N-acetyl-D-glucosamine that due to its rigid structure is insoluble in water. The copolymer becomes fully soluble in dilute acids when the free amino groups of chitosan are protonated that enables electrostatic interactions between the protonated amino groups of chitosan and the negatively charged cyanobacteria (RENAULT et al., 2009). The long chain polymers, like chitosan, can attach onto particles forming “bridging” connections. These bridging connections between the particles can together form a “net” (TRIPATHY and RAJAN DE, 2006; CHEN et al., 2014). However, in conditions where large amounts of negative ions gather around the protonated groups, it becomes shielded, the molecule contracts and also hampers the netting and bridging properties (PAN et al., 2006b; QUN and AJUN, 2006). Consequently, chitosan is not a very efficient coagulant at high pH (MORALES et al., 1985; VANDAMME et al., 2013) and at high ionic strength of the water (PAN et al., 2006a). Given the high pH and considerable

ionic strength of the Jacarepaguá water (see Table 2), chitosan is not an appropriate coagulant to be applied in Jacarepaguá, or any other high ionic strength and high pH water. In addition, the price of chitosan is much higher than that of aluminium salts (GRANADOS et al., 2012).

Contrary to chitosan, PAC (poly-aluminium chloride) turned out an excellent coagulant in Jacarepaguá water. In general, aluminium salts, are widely used in water treatment including cyanobacteria removal (JANČULA and MARŠÁLEK, 2011). PAC has several advantages over other aluminium salt coagulants, such as alum: less pH reduction, lower dose needed, less residual Al, less sulphate added and better flocs at low temperature (GEBBIE, 2001; de JULIO et al., 2010). Use of aluminium formulations is sometimes met with scepticism related to presumed toxic effects (e.g. RENAULT et al., 2009). However, aluminium is the most abundant metal in the Earth crust (>8%) and application of aluminium formulations in waters with neutral pH can be considered safe (JANČULA AND MARŠÁLEK, 2011). The toxicity of metals depends on speciation which is steered by pH (STUMM and MORGAN, 1996), where in case of aluminium the trivalent Al^{3+} prevails at pH lower than 5.5 (DRISCOLL and SCHECHER, 1990; GENSEMER and PLAYLE,1999). As the pH in Jacarepaguá Lagoon keep alkaline in the entire water column low soluble aluminium will be free even near the bottom. In our experiments, no occurrence of this toxic Al species in the water was predicted. Nonetheless, it should be notified that aluminium toxicity in fish has also been ascribed to precipitation of $Al(OH)_3$ on the gills leading to suffocation of the fish (WAUER et al., 2004). Therefore, before applying PAC to Jacarepaguá, albeit in a relative low dose of 8 mg Al L^{-1} - field applications of Al salts are reported to be dosed at 2.6 to 45 mg L^{-1} (COOKE et al., 2005) - additional enclosure studies including the abundant fish *Tilapia rendalli* are recommended.

Red soil in itself removed 33-47% of the cyanobacteria from the water, which may have been caused by some flocculating properties of the RS (PAN et al., 2006b). The RS is a typical laterite soil - rich in iron and aluminium - and predominantly composed of kaolinite, goethite, gibbsite and some anatase (NOYMA et al., 2016). The main component, the clay kaolinite, removed 43% of a *M. aeruginosa* populations when dosed at 200 mg L^{-1} and 88% at 700 mg L^{-1} (Pan et al. 2006b), while 1000 mg L^{-1} removed almost 60% of the red-tide dinoflagellate *Karenia*

brevis (SENGCO and ANDERSON, 2004). The stickiness of *M. aeruginosa* may also cause attachment of clay particles resulting in sedimentation of buoyant *Microcystis* (VERSPAGEN et al., 2006). However, given sediment from Jacarepaguá had no effect on settlement of *M. aeruginosa*, where RS did partly, stickiness seems not have been the main mechanisms operating. Hence, just RS or local sediment are not appropriate to sink the cyanobacteria out of the water column. Similarly, LI and PAN (2013) found that sand alone was ineffective to flock and sink two marine algae and also *M. aeruginosa*. When they added chitosan, however, removal was between 40 and 60%, whereas *Moringa oleifera* (Moringaceae) extract led to more than 90% removal (Li and Pan, 2013). Also PAN et al., (2012) recognised that soils by themselves hardly remove phytoplankton and flocculent addition was needed to facilitate removal.

Indeed, the combination of PAC and RS as ballast improved the settling efficiency at low PAC dose. At a sole PAC dose of 1 and 2 mg Al L^{-1}, although flocks were formed, no difference in settling with the control was observed (*see* Fig. 10). Adding RS, however, greatly improved sedimentation of cyanobacteria flocks at these PAC doses (*see* Fig. 13). The choice for 8 mg Al L^{-1} PAC as optimum dose in combination with RS was based on the efficient removal of cyanobacteria from the water column and acceptable lowering of pH.

The dose of RS could be lowered to 80 mg L^{-1} without losing any efficiency (see Fig. 15). This dose of ballast is quite comparable with the 100 mg L^{-1} of a local sand or soil found in other studies (PAN et al., 2011a; LI and PAN, 2013; 2015). The combination of flocculent and soil has already been applied successfully in an isolated bay of Lake Taihu (China), where adding 25-31 mg L^{-1} (40-50 g m^{-2}) effectively cleared the water of cyanobacteria (Pan et al. 2011b). In Lake Rauwbraken (The Netherlands), PAC (0.83 mg L^{-1}) and a lanthanum modified bentonite (84 mg L^{-1}) effectively removed cyanobacteria from the water column and resulted in water devoid of cyanobacteria nuisance for several years (LÜRLING and VAN OOSTERHOUT, 2013). As in this technique entrapped cyanobacteria in flocks remain intact (CHOW et al., 1999; DRIKAS et al., 2001) - the intactness of precipitated cells is also reflected in unaffected PSII-efficiencies, no release of toxins

and nutrients during treatment occurs, which is a major advantage over using algaecides in treating cyanobacterial blooms.

The experiments in laboratory scale are important to demonstrate, in rapid assays, the possible effects of the lagoon water chemistry on flocculation efficacy. Although physical factors i. e., turbulence can interfere in the flocculation processes, resuspending flocks, the wind-induced mixing might also be beneficial facilitating formation of flocks. The flock and sink approach has been applied successfully to a shallow and small lake (Lake De Kuil, The Netherlands) (GUIDO et al., 2016). Furthermore, this promising approach seems to be applicable for different water characteristic although complementary studies are needed to evaluate the effectiveness of the compounds in larger scales.

Although it is widely recognized that preventing cyanobacterial and harmful algal bloom development through adequate nutrient control in the watershed is far better than eliminating existing blooms, costs and politics may delay such actions that make curative bloom control strategies inevitable (HEISLER et al., 2008). Furthermore, synergistic effects of eutrophication and global change may promote an escalation in cyanobacterial and harmful algal blooms in estuarine and coastal waters (PAERL et al., 2014). Hence, efficient, cheap, fast and safe curative measures to lessen the cyanobacteria and harmful algal bloom nuisance will provide a welcome extension of the water managers' tool-box. Combined coagulant and ballast seems a very promising tool it may give temporal relief from cyanobacteria or harmful algal nuisance in periods when particularly needed, such as around the 2016 Olympics in Jacarepaguá Lagoon.

3.5 **Conclusions**

● Polyaluminium chloride (PAC) flocculated cyanobacteria from a brackish tropical lagoon, while chitosan appeared ineffective as flocculent.

● Positively buoyant cyanobacteria from a brackish tropical lagoon could be flocked and effectively precipitated using a combination of PAC with red soil (RS) or local sediment as ballast.

● Sole use of RS or sediment as ballast was inefficient in removing cyanobacteria.

● Combined use of PAC and ballast seems a very efficient curative measure to lessen cyanobacterial bloom nuisance

3.6 **Acknowledgements**

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4 MANAGING EUTROPHICATION IN A TROPICAL BRACKISH WATER LAGOON: TESTING LANTHANUM MODIFIED CLAY AND COAGULANT FOR INTERNAL LOAD REDUCTION AND CYANOBACTERIA BLOOM REMOVAL

Este capítulo é baseado no manuscrito submetido a revista Estuaries and Coasts numero “ESCO-D-17-00309” e entitulado: Managing eutrophication in a tropical brackish water lagoon: testing lanthanum modified clay and coagulant for internal load reduction and cyanobacteria bloom removal (anexo B).

Abstract

The release of phosphorus (P) stored in the sediment may cause long term delay in the recovery of lakes, ponds and lagoons from eutrophication. In this paper, we tested on a laboratory scale the efficacy of the flocculant polyaluminium chloride (PAC) and a strong P-binding agent (lanthanum modified bentonite, LMB) on their ability to flocculate a cyanobacterial bloom and hamper P-release from a hypertrophic, brackish lagoon sediment. In addition, critical P loading was estimated through PClake. We showed that cyanobacteria could be effectively settled using a PAC dose of 2 mg Al L^{-1} combined with 400 mg L^{-1} LMB; PAC 8 mg Al L^{-1} alone could also remove cyanobacteria, although its performance was improved adding low concentrations of LMB. The efficacy of LMB to bind P released from the sediment was tested based on potentially available sediment P. A dose of 400 g LMB m^{-2} significantly reduced the P-release from sediment to over standing water (either deionized water or water from the lagoon with and without cyanobacteria). In sediment cores, LMB+PAC reduced sediment P flux from 9.9 (± 3.3) to – 4.6 (± 0.3) mg P m^{-2} d^{-1} for the experimental period of 3 months. The internal P load was 14 times higher than the estimated P critical load (0.7 mg P m^{-2} d^{-1}), thus even if all the external P sources would be ceased the water quality will not improve promptly. Hence, the combined LMB+PAC treatment seems a promising in-lake intervention to diminish internal P load bellow the critical load. Such intervention is able to speed up recovery in the brackish lagoon once external loading has been tackled and at a cost of less than 5% of the estimated dredging costs.

Keywords: Geo-engineering, Lake restoration, Phosphorus control, PAC, Phoslock, Sediment release

4.1 Introduction

Eutrophication is one of the main anthropogenic stressors leading to major degradation of coastal waters worldwide (KENNISH, 2002). Water quality problems caused by eutrophication include fish deaths due to anoxia, loss of biodiversity, bad smells and massive plant growth (PAERL and HUISMAN, 2008; CONLEY et al., 2009). Key symptom of eutrophication is a blooming of harmful algae and cyanobacteria, which pose an additional risk to wildlife and humans because of the toxins they may produce (CORREL, 1998; HUSZAR et al., 2000; PAERL et al., 2012). Hence, there is a great need to control these nuisance blooms.

Since blooms are fueled by nutrients, the first step in mitigation would be reducing the nutrient discharge into the receiving waters (COOKE et al., 2005; PAERL et al., 2014). Although some waters will clear up and recover rapidly from such lowered external nutrient loading, many will show a considerable delay in recovery due to internal nutrient cycling (JEPPESEN et al., 1991; SØNDERGAARD et al., 1999; 2001; COOKE et al., 2005). This legacy of nutrients created from decades of uncontrolled excessive external nutrient loading will periodically be recycled between sediment and water column and is viewed as one of the main reasons why many restoration attempts have failed (GULATI and VAN DONK, 2002). Removal of polluted sediments is then a straightforward restoration approach, but it may come with relatively high costs compared to other techniques such as *in situ* fixation or capping (COOKE et al., 2005; PERELO, 2010).

In recent years, the use of solid phase phosphorus (P)-adsorbing compounds has gained interest to tackle the widespread internal loading issue (SPEARS et al., 2013a). The rationale to target stored P lays in the fact that it is the only essential element that can be easily be made to limit algal growth through the formation of insoluble precipitates (GOLTERMAN, 1975). Internal P loading is not only a major issue in inland freshwater systems (SØNDERGAARD et al., 2001), but also occurs in brackish coastal lagoons (MARKOU et al., 2007). While there is a growing number of studies demonstrating efficacy and applicability of solid-phase P sorbents in freshwater systems, studies on brackish coastal waters are virtually lacking.

Nonetheless, eutrophication is considered the most common problem affecting coastal lagoons (ESTEVES et al., 2008; KENNISH et al., 2014). For instance, the coastal system Jacarepaguá lagoon in the western part of Rio de Janeiro city (Brazil) suffers heavily from eutrophication and perennial presence of cyanobacterial blooms (GOMES et al., 2009; DE-MAGALHÃES et al., 2017).

Recently, we have explored the possibility of removing cyanobacteria from Jacarepaguá lagoon water using a coagulant (poly-aluminiumchloride, PAC or chitosan) and red soil or local sediment as ballast (DE-MAGALHÃES et al., 2017). While PAC was effective, chitosan appeared ineffective to flock cells even when combined with ballast compounds (DE-MAGALHÃES et al., 2017). Elevated pH and high alkalinity were identified as factors that may hamper the coagulation of chitosan and impair its ability to effectively remove cyanobacteria from the water column (LÜRLING et al., 2017).

In the present study, we elaborated on these findings and first tested the combination of PAC and the solid phase P adsorbent Phoslock®, which is a lanthanum modified bentonite (LMB) with strong P binding capacity and widely used in freshwater systems (COPETTI et al., 2016), on the ability to remove cyanobacteria from the brackish water of Jacarepaguá lagoon. In addition, we were particularly interested in the performance of LMB as COPETTI et al., (2016) reported that even moderately saline environments of >0.5 ppt will render LMB ineffective. A thorough scientific underpinning of this statement is, however, lacking in that review paper (COPETTI et al., 2016), and also finds no support in the few studies that included more saline environments (HAGHSERESHT 2006; REITZEL et al., 2013). Given the current uncertainty on applicability of LMB in brackish environments, we tested the hypotheses that 1) LMB will block P-release from the sediment of the eutrophic coastal lagoon Jacarepaguá and 2) that a combination of PAC with LMB will clear the water and block the P release effectively.

4.2 **Material and Methods**

4.2.1 Study ecosystem

The Jacarepaguá Lagoon (43º17' - 43º30'W, 22º55' - 23º00'S) is part of a brackish water lagoon complex located in the western part of Rio de Janeiro City (Fig. 16). The Jacarepaguá lagoon is 3.7 km² in area; it has an average depth of 3.3 m; drainage area of 103 km^2; and the freshwater inflow from the six tributaries is about 0.8 m^3 s^{-1} (GOMES et al., 2009). This system has a direct communication with the sea water by the Joatinga channel, giving an average salinity of 5.35 ppt (DE-MAGALHÃES et al., 2017). The lagoon usually presents high pH and alkalinity with perennial relatively high chlorophyll-*a* concentrations (mostly exceeding 100 µg L^{-1}) and long periods of cyanobacteria dominance promoted by the constant sewage input (GOMES et al., 2009; DE-MAGALHÃES et al., 2017).

Figure 16 - Location of the Jacarepaguá lagoon.

Legend: Location of the Jacarepaguá lagoon near to the Olympic 2016 venues and the sediment sampling station (JAC 20). Panel B shows the green water of the lagoon (January 19th 2015) and panel C the main phytoplankton species (*M. aeruginosa* colonies and *P. agardhii* filaments).
Source: Author, 2018.

4.2.2 Sediment and water sampling

On November 2014, 10 L of surface water was collected for experiments with coagulants and ballast. The most important species in this moment was *Microcystis aeruginosa* and the chlorophyll-*a* concentration was 225 µg L^{-1}. Jacarepaguá sediment was collected with a Kajak sediment core sampler on January 19th 2015 at station JAC20 (Fig. 17). At this moment the chlorophyll-*a* concentration, collected by an integration tube, was 226 µg L^{-1} composed mainly by *Microcystis aeruginosa* with some undergrowth of *Planktothrix agardhii* (Fig 17). The pH of the water was 9.04 (± 0.24); salinity was 5.49 ppt and the alkalinity 4.35 mEq L^{-1}. On September 2015 more sediment was collected using the gravity Uwitec Corer sampler at station JAC20 and at this moment the pH was 9.88, salinity 5.17 ppt and the alkalinity was 3.74 mEq L^{-1}. No cyanobacteria bloom was observed, and the phytoplankton community was composed mainly by Cryptophyceae and green algae.

4.2.3 Chemicals and materials

The lanthanum modified bentonite Phoslock® (LMB) was obtained from HydroScience (Porto Alegre, Brazil). This LMB was developed by the Australian CSIRO, as dephosphatisation technique aiming at removing soluble reactive phosphorus (SRP) from the water and blocking the release of SRP from the sediment (DOUGLAS, 2002). The coagulant PAC-AP (polyalumnium chloride; $Al_n(OH)_mCl_{3n-m}$, $\rho \approx 1.37$ kgL^{-1}, 8.9% Al, 21.0% Cl) was obtained from Pan-Americana (Rio de Janeiro, Brazil).

4.2.4 Effect of different concentrations of LMB and PAC on cyanobacteria removal

The first experiment tested the efficacy of a combination of LMB with PAC to settle the cyanobacteria from Jacarepaguá water. Different concentrations of LMB (0

to 400 mg L^{-1}) in presence of two fixed doses of PAC were used. The low PAC dose (2 mg Al L^{-1}) was based on the results from previous experiments in freshwaters (LÜRLING and VAN OOSTERHOUT, 2013; NOYMA et al., 2016); the higher PAC dose (8 mg Al L^{-1}) was based on the effective removal of cyanobacteria from Jacarepaguá water with red soil as ballast (DE-MAGALHÃES et al., 2017). The experiment was run in 75 mL glass tubes that were filled with 60 mL of unfiltered water from Jacarepaguá. The water collected from Jacarepaguá contained cyanobacteria at a chlorophyll-*a* concentration of 222 (± 2) µg L^{-1}; the cells were healthy as indicated by a photosystem II (PSII) efficiency of 0.53 (± 0.03), both determined using a PHYTO-PAM phytoplankton analyser (Heinz Walz GmbH, Effeltrich, Germany).

The experiment included a control without any compound added and was performed with three replicates per treatment. Immediately after adding the designated amount of LMB, the PAC coagulant was added and the content in the test tube mixed briefly using a glass rod. Tubes were placed in the laboratory at 25 °C under stagnant conditions. After one hour 5 mL samples were taken from both the top and the bottom of the tubes in which chlorophyll-*a* concentrations and PSII efficiencies were measured. The 5 mL from the top and the bottom of the tubes were sampled, since an accumulation at the top would indicate a scum formation in the field, which is an unwanted effect, whereas the accumulation at the bottom is the intended effect from the combined coagulant and ballast (DE-MAGALHÃES et al., 2017; MIRANDA et al., 2017). After the top and bottom samples were taken, the pH was measured in the middle of the tubes.

The chlorophyll-*a* concentrations in the top of the tubes and those measured at the bottom of the test tubes, as well as PSII-efficiencies and pH values were statistically evaluated running a one-way ANOVA in the program SigmaPlot version 12.5. Homogeneity of variance was tested by the Equal Variance Test (Brown-Forsythe) and normality, by the Shapiro-Wilk Normality Test. In cases where normality failed data were log-transformed to fulfill this prerequisite. An all pairwise multiple comparison was performed to distinguish means that were significantly different at the 0.05 level (Holm-Sidak method; $p = 0.05$).

4.2.5 LMB dose

The manufacturers advice to dose the LMB in an LMB:P ratio 100:1, with P the "labile" P-pool in the sediment. The ratio LMB:P 100:1 is based on the 1:1 molar La:P from the precipitation reaction equaling a 4.485:1 La:P weight ratio and a 4.5% La in LMB. Based on the 0.05 g P / kg (wet sediment) we estimated a dose of 400 and 507.5 g LMB m^{-2} assuming a communicating sediment depth of 8 cm and 10 cm respectively, which are consistent with LMB doses applied in the field (DITHMER et al., 2016b).

4.2.6 Sediment P extraction

To determine the dose of LMB needed in the experiments, an estimate of the potentially releasable P in the sediment was required. Hereto, a sequential extraction protocol modified from PALUDAN & JENSEN, (1995) and used by CAVALCANTE et al., (2018) to measure different P forms in the sediment was adopted. One gram of wet sediment was brought into each of four 50 mL Falcon tubes to which, as a first step, 25 mL anoxic demineralized water was added to extract the immediately available P. The tubes were shaken for 30 minutes (oxygen at the start was 0.21 and at the end 0.44 mg L^{-1}). The tubes were centrifuged and the supernatant collected. A second aliquot of 25 mL anoxic demineralized water was added to the pellets and shaken for five minutes, where after the tubes were centrifuged and the supernatants joined, filtered through 0.6 µm glass fiber filters (GF-3, Macherey-Nagel), acidified with 0.5 mL 2 M H_2SO_4 and stored in the refrigerator until P analysis. In the second step, to the pellets 25 mL of anoxic Bicarbonate/Dithionite (BD: 0.11 M $NaHCO_3$ and 0.11 M $Na_2S_2O_4$) was added to extract P bound to Fe-hydroxides and Mn-compounds from the sediment pellets. The tubes were shaken for 30 minutes, subsequently centrifuged and the supernatant collected. To the pellets, another 22 mL anoxic BD was added and tubes were shaken for 5 minutes, centrifuged and

supernatants joined. The joined 47 mL supernatants were aerated for half an hour, filtered through 0.6 µm glass fibre filters, acidified with 3 mL 2 M H_2SO_4 and stored in the refrigerator for P analysis. In the third and last step, to the pellets 25 mL 0.1 M NaOH was added aiming to extract P bound to metal oxides of Al. The tubes were shaken for 30 minutes, centrifuged, and supernatants collected, followed by a second extraction with 25 mL 0.1 M NaOH for five minutes and a washing step for five minutes with 23.5 mL demineralized water. The three joined supernatants (73.5 mL) were filtered as before, acidified with 1.5 mL 2 M H_2SO_4 and stored in the refrigerator. The filtrates were analysed on their SRP and total phosphorus (TP) concentrations using a Flow Injection Analysis System (model 2500, FIAlab, USA). The dry weight of the sediment was determined by weighing triplicate samples of 10 mL sediment before and after drying at 105 °C.

4.2.7 Effect of different over-standing water on sediment phosphate release

Fifty gram wet sediment from Jacarepaguá, corresponding to a 2.43 mg of releasable P in the sediment, considering the P content determined as described above, was transferred into 250 mL Schott glass bottles. To six bottles 100 mL demineralized water was added, to nine bottles 100 mL filtered Jacarepaguá water (0.6 µm glass fiber filters; GF-3, Macherey-Nagel) was added, while to nine other bottles 100 mL unfiltered Jacarepaguá water was added, which was collected on January 19th 2015. Three bottles of each series were left untreated (control) and three were treated with 400 g m^{-2} LMB, while the two series with filtered and unfiltered Jacarepaguá water also included a treatment with PAC (8 mg Al L^{-1}) and LMB (400 g m^{-2}) in triplicates. This dose of PAC was found effective in flocculating the cyanobacteria out of the water column without strong effects on the pH of Jacarepaguá water (DE-MAGALHÃES et al., 2017). PAC was not included in the demineralized water series, because of strong effects on pH (GEBBIE, 2001). We calculated a dose of 400 g LMB m^{-2} assuming a communicating sediment depth of 8 cm which is consistent to the La profile in 10 LMB treated lakes where La was mixed

in the sediment from ~5 cm to more than 10 cm (DITHMER et al., 2016b). The experimental bottles were placed at 25°C at low light (≅ 1 µmol photon m^{-2} s^{-1}) in day-night regime (13 hours light:11 hours dark). Initially and after 7, 14 and 21 days samples were taken, filtered through 0.6 µm glass fibre filters (GF-3, Macherey-Nagel), and analysed on their SRP concentrations using a Flow Injection Analysis System (model 2500, FIAlab, USA). Differences in SRP concentrations between start and one week incubations were used to derive an estimate of SRP fluxes using the known water volume (100 mL) and the surface area of the sediment at the Schott glass bottles (28.27 cm^2).

4.2.8 Treating sediment cores with PAC or LMB+PAC – short term experiment

On January 19th 2015, seven sediment cores were drilled from Jacarepaguá using a Kajak core sampler. The cores contained between 18 and 30 cm length of black sediment and 9 to 21 cm over-standing, cyanobacteria dominated water. Hereto, considering a communicating sediment depth of 8 cm, and the results of the extraction described above, the cores contain an estimated amount of 10.15 mg of P releasable to the water column. Two cores were treated with sole PAC (8 mg Al L^{-1}), two cores with LMB (400 g m^{-2}) plus PAC (8 mg Al L^{-1}), while three cores remained untreated (controls). The cores were incubated in the laboratory at 25°C at low light (≅ 1 µmol photon m^{-2} s^{-1}) in day-night regime (13 hours light: 11 hours dark). Initially and after 1.5, 3.5, 18, 42, 90, 138, 186 and 306 hours water samples were taken and analysed on their chlorophyll-*a* concentrations. Additional samples taken before, just after application and after 138 and 306 hours incubation, were filtered through 0.6 µm glass fiber filters (GF-3, Macherey-Nagel) and analysed on their SRP concentration as previously described. The differences between SRP concentrations from the start and after incubation of 306 hours were used to estimate the SRP fluxes using the formula: $\{(P_{final} - P_{start}) \times \text{water height}\}/\Delta t$, with P in mg m^{-3}, water height in m and Δt in days (d).

4.2.9 Treating sediment cores with LMB+PAC- long term experiment

On September 29th 2015, additional sediment cores were taken from Jacarepaguá using a gravity Uwitec Corer sampler. The tubes contained between 18 and 28 cm length of black sediment and 32 to 43 cm of over-standing water. The potential available P was determined as outlined above and the SRP concentration in the water was determined. Both were used to estimate the dose of LMB required assuming a 10 cm communicating sediment depth. The 10 cm communicating sediment depth contain a calculated amount of 12.68 mg of P releasable yielding a dose of 507.5 g m^{-2} to be added together with PAC (8 mg Al L^{-1}) to each of four replicate cores (treatment), while four other cores remained untreated (controls). The chlorophyll-*a* concentration of the over-standing water was 86 (± 1) μg L^{-1}. The cores were closed with a rubber stopper and placed in the laboratory at 25°C in the dark. The experiment lasted 96 days to give insight in the durability and efficacy of the treatment. The experiment was conducted under anoxia 0.20 (± 0.45) mg L^{-1} at a circumneutral pH 7.01 (± 0.54). 10 ml of water from the middle of the core tubes were sampled initially and after 1, 3, 15, 22, 29, 35, 64 and 96 days and filtrated before been analysed using a Flow Injection Analysis System (model 2500, FIAlab, USA) for SRP measurements. The treatment took place on October 1st, i.e. two days after collection, because the sediment P had to be determined prior to application. Consequently, the course of SRP concentrations was statistically evaluated running a rmANOVA in the toolpack SPSS (version 22) using the whole period as well as using only the data obtained after application (days 3,..., 96). The differences between SRP concentrations from start and after 96 days of incubation were used to estimate the SRP fluxes using the formula: $\{(P_{final} - P_{start}) \times \text{water height}\}/\Delta t$, with P in mg m^{-3}, water height in m and Δt in days (d).

4.2.10 Comparison of SRP fluxes with estimated critical P loadings

The PClake metamodel is used to estimate the critical P load sufficient to cause a shift between a clear water state (P load below its critical value) and a turbid water state (P load above its critical value) (MOOIJ et al., 2010, PBL 2015), available at http://themasites.pbl.nl/modellen/pclake/index.php. In the clear water state blooms of cyanobacteria are not expected as they are P-limited. PCLake simulates the influence of phosphate on lakes based on water and sediment P, transparency, amount of water plants, phytoplankton concentration, fish stock and swamp and bank vegetation, whilst taking into consideration soil type, size and depth of a lake. PCLake simulations have been run by the model builders using a whole range of P loads for a number of lake types and both starting conditions. In these 100.000 simulations depth, lake surface, retention time, soil type, swamp area defined the lake types. All results are stored in a database and the critical transitions determined for each combination. The critical transition is the P-load yielding a transparency of half the water column depth. In case of new combinations, the critical P loads are estimated using a neural network (http://www.pbl.nl/dossiers/water/modellen/WerkingModelPCLake). PClake was run with the following parameters based on previous Jacarepaguá Lagoon studies (BARBOSA and ALMEIDA, 2001; FERRÃO-FILHO et al., 2002; GOMES et al., 2009). The input parameters were: average depth of 3.3m, swamp area 0.1, fetch 4000m, discharge (19 mm d^{-1} = residence time of 176 days), average depth = 3.3 m, background extinction = 0.5 m^{-1}, and sand as soil type. We compare the SRP-fluxes derived from our current experiments to the PClake critical P loadings. An additional critical P load estimate was made, targeting a TP concentration of 30 µg L^{-1}, which correspond to a decrease of 98% of TP in Jacarepaguá Lagoon (DE-MAGALHÃES et al., 2017), using the VOLLENWEIDER (1976) model: $P_{critical} = P_{target} \times (1 + \sqrt{\tau}) \times z_m \times \tau^{-1}$, where $P_{critical}$ is the critical P load (g m^{-2} $year^{-1}$), P_{target} is the target in-lagoon P concentration (g m^{-3}), τ is the water retention time (year) and z_m is mean water depth

(m). The same model was used to derive an estimate of the actual load based on the current in-lagoon P concentration.

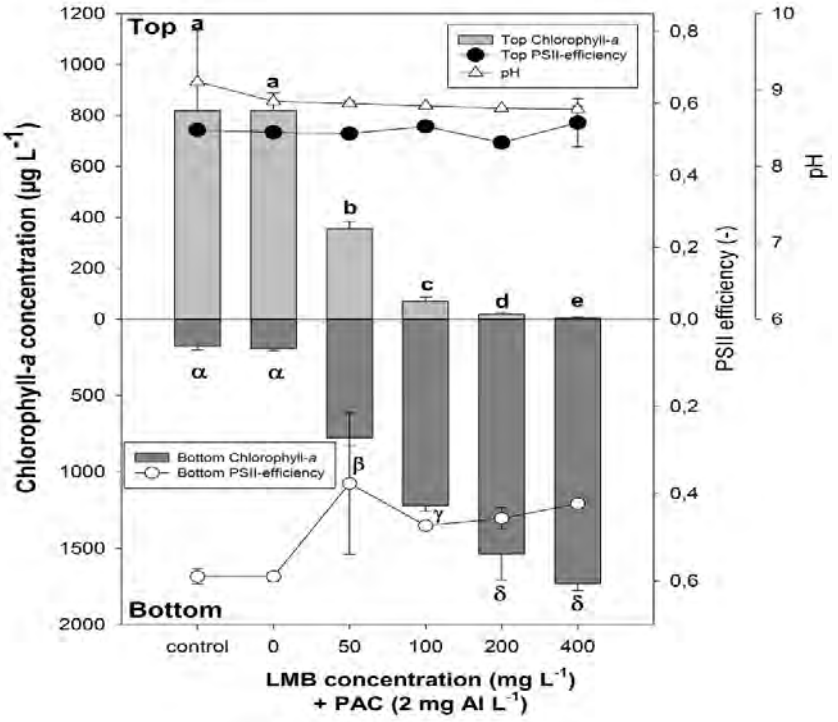
4.3 **Results**

4.3.1 Effect of different concentrations LMB and PAC on cyanobacteria removal

With the PAC dose fixed at 2 mg Al L^{-1} the chlorophyll-*a* concentrations in the top of the test tubes declined with increasing LMB dose. The F-test revealed a significant difference among the treatments ($F_{5,12}$ = 135.0; p< 0.001). The pairwise multiple comparison revealed no difference between the control and the sole PAC treatment (0 mg LMB L^{-1}) while with higher LMB dose all chlorophyll-*a* concentrations in the top were significantly different and decreased with higher concentrations of LMB as ballast (Fig. 17). Also, in the bottom of the test tubes significantly different ($F_{5,12}$ = 495.4; p< 0.001) chlorophyll-*a* concentrations were found. The *post-hoc* comparison, considering the top of the bottles revealed four homogenous groups that were significantly different from each other: 1) the lowest chlorophyll-*a* concentrations were in the control and the 0 mg LMB L^{-1} treatment; 2) significantly higher chlorophyll-*a* concentrations were measured in the bottom of the tubes treated with concentrations 50 mg LMB L^{-1} treatment; 3) even higher chlorophyll-*a* concentrations were measured in the bottom of the tubes treated with concentrations 100 mg LMB L^{-1} treatment; 4) the highest chlorophyll-*a* concentrations were measured in the bottom of the tubes treated with 200 and 400 mg LMB L^{-1} (Fig. 17). PSII-efficiencies in the top of the tubes were also statistically different ($F_{5,12}$ = 6.19; p = 0.005), the *post-hoc* comparison revealed that the PSII in the 200 mg LMB L^{-1} treatment was lower than in the 100 and 400 mg LMB L^{-1}. Nonetheless, values varied on average between 0.49 and 0.55. PSII efficiency was also statistically different in the bottom of the tubes (H_5 = 13.8; p = 0.017). The pairwise multiple comparison test revealed that PSII in the

control (0.59) was significantly higher than in the 400 mg LMB L^{-1} treatment (0.42) (Fig. 18). Although pH in the control was significantly higher than the treatments ($F_{5,12}$ = 94.1; p < 0.001), the differences were relatively small varying from 9.1 (control) to 8.7 (400 mg LMB L^{-1}; Fig. 17).

Figure 17 - Chlorophyll-a concentrations (µg L^{-1}) in the top and bottom of the test tubes treated with PAC 2 mg Al L^{-1} and it combination with lanthanum modified clay.

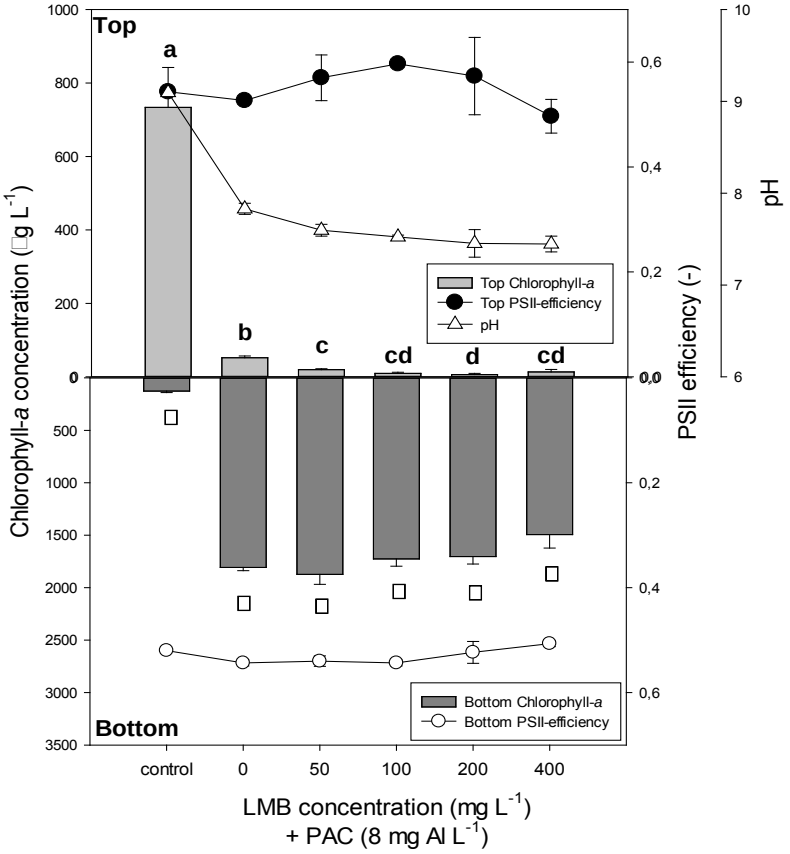


Legend: Chlorophyll-a concentrations (µg L^{-1}) in the top 5 mL (top light grey bars) and bottom 5 mL (lower dark grey bars) of 60 mL cyanobacteria suspensionsfrom Jacarepaguá Lagoon incubated for one hour in the absence (control) or presence of the coagulant PAC (2 mg Al L^{-1}) and different concentrations of lanthanum-modified bentonite, LMB (0 - 400 mg L^{-1}). Also included the Photosystem II efficiency (PSII) of the cyanobacteria collected at the water surface (filled circles) and at the bottom (open circles). Error bars indicate one standard deviation (n = 3). Similar symbols (a,..,δ) above/below the bars indicate homogeneous groups that are not different at the 95% level (Holm-Sidak test).

Source: Author, 2018.

In the series with PAC dosed at 8 mg Al L^{-1} and concentration range of LMB, chlorophyll-*a* concentrations in the top of the test tubes were significantly different among treatments ($F_{5,12}$ = 66.7; p < 0.001). The *post-hoc* comparison revealed four homogeneous groups: 1) the control; 2) the 0 mg LMB L^{-1} treatment, i.e. the sole PAC treatment; 3) the combined PAC and 50, 100 and 400 mg LMB L^{-1} treatments and 4) the 100, 200 and 400 mg LMB L^{-1} treatments combined with PAC (Fig. 19). The bottom chlorophyll-*a* concentrations were also significantly different ($F_{5,12}$ = 217.7; p < 0.001). Three significantly different groups were detected: 1) the control 2) the 0, 50, 100 and 200 mg LMB L^{-1} treatments combined with PAC, and 3) the 400 mg LMB L^{-1} treatment also combined with PAC (Fig. 18). PSII-efficiencies in the top of the test tubes were similar ($F_{5,12}$ = 2.78; p = 0.068) and on average 0.55 (± 0.05). In the bottom, the ANOVA indicated significant differences ($F_{5,12}$ = 6.50; p = 0.004), where the *post-hoc* comparison indicated PSII in the 400 mg LMB L^{-1} treatment was significantly lower than those in the 0, 50 and 100 mg LMB L^{-1} treatments. However, differences were very small, as were within group variations. The mean PSII-efficiency at the bottom was 0.53 (± 0.02) (Fig. 3). The pH was significantly different ($F_{5,12}$ = 288.3; p < 0.001) and three different groups were found: 1) the control; 2) the 0 mg LMB L^{-1} treatment, i.e. the sole PAC treatment; and 3) all PAC + LMB treatments (Fig. 18).

Figure 18 - Chlorophyll-a concentrations (µg L^{-1}) in the top and bottom of the test tubes treated with PAC and it combination with lanthanum modified clay.



Legend**:** Chlorophyll-a concentrations (µg L^{-1}) in the top 5 mL (top light grey bars) and bottom 5 mL (lower dark grey bars) of 60 mL cyanobacteria suspension from Jacarepaguá Lagoon incubated for one hour in the absence (control) or presence of the coagulant PAC (8 mg Al L^{-1}) and different concentration of lanthanum-modified bentonite, LMB (0 - 400 mg L^{-1}). Also included are the Photosystem II efficiencies (PSII) of the cyanobacteria collected at the water surface (filled circles) and at the bottom (open circles) as well as the pH of the water (open triangles). Error bars indicate one standard deviation (*n* = 3). Similar symbols (a,.., γ) above/below the bars indicate homogeneous groups that are not different at the 95% level (Holm-Sidak test).

Source: Author, 2018.

4.3.2 Effect of different over-standing water on sediment phosphate release

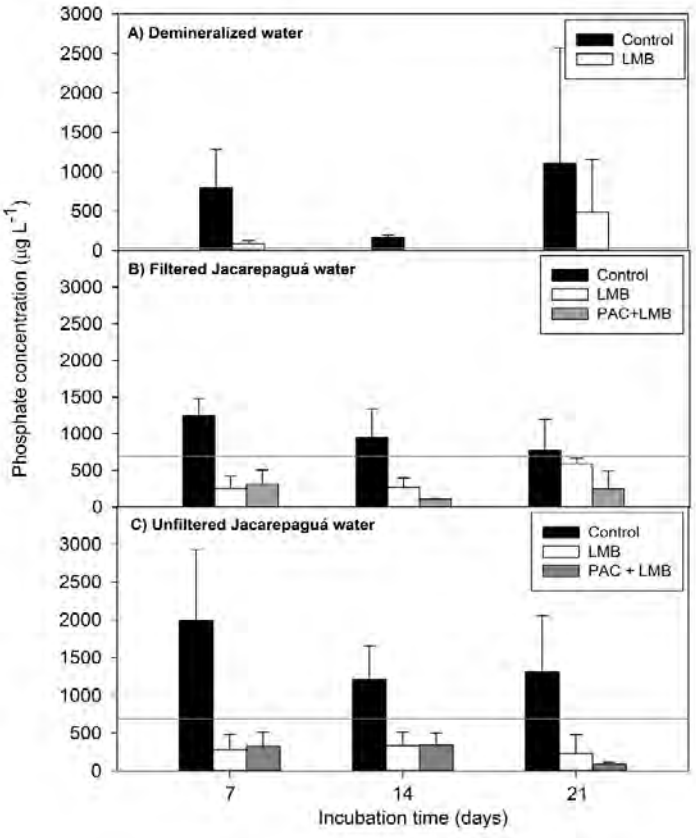
The initial SRP concentration in the Jacarepaguá lagoon was 786 µg L^{-1} in the filtered water and 783 µg L^{-1} in the unfiltered water, while it was below the detection limit (3 µg L^{-1}) in the demineralized water. The SRP concentrations in the filtered and unfiltered lagoon water standing over Jacarepaguá sediment were reduced by treatments with LMB or PAC+LMB, while it was the same in the controls (Fig. 19). Contrary, in over standing demineralized water SRP concentrations seems to increase in treatments with LMB and control (Fig. 19), however the rmANOVA indicated no time effect ($F_{1.5,6.0}$= 2.12; p = 0.200), no treatment effect ($F_{1,4}$= 1.60; p = 0.274) and no time x treatment interaction ($F_{1.5,6.0}$= 0.36; p = 0.655), (Fig. 19A). The SRP fluxes, from demineralized water, determined after one-week incubation were not significantly different (t_4 = 2.25; p = 0.065), despite they were on average 4.0 (± 2.5) mg P m^{-2} d^{-1} in the control and 0.4 (± 0.2) mg P m^{-2} d^{-1} in the LMB treatment (Fig. 24).

In the series where Jacarepaguá sediment was incubated with filtered lagoon water, the rmANOVA indicated no time effect ($F_{2,12}$ = 1.15; p = 0.351), a significant treatment effect ($F_{2,6}$ = 107.5; p < 0.001) and no time x treatment interaction ($F_{4,12}$ = 0.79; p = 0.552). Tukey's *post-hoc* comparison revealed that SRP concentrations in the LMB and LMB+PAC treatments were significantly lower than in the controls (Fig. 19B). Likewise, the SRP fluxes were significantly different ($F_{2,8}$ = 22.8; p = 0.002). Tukey's test showed that controls differed from treatments with values of 2.3 (± 1.2) mg P m^{-2} d^{-1} in the control, -2.7 (± 0.9) mg P m^{-2} d^{-1} in LMB treatment and -2.4 (± 0.9) mg P m^{-2} d^{-1} in LMB+PAC treatment. The negative values indicate a net removal of SRP from the over-standing water and thus a flux towards the sediment (Fig. 24).

The treatment effects in the series with sediment and unfiltered water were comparable to those obtained with filtered water (Fig. 19B and C). The rmANOVA indicated no time effect ($F_{2,12}$ = 1.90; p = 0.192), a significant treatment effect ($F_{2,6}$ = 13.1; p = 0.006) and no time x treatment interaction ($F_{4,12}$ = 1.37; p = 0.301). Tukey's *post-hoc* comparison revealed that SRP in the LMB and LMB+PAC treatments were significantly lower than in the controls (Fig. 19C). The SRP fluxes were significantly

different ($F_{2,8}$ = 8.87; p = 0.016) and Tukey's test showed that the control differed from treatments with values of 6.1 (± 4.8) mg P m^{-2} d^{-1} in the control, -2.5 (± 1.0) mg P m^{-2} d^{-1} in LMB treatment and -2.3 (± 0.9) mg P m^{-2} d^{-1} in LMB+PAC treatments. Again, the negative values indicate a net removal of SRP from the over-standing water and thus a flux towards the sediment (Fig. 23).

Figure 19 - Phosphate concentrations (µg L^{-1}) in demineralised water, filtered and unfiltered Jacarepaguá water after treated with either LMB or PAC + LMB.



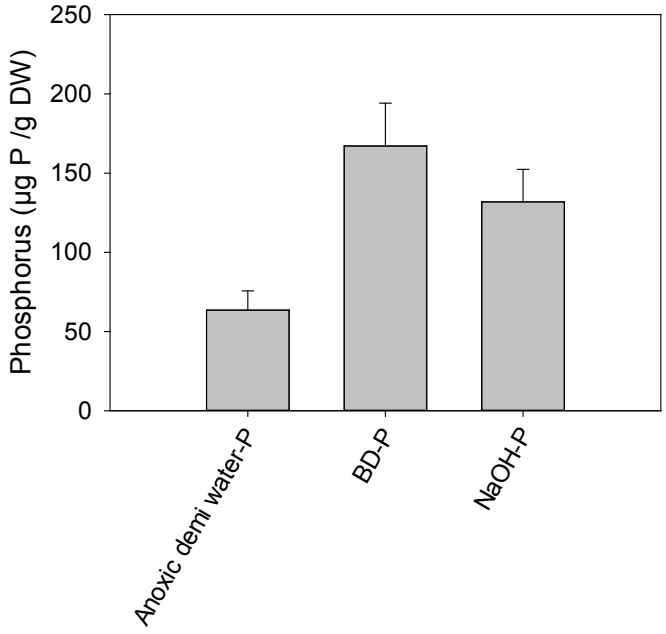
Legend: Phosphate (SRP) concentrations (µg L^{-1}) after 7, 14 and 21 days in 100 mL demineralised water (A), filtered (B) and unfiltered (C) Jacarepaguá water standing above 50 g Jacarepaguá sediment that was untreated (controls) or treated with either LMB (400 g m^{-2}) or PAC + LMB (PAC at 8 mg Al L^{-1}). Error bars indicate one standard deviation (n = 3). The grey line represents the initial SRP values at day '0" in each type of water used

Source: Author, 2018.

4.3.3 "Labile" P-pool in Jacarepaguá Lagoon sediment

The average value from the phosphate concentration sum, for all three extraction steps was 362.5 µg P/g DW. The major part of the phosphorus was extracted in step 2, with BD (167.1 ±27.1 µg P/g DW). The P sorbed by clay minerals and oxides of AI extracted using NaOH contributed with 131.8 (±20.5) µg P/g DW. Lower contribution of loosely adsorbed P (extracted with anoxic demineralized water) was observed in a concentration of 63.5 (±12.1) µg P/g DW (Fig. 20). Considering 14% of dry weight in each ml of sediment it yields a concentration of 51.5 µg P/ml.

Figure 20 – Concentrations of Phosphorus in the Jacarepagua Lagoon sediment

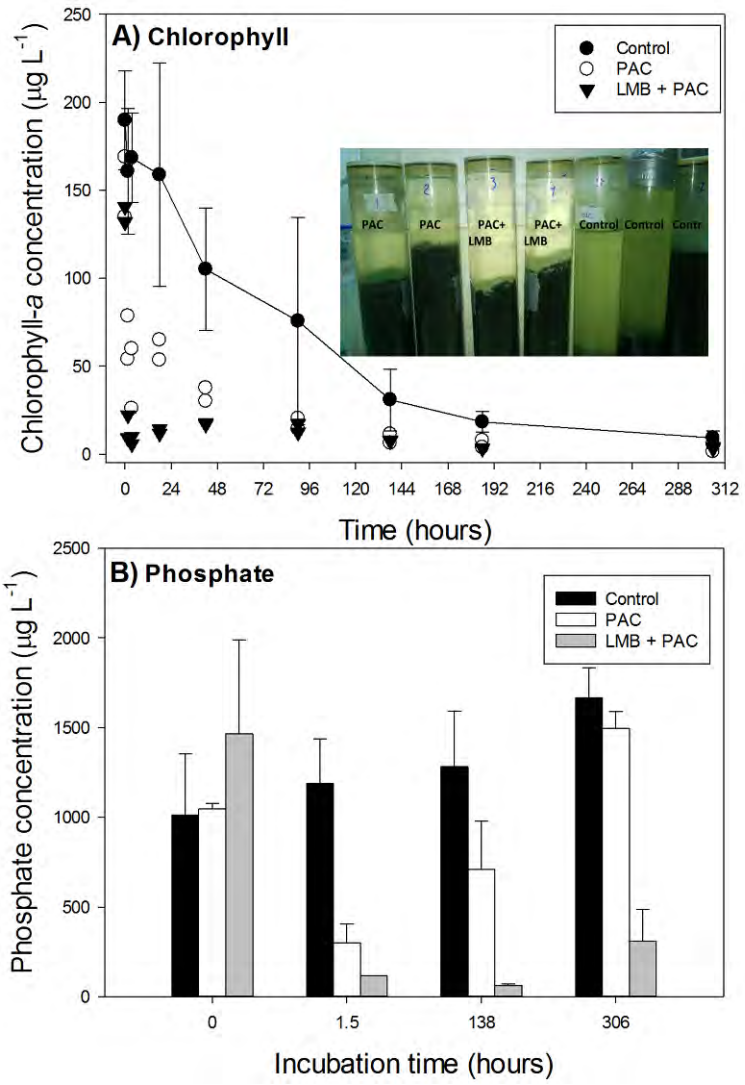


Legend: Average concentrations of P-fractions (µg P/g DW) in Jacarepaguá Lagoon sediment core. Error bars indicate one standard deviation (n = 3). BD= strongly reducing reagent (anoxic Bicarbonate/Dithionite).
Source: Author, 2018.

4.3.4 Treating sediment cores with PAC or LMB+PAC – short term experiment

The sediment cores treated with PAC+LMB or only PAC caused a rapid decline in both the chlorophyll-*a* and the SRP concentrations in the water column (Fig. 21A and B). Already after 1.5 hours chlorophyll-*a* concentrations in the sole PAC treatment were 59% lower than in the control, while in the LMB + PAC treatment it was more than 90% lower. The rmANOVA indicated a significant time effect ($F_{3.5,14.3} = 34.3$; $p < 0.001$), a significant treatment effect ($F_{2,4} = 11.1$; $p = 0.023$) and a significant time x treatment interaction ($F_{7.1,\ 14.3} = 3.84$; $p = 0.015$). The chlorophyll-*a* concentrations in the control also gradually decreased to values similar as in the treatments (Fig. 21A). Tukey's test revealed that only the control and the LMB+PAC treatments were significantly different from each other. The SRP concentrations were strongly influenced by the treatments where PAC reduced the SRP concentrations by 72% within 1.5 hours, while LMB+PAC caused a 92% reduction (Fig. 21B). However, SRP concentrations in PAC treatments started to increase again and after 306 hours they were similar to the control ($t_3 = 1.25$; $p = 0.299$), while SRP in the PAC + LMB treatments were still significantly lower (Tukey's test following one-way ANOVA; $F_{2,6} = 49.2$; $p = 0.002$). The SRP fluxes were on average 9.2 (± 6.7) mg P m^{-2} d^{-1} in the control, 3.6 (± 1.7) mg P m^{-2} d^{-1} in PAC treatment and -10.4 (± 5.5) mg P m^{-2} d^{-1} in LMB+PAC treatment. The ANOVA indicated that SRP fluxes were significantly different ($F_{2,6} = 7.70$; $p = 0.043$), (Fig 23), but this was not confirmed by the Tukey *post-hoc* comparison yielding a marginal difference between the control and LMB+PAC treatment ($p = 0.052$).

Figure 201 - Chlorophyll-a and SRP concentrations in the short term experiment.



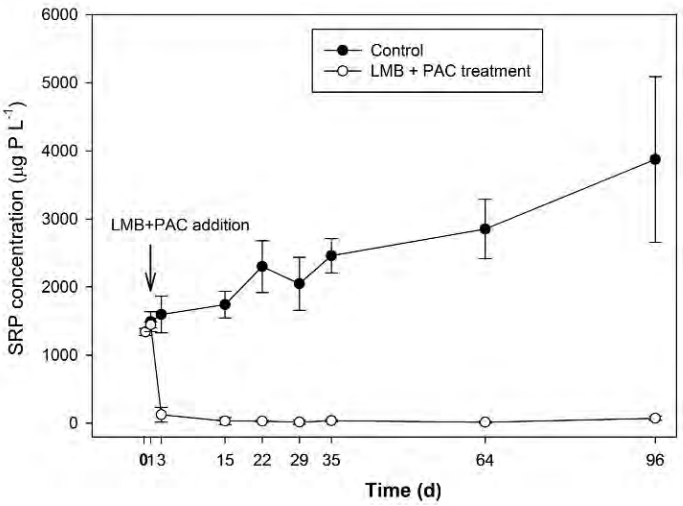
Legend: Course of the chlorophyll-*a* concentrations (upper panel A) and of SRP concentrations (lower panel B) in a short term experiment in which sediment cores from Jacarepaguá lagoon (collected January 19th 2015) were left untreated (Control; *n* = 3) or were treated with either PAC (8 mg L^{-1}; *n* = 2), or with PAC (8 mg L^{-1}) and LMB (400 g m^{-2}; *n* = 2)

Source: Author, 2018.

4.3.5 Treating sediment cores with LMB + PAC-long term experiment

When sediment cores from Jacarepaguá were treated with PAC+LMB a strong reduction in SRP concentrations could be observed (Fig. 22). The rmANOVA on SRP data over the whole period indicated a significant time effect ($F_{3.4,16.8}$ = 7.29; p = 0.002), a significant treatment effect ($F_{1,5}$ = 136.0; p < 0.001) and a significant time x treatment interaction ($F_{3.4,16.8}$ = 16.4; p < 0.001). To check whether the interaction effect was caused by the initial data obtained prior to the treatment (days 0 and 1), an additional rmANOVA was run on data after the application (days 3,...,96). This rmANOVA yielded similar results; a significant time effect ($F_{3.3,16.7}$ = 7.22; p = 0.002), a significant treatment effect ($F_{1,5}$= 146.7; p < 0.001) and a significant time x treatment interaction ($F_{3.3,16.7}$ = 7.62; p = 0.002). The time x treatment interaction effect was caused by the gradual increase in SRP in the controls, while SRP in the treatments remained equally low over the course of the experiment (Fig. 22). SRP in the treatments was on average only 2% of the values in the control. The SRP fluxes were 9.9 (± 3.3) mg P m^{-2} d^{-1} for the control and -4.6 (± 0.3) mg P m^{-2} d^{-1} for the PAC+LMB treatments (Fig. 23).

Figure 212 - the SRP concentrations in the long term experiment where the sediment cores were treated with PAC (8 mg L^{-1}) and LMB (507.5 g m^{-2}; n = 4).



Legend: Course of the SRP concentrations in sediment cores collected on September 29th 2015 in Jacarepaguá lagoon that were left untreated (Control; *n* = 4) or were treated with PAC (8 mg L^{-1}) and LMB (507.5 g m-2; *n* = 4).
Source: Author, 2018.

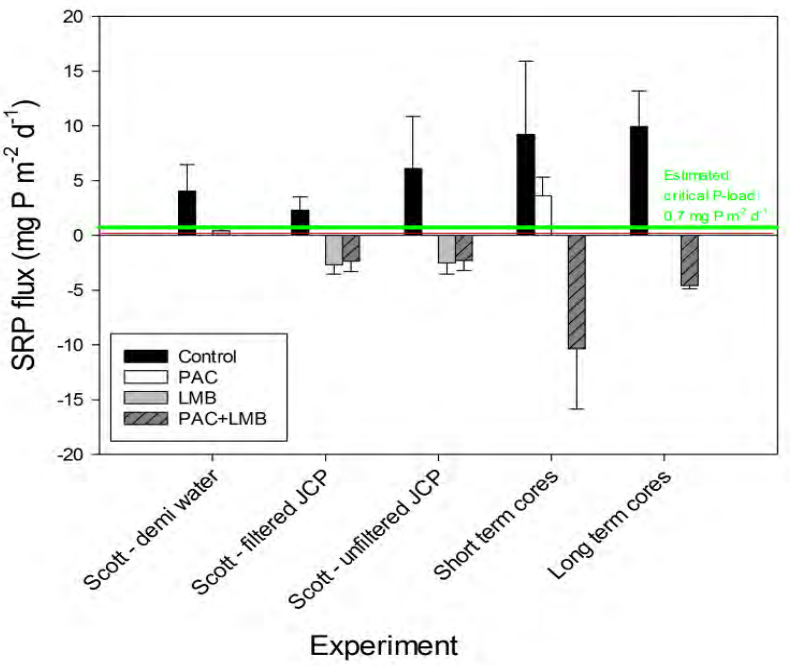
4.3.6 Comparison of SRP fluxes with estimated critical P loadings

Based on the output from the PCLake Metamodel, a critical SRP flux of 0.7 mg P m^{-2} d^{-1} indicates the shift from a clear to turbid stable state in Jacarepaguá lagoon. While after the turbid stable state is stablished only decreasing the SRP flux to values lower than 0.2 mg P m^{-2} d^{-1} would shift the water from the turbid to clear. The Vollenweider (1976) model yielded -for a target in-lagoon P concentration of 30 µg L^{-1}- a critical P load of 0.95 mg P m^{-2} d^{-1} (Table 3). These values are considerably lower than the fluxes that have been estimated in the controls of the different experiments conducted and higher than the LMB treatments in this study (Fig. 23).

Table 3 - Critical P loadings from the transitions from clear to turbid water and vice versa derived using the PCLake Metamodel with the following input data: residence time = 173.7 days, discharge 19 mm d-1; average depth of 3.3 m; background extinction of 0.5 m^{-1}; maximum fetch of 4000 m; relative surface swamp area of 0.1; and sand as the soil type, as well as the critical P load based on teh Vollenweider (1976) model with a target in-lagoon P concentration of 30 µg L^{-1}.

Model	Critical P load per day (mg P m^{-2} d^{-1})	Critical P load per year (g P m$years^{-1}$)
PCLake – clear to turbid	0.66	0.24
PCLake – turbid to clear	0.17	0.06
Vollenweider	0.95	0.35

Figure 223 - Fluxes of SRP in the different experiments and treatments performed in this study.



Legend: Estimated SRP fluxes in the different experiments and treatments performed in this study. Negative values indicate a net SRP removal from over-standing water and thus na accumulation in the sediment, whereas positive values indicate a net release from the sediment (internal loading). The green line represents the estimated critical transition from clear to turbid water, while the grey line represents the critical transition from turbid to clear based on the PCLake Metamodel.

Source: Author, 2018.

4.4 **Discussion**

The results of this study are in agreement with our hypotheses that LMB will block P-release from the sediment of the eutrophic coastal lagoon Jacarepaguá and that a combination of PAC with LMB also clears the water effectively from cyanobacteria. The LMB strongly reduced the internal loading from the nutrient rich sediment from Jacarepaguá lagoon. These results add to the growing body of evidence that LMB is an effective eutrophication management agent. Meanwhile, LMB has been used in dozens of freshwater systems where it in general led to an improved water quality (e.g., COPETTI et al., 2016; SPEARS et al., 2013; 2016; EPE et al., 2017). In freshwater lakes with cyanobacterial blooms, the combination of LMB with a coagulant clearly improved water quality through effective control of the bloom and internal SRP loading (LÜRLING and VAN OOSTERHOUT, 2013; WAAJEN et al., 2016a). A growing number of studies show that LMB is effective in reducing the SRP efflux from freshwater sediments (e.g., WAAJEN et al., 2016a,b), but reports on its efficacy in eutrophic coastal lagoons is still limited. Few studies have reported that LMB could adsorb SRP effectively in saline water (HAGHSERESHT, 2006; ZAMPARAS et al., 2012) and brackish water (REITZEL et al., 2013), while reports on effective SRP efflux reduction from brackish and saline sediments are even more rare (DOUGLAS et al., 1999). Hence, our study is one of the few that demonstrates the effectiveness of LMB in hampering the SRP efflux from a brackish sediment and the first that shows that combined with PAC and LMB can control the sediment SRP release for at least three months. In our short term experiment, we could see that PAC alone (at 8 mg Al L^{-1}) was ineffective in hampering sediment P efflux as within two weeks SRP was as high as in the control, but when combined with LMB, the SRP remained at 2% of the control for the entire experimental period of three months.

Our results also refute the claim that even moderately saline environments of >0.5 ppt will render LMB ineffective, because La would be freed from the clay matrix and therewith prohibit formation of a reactive layer for the absorption of labile P species at the sediment-water interface (COPETTI et al., 2016). Liberation of some of

the La from the clay matrix is likely in more ion rich environments, but formation of “soluble La species” (COPETTI et al., 2016) is less likely, since any La will immediately react with oxyanions in the water to form complexes (BYRNE and KIM, 1993), including precipitates with phosphate (FIRSCHING and KELL, 1993). High pH and elevated alkalinity as in Jacarepaguá lagoon imply a higher proportion of hydroxyl- and carbonate ions in the water that could interfere with La-phosphate precipitation (BYRNE and KIM, 1993; JOHANNESSON and LYONS, 1994). Nonetheless, our results show that such interference in the water of Jacarepaguá is insufficient to render LMB ineffective and that sufficient La remained to effectively reduce the SRP efflux from the brackish sediment of Jacarepaguá lagoon. Effective blocking of sediment P release has also been found in a short-term (4 d) experiment, where 0.1 g of LMB and 1.0 g of bottom sediment from Swan River were incubated with 30 mL autoclaved water of 0.5 and 30 ppt salinity (HAGHSERESHT, 2006). It would be advisable to conduct additional research with LMB under more saline conditions to test the claim that “soluble La species” are released into the saline water and to evaluate the efficacy of LMB in more saline conditions.

The main reason for including PAC is the year round presence of a relatively high biomass of phytoplankton in Jacarepaguá lagoon (GOMES et al., 2009) and the incapacity of solely ballast to precipitate cyanobacteria, whilst their combination is highly effective (NOYMA et al., 2017). The effectiveness of ballast compounds and a low dose coagulant is, however, inversely related to cyanobacterial biomass – more biomass requires more ballast to effective settling (NOYMA et al., 2017). Our results showed that 2 mg Al L^{-1} PAC in itself was insufficient to settle the cyanobacteria, but with a dose of 400 mg LMB L^{-1} effective removal could be achieved. It should be noted, however, that such LMB dose comes down to 4884 tons for the entire lagoon. Increasing the PAC dose to 8 mg L^{-1}, which proved to be the best concentration in our previous studies with red soil as ballast (DE-MAGALHÃES et al., 2017), showed that comparable results could be achieved with 100 mg LMB L^{-1}, which is 1221 tons for the entire lagoon.

Of course the main reason for applying LMB is not the needed ballast weight, but the effectiveness in reducing the sediment SRP-efflux. In the first trials we used 400 g m^{-2}, but this was increased to 507.5 g m^{-2} in the last sediment core experiment

as we increased the communicating sediment depth to 10 cm and included the water column P in the calculations. This dose is in close vicinity with the average dose of 388 g LMB m^{-2} (range 159-530) given in COPETTI et al., (2016) and the 348 g LMB m^{-2} (range 6-667) listed in SPEARS et al., (2013). Considering the total sediment area of the lagoon (3.7 km^2) a 507.5 g m^{-2} dose implies 1878 tons of LMB would be needed, which with an average water depth of 3.3 m yields a dose of 154 mg LMB L^{-1} in the lagoon. Common application of LMB is as a slurry from the water surface - LMB granules are mixed with surface water just before spraying on the water (COPETTI et al., 2016). Since this LMB dose is between suboptimal and optimal when combined with 2 mg Al L^{-1} of PAC (see Fig. 18), a dose of 8 mg Al L^{-1} of PAC seems better suited (see Fig. 19). Although, 8 mg Al L^{-1} of PAC by itself was already sufficient to precipitate the cyanobacteria, the short term sediment core experiment clearly evidenced it was ineffective in hampering the sediment P-efflux (see Fig. 22). Using a higher dose of PAC to counteract the sediment P release is not recommended for several reasons despite the cost of PAC is only about 15-20% that of LMB. First, the minimum dose needed, based on an Al:P ratio of minimally 10:1 (cf. DE VICENTE et al., 2008; EGEMOSE et al., 2010), would boil down to at least 16 mg Al L^{-1}. At such PAC dose, the pH in Jacarepaguá water will drop and depending on the pH at application could drop to pH values below 6 (DE-MAGALHÃES et al., 2017). Second, the Al polymerization seems to be the most important factor for acute hypoxic death in fish (POLÉO, 1995) and thus negative effects of a relatively high Al dose are likely on the abundant fish, such as *Tilapia rendalli*, which is an important feed and source of income to fishermen living adjacent to the lagoon. Finally, Al-flocks are easily resuspended and hence distributed, while LMB is not (EGEMOSE et al., 2010). In fact, LMB strongly increased sediment stability/consolidation and the resuspension data obtained by EGEMOSE et al., (2010) drove them to conclude that wind driven events will most probably not cause any resuspension of LMB in contrast to Al flocks. Nonetheless, the influence of wind driven resuspension on flocks and P-binding capacity in a large shallow system like Jacarepaguá lagoon needs to be determined.

The combination of a higher dose of PAC (8 mg L^{-1}) with dose of LMB targeting both water column and sediment P, not only ensures a stripping of the

water column of cyanobacteria and phosphate, which is around 0.8 mg SRP L^{-1} despite cyanobacteria flourishing (DE-MAGALHÃES et al., 2017), but also sufficient SRP binding capacity to counteract any P that might diffuse from a bit deeper than 10 cm sediment as the PAC brings an additional SRP binding capacity equal to about 5 cm of sediment.

The negative P-flux and the low SRP concentration in the long term experiment (-4.6 ± 0.3mg P m^{-2} d^{-1}) showed the strong P binding capacity of LMB + PAC. This P binding occurred in cores that had very low oxygen concentrations, which is common for Jacarepaguá lagoon, and is in line with other studies that also found good P adsorption by LMB under anoxia (ROBB et al., 2003; AKHURST et al., 2004; ROSS et al., 2008). The combination of a low dose PAC with a sediment P target dose of LMB has been applied in a whole lake application in 2008 (LÜRLING and VAN OOSTERHOUT, 2013). The hypertrophic water with dominance of cyanobacteria in Lake Rauwbraken (The Netherlands) was changed to a mesotrophic clear water state with total P concentrations for more than four years being less than 10% pre-application concentrations (LÜRLING and VAN OOSTERHOUT, 2013). It should be noted, however, that Lake Rauwbraken, unlike Jacarepaguá lagoon, has no major inflows of nutrient rich water, but rather diffuse sources via ground water, litter fall and birds (LÜRLING and VAN OOSTERHOUT, 2013). In Jacarepaguá the external load is overwhelming with an average discharge of 0.8 m^3 s^{-1} (GOMES et al., 2009) from the tributaries and an average total P concentration of 1477 mg m^{-3}, the external load comes to 27.6 mg P m^{-2} d^{-1} (~10 g P m^{-2} $year^{-1}$). Given such ongoing external P loading in Jacarepaguá lagoon it is beyond doubt that first these external sources should be tackled before massive in-lake rehabilitation actions are undertaken.

External load reductions could reduce the eutrophication symptoms within several years depending on efficacy of P load reduction and retention time (FASTENER et al., 2016). Although the retention time in Jacarepaguá is around 0.5 years, suboptimal mixing and particular the high internal P load could hamper delay in recovery for many years (FASTENER et al., 2016). In Jacarepaguá lagoon the internal P flux of ~10 mg P m^{-2} d^{-1} (or ~3.6 g P m^{-2} $year^{-1}$) is ~ 14 times higher than the critical load, here calculated. Although the model has not been developed for

brackish water, and estimated critical loadings come with some uncertainties (JANSE et al., 2010), the internal P loading was substantially larger than the critical loading. Reducing the P loading to below the critical P load is the only option for rehabilitation (VOLLENWEIDER, 1976; JANSE et al., 2008). Thus, even when external loadings are completely stopped, the water quality in Jacarepaguá lagoon will not improve rapidly unless internal loading is tackled adequately. Consequently, additional in-lake actions seem inevitable in this system. Treatments with only LMB or LMB+PAC could bring the internal P load below the critical load, but as emphasized the external load should also be strongly controlled by implementing efficient waste water treatment in the catchment. Furthermore, those catchment treatments should keep the P load below the critical load to ensure enduring improved water quality.

The effective control of the sediment P release from Jacarepaguá sediment becomes important in view of the planned but not yet executed dredging plans for the lagoon. According to media reports the dredging project will cost $250 million (http://www.dailymail.co.uk/wires/ap/article-2947878/Rio-official-visits-filthy-lagoon-near-Olympic-Park.html). Of course, as mentioned before, such actions should only be undertaken once external loading has been reduced drastically, but then LMB, or LMB+PAC might prove a much cheaper option, or could be considered as addition to dredging. The effective dose used here (507.5 g m^{-2}) will boil down to around 1878 tons of LMB for the entire lagoon. With a pricing between $2500 and $3000 per ton of LMB, the total material costs to tackle the internal load would be between $4.7- and $5.6 million. Assuming that also the entire water column needs to be stripped of 1 mg P L^{-1}, which requires an additional 1000 tons ($2.5 – 3.0 million) and including operational costs a total budget of around $10 million would suffice. This is only 4-5% of the estimated dredging costs. Moreover, it remains to be seen if the planned dredging and storage of sediment in geotextiles in a newly to create island in the lagoon will sufficiently reduce in-lake nutrients to improve water quality. The in-lagoon P concentrations need to be pushed below the threshold concentration needed to minimize the risk on cyanobacterial blooms (FASTNER et al., 2016). The here tested combination of PAC and LMB proved an efficient method to settle cyanobacteria out of the water column and to block the sediment P release. Hence, the combination seems promising to test at a larger scale *in-situ* using enclosures.

4.5 **Conclusions**

● Positively buoyant cyanobacteria could be precipitated using low dosage PAC (2 mg Al L^{-1}) combined with higher LMB dose and solely with a higher dose of PAC (8 mg Al L^{-1}) or also combined with lower LMB dose.

● The determined internal P loading from the sediment exceeded estimated critical P loading for rehabilitation meaning that only external load reduction will not improve water quality in the lagoon and that both internal and external P load should be tackled.

● The PAC dose used (8 mg Al L^{-1}) was not capable to block P release from the sediment, but the LMB proved highly efficient in a brackish system.

● In all treatments with LMB and LMB+PAC negative SRP fluxes were determined meaning a net removal of P from the water column towards the sediment.

● In a three month sediment core experiment combined LMB+PAC treatment kept SRP as low as 2% of the controls underpinning the strong and robust interception of P released from the heavily P enriched sediment of Jacarepaguá lagoon.

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5 DISCUSSÃO GERAL

A Lagoa de Jacarepaguá continua sofrendo com o intenso acumulo de nutrientes e constantes florações de cianobactérias como também observado em estudos anteriores (FERRÃO FILHO et al., 2002a; GOMES et al., 2009). Durante o presente estudo foram observadas florações em quase todo os meses, representadas principalmente pela espécie *M. aeruginosa*. O crescimento dessa espécie é favorecido em todo o globo em condições de abundância e aporte exagerado de nutrientes, tendo uma distribuição geográfica abrangente com exceção apenas do continente antártico (FRISTACHI & SINCLAIR, 2008). Cepas dessa espécie podem produzir toxinas do tipo microcistinas, que exercem importantes alterações no ambiente, provocando mudanças na estrutura das comunidades e ocasionando eventos de intoxicação e mortandade de peixes, além da contaminação humana.

Na Lagoa de Jacarepaguá as florações de *M. aeruginosa* já vêm sendo estudadas desde 1996 onde DOMINGOS (2001) observou entre o período de 1996 e 1997, florações associadas a morte da população de macrófitas aquáticas devido ao aumento da salinidade. Posteriormente, Gomes et al 2009 observaram períodos mais intensos de florações de *M. aeruginosa* com posterior desaparecimento das cianobactérias, dando oportunidade ao crescimento de clorofíceas, diatomáceas e pequenos flagelados, que coincidem com períodos de queda da temperatura da água. Levando em consideração o clima tropical em que a Lagoa de Jacarepaguá está localizada e a relação positiva das florações de *M. aeruginosa* com o aumento da temperatura da água, é esperado que o problema dessas florações se agrave ainda mais devido ao cenário de aquecimento global, caso não haja redução das cargas de nutrientes (PEARL & HUISMAN, 2008).

Neste trabalho de doutorado observou-se que os eventos de florações de *M. aeruginosa* continuam constantes e a ocorrência das florações perduram a maior parte do ano. As temperaturas da Lagoa de Jacarepaguá permanecem elevadas em quase todo o período onde apenas em alguns momentos caem para temperaturas próximas a 20°C, que desfavorece o crescimento de *M. aeruginosa* (GOMES et al.,

2009; YANG et al., 2018). Além disso, apesar da conexão com o mar através do canal da Joatinga, a salinidade da água tem se mantido baixa, entre 4 S, na maior parte do ano, não sendo prejudicial ao crescimento de *M. aeruginosa* uma vez que esta apresenta ampla faixa de resistência à salinidade (DOMINGOS 2001; TONK et al., 2007; ROBSON E HAMILTON, 2003). A morfologia da lagoa, somada a sua localização e a amplitude máxima da maré, de 1,5 m na barra do canal de Joatinga, faz com que a troca de suas águas com o mar seja desfavorecida, diminuindo a entrada de água salgada e intensificando o problema do acúmulo de nutrientes (MARQUES, 1990; ZEE et al.,1992).

Devido a elevada carga de nutrientes e elevadas temperaturas é esperado a intensificação das florações de cianobactérias, caso não haja nenhuma intervenção humana sobre as fontes difusas e pontuais de nutrientes que entram no local. Uma vez identificadas, essas fontes externas de incremento de nutrientes devem ser primeiramente tratadas (COOKE et al., 1993). Entretanto, em grande parte dos casos apenas a redução das fontes externas não é suficiente para a melhoria da qualidade da água.

Estudos têm demostrado que apenas a metade dos lagos tratados apresentam alguma melhoria devido apenas à redução das fontes externas de nutrientes (CULLEN & FORSBERG, 1988) e, mesmo que haja alguma resposta, esta pode aparecer após décadas (VAN LIERE & GULATI, 1992). Nesses casos, as fontes internas que acumularam durante longos períodos de eutrofização, são as principais responsáveis, tendo o sedimento um papel fundamental para essa demora (SØNDERGAARD et al., 1993; SCHARF, 1999; SØNDERGAARD et al., 2003).

Nosso estudo demonstrou que devido ao período prolongado de acúmulo de nutrientes e de intensas florações de cianobactérias, o sedimento da Lagoa de Jacarepaguá apresenta elevado fluxo de fósforo, em torno de 9,9 (±3,3) mg P m^{-2} d^{-1} (Capítulo 3). Esse fluxo é comparável a outros ambientes eutrofizados e capaz de provocar uma demora na melhoria da qualidade da água por anos, mesmo se o lançamento de esgoto for interrompido totalmente. Assim sendo, medidas que removam ou bloqueiem a liberação do fósforo contido no sedimento se fazem necessárias para uma melhora eficaz e duradoura.

Dentre todas as medidas de mitigação apresentadas (ver introdução), a que utiliza conjuntamente coagulantes e adsorventes de fósforo, além de menos custosas, são promissoras (LÜRLING & FASSEN, 2012; DE-MAGALHÃES et al., 2017). A utilização de coagulante, além de ser capaz de remover parte do fósforo da coluna da água, tem como principal objetivo a remoção das florações para o sedimento no fundo onde podem ser decompostas lentamente junto com suas toxinas, não promovendo perigo às comunidades pelágicas presentes na lagoa e evitando a queda de oxigênio provinda da decomposição dessa biomassa na coluna de água. A utilização de lastro visa além de auxiliar na foculação fazer também o capeamento do sedimento.

Os coagulantes testados, PAC e quitosana apresentaram diferentes respostas na capacidade de flocular florações de *M. aeroginosa* na água da Lagoa de Jacarepaguá. Enquanto a utilização de PAC 8 mg Al L^{-1} apresentou elevada eficiência em precipitar as algas nos testes de laboratório, a quitosana, mesmo nas concentrações mais elevadas e combinada com lastro, foi incapaz de promover a floculação. O principal mecanismo que afeta a eficiência da quitosana é a concentração de ânions em torno da camada positivamente carregada dos grupos amina da quitosana (TSAIH & CHEN, 1997; STRAND et al., 2003; QUN & AJUN, 2006). Em aguás com pH elevado, as hidroxilas e os carbonatos aniônicos prevalecem na água podendo causar um distúrbio na interação entre os grupos amino protonados da quitosana e a carga negativamente carregada de cianobctérias (RENAULT et al., 2009). Além disso, a eficiência da quitosana depende também de caracteristicas intrínsecas do produto como peso molecular, fração molar da acetilação e a densidade da carga (YANG et al, 2016; STRAND et al, 2003). Comparando os resultados aqui obtidos com a aplicação da mesma quitosana na água do reservatório do Funil (RJ) (NOYMA et al 2016), observamos que ela funcionou muito bem em pH neutro e em baixa alcalinidade, sendo estas apontadas como as principais variáveis que afetaram a sua eficiência em nossos experimentos.

A utilização de PAC na Lagoa de Jacarepaguá se mostrou eficiente mesmo sozinha, para flocular a floração de *M. aeruginosa*. A escolha de PAC sobre outros coagulantes à base de alumínio deve-se à vantagem de ter um menor efeito redutor no pH, necessitar de menor dose para formar grandes flocos e produzir menor

quantidade de alumínio residual (GEBBIE 2001; DE JULIO et al., 2010). Apesar de ser eficiente sozinho, a utilização em conjunto com lastro foi capaz de maximizar significaticamente esse efeito. Em experimentos de laboratório LÜRLING & FASSEN (2013b) demonstraram que a utilização de lastro tornou possível a floculação da floração de *M. aeruginosa*, utilizando baixa dose de PAC.

O presente estudo mostrou que todos os latros testados, solo vermeho, sedimento da lagoa (Capítulo 2) e BML (Capítulo 3), são capazes de aumentar a eficiência de PAC nessa floculação. Em alguns casos, em vez do coagulante, apenas o lastro já é capaz de se agregar e precipitar as algas, o que funciona bem em ambientes marinhos devido à alta força iônica (SENGCO et al., 2001; SENGCO & ANDERSON, 2004). Apesar de funcionarem bem em aguás marinhas, em águas doces se mostram ineficientes, trazendo então a necessidade da utilização conjunta com um coagulante (LI & PAN 2013). LI & PAN (2013) por exemplo, mostraram que a utilização de areia sozinha foi incapaz de flocular *M. aeruginosa* tendo conseguido aumentar a eficiência para 40-60 % com adição de quitosana e 90% utilizando extrato de *Moringa oleifera*. Também PAN et al. (2012) reconheceram que a adição apenas de solo dificilmente removeria o fitoplâncton sem que um coagulante não fosse usado como facilitador. Assim, como em ambientes de água doce que apresentam baixa força iônica, a utilização somente de lastro na lagoa de Jacarepaguá não foi suficiente para precipitar *M. aeruginosa* sendo que bons resultados foram alcançados com a utiliazação de PAC 8 Al mg L^{-1} e a sua adição conjunta com lastro aumentou ainda mais a eficiência da remoção. A técnica “Flock and sink” utilizando PAC e lastro se mostrou um método eficiente para a remoção de *M. aeruginosa* na lagoa costeira de Jacarepaguá.

Apesar do sucesso da utilização conjunta de baixas doses de PAC e lastro (solo vermelho ou sedimento), a floculação isoladamente é uma medida a ser utilizada em períodos específicos, viabilizando água para alguns usos. Nas condições em que a Lagoa de Jacarepaguá se encontra podemos prever que, mesmo após uma efetiva redução do aporte externo, a melhoria da qualidade da água demore décadas devido ao estoque de fósforo presente no sedimento. Com isso, medidas que removam ou aprisionem o fósforo, como a adição de adosrvente de fósforo em vez de simplesmente lastro se fazem necessárias.

A aplicação de PAC e bentonita modificada com lantânio (BML) com o intuito de flocular as cianobactérias e prender o fósforo no sedimento da Lagoa de Jacarepaguá foram testadas em laboratório. A argila modificada com lantânio foi bem sucedida em reduzir a liberação de fósforo pelo sedimento, quando testada a eficiência de somente PAC e "Flock and Lock" nos testemunhos da lagoa onde as maiores reduções de fósforo foram observadas na utilização conjunta dos dois (Figura 22; Cap 3). Nesse experimento, apesar da rápida precipitação das florações e remoção de fósforo, a utilização apenas de PAC apresentou um retorno para concentrações iniciais de fósforo ao fim do experimento.

A utilização da argila modificada com lantânio tem se mostrado eficiente em mitigar a eutrofização em dezenas de lagos de água doce, onde melhorou significativamente a qualidade da água (e.g., COPETTI et al. 2016; SPEARS et al. 2013; 2016). Alguns estudos têm demonstrado que a argila modificada com lantânio também é eficiente em adsorver fósforo da coluna de água no mar e em ambientes salobros (HAGHSERESHT, 2006; ZAMPARAS et al., 2012). Sendo assim, este trabalho somado a outros, refuta a redução da eficiência da BML devido a liberação de lantânio (La) livre da matriz de argila na presença de salinidade > 0.5 ppt (COPETTI et al. 2016). A liberação de La da matrix é mais provável que ocorra em ambientes ricos em íons, porém mesmo assim a formação de espécies de La solúvel é menos provável que ocorra, já que o La imediatamente reage com oxônios presente na água, incluindo o próprio fósforo para formar complexos (BYRNE & KIM 1993; FIRSCHING & KELL 1993).

Nossos resultados mostram que, se utilizado BML em períodos onde apenas a floculação de algas é desejada, esta pode ser alcaçada com a utilização de uma dose de 8 mg Al L^{-1} de PAC, somadas à dose de 100 mg BML L^{-1}. Considerando as dimensões da lagoa essa dose daria a quantidade de 1221 toneladas de BML a ser aplicada em toda a lagoa. Quando desejada também a redução do fluxo interno de fósforo uma dose entre 400 g m^{-2} e 507.5 g m^{-2} deve ser aplicada considerando a quantidade de fósforo na coluna de água e sua inativação nos primeiros 10 cm de sedimento da lagoa. Considerando a área total de sedimento da lagoa (3,7 km²) a dose de 507,5 g m^{-2} a ser aplicada resultaria na aplicação total de 1878 toneladas de BML, considerando 3,3 m da coluna d'água daria uma dose de 154 mg BML L^{-1} na

lagoa. Uma aplicação com a dose utilizada neste trabalho (507,5 g m^{-2}) iria fazer necessária a utilização de 1878 toneladas de BML para toda a lagoa com o preço entre US$2500 e US$3000 por tonelada de BML, o custo total ficaria entre US$ 4,7 e 5,6 milhões, que seria apenas 2% do custo estimado da dragagem.

O tratamento utilizando BML ou BML+PAC em experimentos de laboratório se mostraram eficazes para a melhoria da qualidade da água e seu custo mais baixo, quando comparado à dragagem (http://www.dailymail.co.uk/wires/ap/article-2947878/Rio-official-visits-filthy-lagoon-near_Olympic-Park.html), faz com que sua utilização deva ser considerada. Sendo assim, devido às altas eficiências, durabilidade e baixos custos, a combinação de PAC e BML se mostrou promissora para precipitação das cianobactérias e bloqueio do fluxo de fósforo pelo sedimento da Lagoa de Jacarepaguá, sendo capaz de alternar o estado túrbido da lagoa para um estado claro, uma vez que o aporte externo seja primeiramente controlado. Essa medida apresentada nessa tese é uma solução viável e traz a esperança de uma melhoria de qualidade de vida, viabilizado novamente a água da lagoa de Jacarepaguá para seus usos múltiplos como recreação, esportes, pesca e paisagismo.

CONCLUSÃO

- A Lagoa de Jacarepaguá apresentou densas florações de *M. aeruginosa* na maior parte do ano e nos períodos de ausência de floração o fitoplâncton foi composto principalmente pelos grupos funcionais X1, J, F, X2, Y, C, MP, e P.

- As florações de *M. aeruginosa* foram favorecidas pela elevada concentração de nutrientes presente durante todo o ano e controladas principalmente pela temperatura da água e salinidade.

- A utilização apenas de lastro (solo vermelho, sedimento local ou LMB) sozinho é ineficiente em flocular as florações de *M. aeruginosa* da água da Lagoa de Jacarepaguá.

- Quitosana, mesmo em altas doses e combianado com lastro, não foi eficiente em flocular a biomassa de *M. aeruginosa*, prejudicado principalmente pelo alto pH da lagoa.

- O floculante PAC em baixa dose quando combinado com lastro, é capaz de precipitar a floração de *M. aeruginosa*. Na dose de 8 mg Al L^{-1}, PAC sozinho foi capaz de precipitar a floração de *M. aeruginosa* sem promover grandes alterações no pH e não forma Al^{+3}, fração tóxica do alumínio. Quando combinado com lastro (solo vermelho, LMB ou sedimento) sua eficiência foi significativamente melhorada.

- A utilização de apenas LMB foi capaz de bloquear a liberação de fósforo do sedimento. Contudo, no experimento de longa duração, a combinação de LMB+PAC foi capaz de bloquear o fluxo de P do sedimento.

PERSPECTIVAS

Esta tese trouxe avanços sobre o conhecimento e aplicabilidade de técnicas capazes de mitigar as florações de cianobactérias e a eutrofização. Os resultados mostram que a aplicação de floculante junto a argila modificada com lantâneo tem potencial de promover o retorno das atividades de pesca, lazer e turismo da lagoa, trazendo renda e benefícios para a sociedade. Vale ressaltar, entretanto, que para conseguir a longevidade do tratamento, é fortemente recomendado que primeiramente seja realizado a redução das fontes externas de nutrientes que entram na lagoa. Uma vez reduzida essas fontes, a técnica “Flock and Lock” se mostra capaz de reduzir o fósforo presente na água, aprisionando-o no sedimento de forma eficiente, duradoura e mais barata em relação a outras técnicas. Com os resultados desta tese, outras perguntas podem ser levantadas como: quais os efeitos da ressuspensão do sedimento no sucesso dessa técnica? Qual seu efeito nos diferentes componentes da cadeia trófica? Qual o destino das toxinas? Abrindo assim, novos caminhos de pesquisas para esta área do conhecimento.

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ANEXO A – Artigo publicado referente ao capítulo 2

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Efficacy of Coagulants and Ballast Compounds in Removal of Cyanobacteria (*Microcystis*) from Water of the Tropical Lagoon Jacarepaguá (Rio de Janeiro, Brazil)

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Abstract Eutrophication is considered the most important water quality problem in freshwaters and coastal waters worldwide promoting frequent occurrence of blooms of potentially toxic cyanobacteria. Removal of cyanobacteria from the water column using a combination of coagulant and ballast is a promising technique for mitigation and an alternative to the use of algaecides. In laboratory, we tested experimentally the efficiency of two coagulants, polyaluminium chloride (PAC) and chitosan (made of shrimp shells), alone and combined with two ballasts: red soil (RS) and the own lagoon sediment, to remove natural populations of cyanobacteria, from an urban brackish coastal lagoon. PAC was a very effective coagulant when applied at low doses (≤8 mg Al L^{-1}) and settled the cyanobacteria, while at high doses (≥16 mg Al L^{-1}) large flocks aggregated in the top of test tubes. In contrast, chitosan was not able to form flocks, even in high doses (>16 mg L^{-1}) and did not efficiently settle down cyanobacteria when combined with ballast. The RS itself removed 33–47 % of the cyanobacteria. This removal was strongly enhanced when combined with PAC in a dose-dependent matter; 8 mg Al L^{-1} was considered the best dose to be applied. The lagoon sediment alone did not promote any settling of cyanobacteria but removal was high when combined with PAC. Combined coagulant and ballast seems a very efficient, cheap, fast and safe curative measure to lessen the harmful cyanobacteria bloom nuisance in periods when particularly needed, such as around the 2016 Olympics in Jacarepaguá Lagoon.

Keywords Bloom control · Chitosan · Cyanobacteria · Eutrophication · Mitigation · PAC

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Introduction

Anthropogenic activities have led to major degradation of coastal waters worldwide (Kennish 2002), where eutrophication is one of the main stressors having a severe impact on water quality (Smith and Schindler 2009; Kennish et al. 2014; Paerl et al. 2014). One of the key symptoms of eutrophication is the development of harmful algal blooms (Heisler et al. 2008). There is broad scientific consensus that harmful algal blooms in coastal areas have increased worldwide over the last decades (Anderson et al. 2012; Paerl et al. 2014). Such blooms may have large consequences for ecosystem functioning and ecosystem services. Particularly, coastal lagoons with relative long water residence time are vulnerable to nutrient enrichment (Kennish et al. 2014) that may lead to such harmful algal blooms (Heisler et al. 2008). Augmented human population growth, urbanization and industrialization of the coastal area are considered the most important driver of eutrophication (Kennish 2002; Kennish et al. 2014). Cultural eutrophication

is also viewed as the most common problem affecting Neotropical coastal lagoons (Esteves et al. 2008).

A severely impacted coastal lagoon is Jacarepaguá in the western part of Rio de Janeiro (Brazil), where water and sewage treatment are inadequate leading to heavy blooms of cyanobacteria, especially *Microcystis aeruginosa*, of which the toxins even accumulate in fish used for consumption (Magalhães et al. 2001). It is straightforward that restricting or complete stopping of the excessive external nutrient input is the first step to manage eutrophication (Cooke et al. 2005). In Jacarepaguá Lagoon, also the accumulated nutrients in the organic-rich sediments are expected to delay recovery when external load reductions have been done (Jeppesen et al. 1991; Søndergaard et al. 1999; Cooke et al. 2005). Since Jacarepaguá Lagoon is located adjacent to the 2016 Olympic Park, authorities are discussing dredging as a measure to mitigate the cyanobacterial nuisance. However, this seems shutting the stable door after the horse has bolted as external nutrient inputs have not been reduced and the water will keep rich in nutrients and infested cyanobacteria. Nowadays, cyanobacteria in Jacarepaguá Lagoon are present perennially and build more frequent and longer-lasting perennial blooms that without additional measures will maintain a high risk for ongoing cyanobacterial blooms even after dredging. Therefore, we explored the possibility for efficient, cheap, fast and safe curative measures to lessen the cyanobacteria nuisance in periods when particularly needed, such as around the 2016 Olympics.

Algaecides are among the commonly used curative measures, but their application may come with shortcomings such as toxins and nutrient release or unwanted ecotoxicological side effects (Jančula and Maršálek 2011; Merel et al. 2013). Likewise, although found effective against *Planktothrix agardhii* (Matthijs et al. 2012), diluted hydrogen peroxide is not considered the intervention of first choice against *M. aeruginosa*—the dominant cyanobacterium in Jacarepaguá Lagoon—as toxins may be liberated (Lürling et al. 2014), extracellular polymeric substances may protect *Microcystis* against peroxide making higher doses necessary (Gao et al. 2015), and positively buoyant cyanobacteria biomass may accumulate at the surface (Wang et al. 2012; Barrington et al. 2013) aggravating nuisance. Instead, we explored the stripping of the water column from cyanobacteria with a coagulant and ballast (e.g. Li and Pan 2013; Lürling and Van Oosterhout 2013; Noyma et al. 2016) as a promising alternative to the use of algaecides.

In this technique, cyanobacteria in the water column are flocked and the aggregates of intact cells/colonies are settled to the sediment with entrapped ballast. As ballast, natural soils and clays are commonly used (Pan et al. 2006a, b, 2011a, b; Zou et al. 2006). In stratifying inland waters with much lower external phosphorus (P) load than internal loading, cyanobacteria removal with flocculants and a lanthanum-modified clay as ballast—to chemically inactivated phosphorus released from the sediment—has also yielded very promising results (Lürling and Van Oosterhout 2013; Waajen et al. 2016). Recently, Noyma et al. (2016) showed that buoyant cyanobacteria (primarily *M. aeruginosa*) from the freshwater Funil Reservoir (Rio de Janeiro, Brazil) could be flocked and effectively precipitated using a combination of polyaluminium chloride (PAC) or chitosan (made of shrimp shells) with a local red soil (collected from the banks of the reservoir, consisting mainly of kaolinite clay) as ballast. Based on those results, we hypothesized that the cyanobacteria flourishing in Jacarepaguá Lagoon could also be effectively removed from the water column using a combination of PAC or chitosan with red soil as ballast. To test this hypothesis, we ran several controlled experiments in laboratory with cyanobacteria and water from Jacarepaguá Lagoon that were exposed to different concentrations of PAC and chitosan alone and in the presence of red soil. In addition, we tested the local sediment as potential ballast compound.

Material and Methods

Jacarepaguá Lagoon

The Jacarepaguá Lagoon (43° 17′–43° 30′ W, 22° 55′–23° 00′ S) is part of a lagoon complex located in the coastal plain of at the southern coast of Rio de Janeiro, Brazil (Fig. 1). This complex consists of four main elongated lakes: Jacarepaguá, Camorim, Tijuca and Marapendi (Gomes et al. 2009). The Jacarepaguá Lagoon has a surface area of 3.7 km^2, an average depth of 3.3 m and little water exchange with the sea since it communicates with the sea through the Camorim and Tijuca lagoons. Jacarepaguá complex has the largest drainage area of the region (103 km^2) and a water inflow from rivers of about 0.8 $m^3\ s^{-1}$ (Gomes et al. 2009). The main tributaries of Jacarepaguá Lagoon flow through urban settlements surrounding the lagoon transporting not only sediment but also industrial and household sewage (Gomes et al. 2009).

Sampling

On 18th November, 16th December 2014 and 19th January 2015, samples were taken at two stations in Jacarepaguá Lagoon (JAC 18–22° 58′ 36.8″ S 43° 22′ 48.5″ W, depth 1.2 m and JAC 20–22° 59′ 14.1″ S 43° 24′ 9.6″ W, depth 1.3 m; Fig. 1a). Water transparency in each sampling station was measured using a Secchi disk. In situ, water temperature,

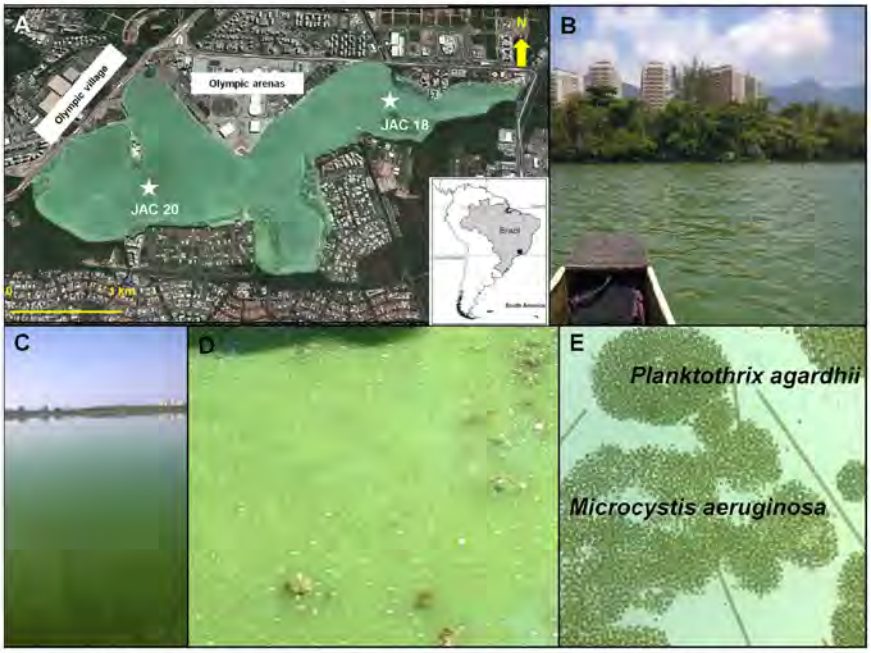

Fig. 1 Panel **a** shows the close vicinity of some of the 2016 Olympic arenas, the Olympic park of Jacarepaguá lagoon and the two sampling stations (JAC 18, JAC 20). Panel **b** shows some of the Olympic park buildings as seen from the lagoon. Panels **c**, **d** show the green water of the lagoon (January 19th 2015) and panel **e**, the main phytoplankton species (*M. aeruginosa* colonies and *P. agardhii* filaments)

conductivity, salinity, pH, dissolved oxygen concentrations and saturation were measured with a multiparameter sonde (YSI model 600R) at three depths: top, 0.5 m and bottom. Dissolved and total nitrogen and phosphorus, chlorophyll-*a* and quantitative phytoplankton samples were collected with an integration tube (4.5 cm diameter) integrating 1 m of water column. Phytoplankton samples were fixed with Lugol's solution, and nutrient samples were kept frozen until analysis.

Sample Analysis

The soluble reactive phosphate (SRP), ammonium ($N\,NH_4^+$), nitrate ($N\,NO_3^-$), nitrite ($N\,NO_2^-$) and total phosphorus (TP) were measured using flow injection analysis according to manufacturer instructions (FIAlab 2500, FIALab Instruments Inc., Seattle, Washington). Chlorophyll-*a* concentrations were measured using a PHYTO-PAM phytoplankton analyser (Heinz Walz GmbH, Effeltrich, Germany). Phytoplankton populations were enumerated according to the settling technique (Utermöhl 1958) in random fields (Uhelingher 1964) using an inverted microscope (Olympus, CKX41).

Chemicals and Materials

At station JAC 20, 10 L of surface water were collected for experiments with flocculants and ballasts. The dominant species was *M. aeruginosa* (Kützing) Kützing with some undergrowth of *P. agardhii* (Gomont) Anagnostidis & Komárek. Jacarepaguá sediment was collected with a plastic core sampler on January 19th 2015. Red soil (RS) used as ballast was collected from the banks of the Funil Reservoir (22° 30′ S, 44° 45′ W, Rio de Janeiro, Brazil). Prior to use, RS was dried and grinded using pestle and sieved over 0.5 mm. This soil has been characterized according to particle size and mineralogical composition, and consisted of 99 % fine earth (<2 mm) comprised mainly of clay (≅50 %). Kaolinite was most abundant, followed by goethite and mica (for details, see Noyma et al. 2016).

The coagulant PAC-AP (polyaluminium chloride; $Al_n(OH)_mCl_{3n-m}$, $\rho \approx 1.37$ kg L^{-1}, 8.9 % Al, 21.0 % Cl) was obtained from Pan-Americana (Rio de Janeiro, Brazil), whereas chitosan made of shrimp shells was obtained from Polymar Ciência e Nutrição S/A (Ceará, Brazil). The chitosan was acidified with a 1 % hydrochloric acid as the protonation of amino groups makes chitosan positively charged that allows

flocculation (Pan et al. 2006b). PAC was diluted 100 times in demineralised water prior to use.

Experiments

Aliquots of 60 mL cyanobacteria suspensions from Jacarepaguá Lagoon were transferred to 75-mL glass tubes (25 × 200 mm). The initial cyanobacterial chlorophyll-*a* (μg L^{-1}) as well as the Photosystem II (PSII) efficiency was determined using a PHYTO-PAM phytoplankton analyser (Heinz Walz GmbH, Effeltrich, Germany). Cyanobacteria suspensions were treated with the designated compound(s) (treatment) or left untreated (controls). Suspensions were mixed at start and placed in the laboratory at 25 °C under stagnant conditions. After 1 h, 5-mL samples were taken from both the top and the bottom of the tubes in which chlorophyll-*a* concentrations and PSII efficiencies were measured. The pH was measured in the tubes.

In the first experiment, the effect of the flocculants PAC and chitosan on the vertical distribution of the cyanobacteria was studied. The initial cyanobacteria chlorophyll-*a* concentration was 205 (±8) μg L^{-1}. The cells were in good physiological conditions as shown by the PSII efficiency of 0.40 (±0.04). PAC was dosed at 0, 1, 2, 4, 8, 16 and 32 mg Al L^{-1} and chitosan at 0, 1, 2, 4, 8, 16 and 32 mg L^{-1}. We tested this range considering that these flocculants are efficient to remove algae at low doses as 2 mg L^{-1} (Divakaran and Sivasankara Pillai 2002; Noyma et al. 2016). Immediately after adding the flocculants from the prepared stocks, the contents in each test tube were mixed briefly using a glass rod. Tubes were left untouched for 1 h, then top and bottom samples were taken and analysed as mentioned above. The aluminium species prevailing in the PAC treatments was modelled using the program CHEAQS Next (Verweij 2015). As the input in the model were served the measured pH, the added Al concentration, a carbonate concentration of 229 mg L^{-1} as calculated from alkalinity and a phosphate concentration of 1 mg L^{-1}.

In the second experiment, the effect of different concentrations of flocculants, PAC or chitosan, on the vertical distribution of the cyanobacteria was studied in the presence of a fixed dose of RS (320 mg L^{-1}). The RS dose was applied as a slurry and the dose was based on a previous study in which 320 mg L^{-1} appeared sufficient to sink positively buoyant *M. aeruginosa* out of water from the Funil Reservoir, Brazil (Noyma et al. 2016). Similar to the first experiment, PAC was dosed from 0 to 32 mg Al L^{-1} and chitosan from 0 to 32 mg chitosan L^{-1}. Both series included a control that received no RS and no coagulant. The cyanobacteria suspension used was the same as for the first experiment. Immediately after adding the RS—by making slurry with some of the water from the test tube—the designated amount of coagulant was added and the content in the test tube mixed briefly using a glass rod. Tubes were then left untouched for 1 h, after which top and bottom samples were taken and analysed as mentioned above.

In the third experiment, the effect of different concentrations of RS (0 to 320 mg L^{-1}) in the presence of a fixed dose of PAC (8 mg Al L^{-1}) on the vertical distribution of the cyanobacteria was studied. The PAC dose was based on the results from the previous experiments. Based on the outcomes of the previous experiments, chitosan was no longer included in this experiment. The initial cyanobacteria chlorophyll-*a* concentration was 222 (±2) μg L^{-1} with healthy cells as reflected in a PSII efficiency of 0.53 (±0.03). The experiment included a control without any compound added and was performed with three replicates per treatment. Immediately after adding the designated amount of RS, the PAC flocculent was added and the content in the test tube mixed briefly using a glass rod. Tubes were treated as mentioned before.

In the fourth experiment, wet sediment from Jacarepaguá Lagoon was tested on its ability to settle cyanobacteria out of the Jacarepaguá water. To apply the sediment, slurry was made with 10 g L^{-1} wet sediment of which 1.92 mL was pipetted into 60 mL cyanobacteria suspension (dose of 320 mg wet sediment L^{-1}). In another treatment, the flocculent PAC was dosed at 8 mg Al L^{-1} immediately after the sediment. An additional control with only PAC addition was included. Immediately after dosing, the contents in each test tube were mixed briefly using a glass rod. The treatments were run in triplicates as outlined above.

Statistical Analyses

For the third (effect of different concentrations of RS in the presence of a fixed dose of PAC) and fourth (ability of wet sediment to settle cyanobacteria out) experiments, the chlorophyll-*a* concentrations in the top and those measured at the bottom of the test tubes, as well as PSII efficiencies and pH values were statistically evaluated through a one-way ANOVA. Chlorophyll-*a* concentrations were log-transformed to meet the requirement of homogeneity in variance (Equal Variance Test; Brown-Forsythe). An all pairwise multiple comparison was performed to distinguish means that were significantly different at the 0.05 level (Holm-Sidak method).

Results

Water Quality in Jacarepaguá Lagoon

The water of the tropical lagoon Jacarepaguá was warm, brackish, cyanobacteria-infested, with high pH and low transparency (Table 1). During the studied period, the water temperature was reached 30.5 ± 4.1 °C in the upper water layer and 28.9 ± 3.3 °C near the bottom. Despite these small

Table 1 Average values and range of limnological variables, measured in November and December (2014) and January (2015), at two different sites in Jacarepaguá lagoon: JAC 18 and JAC 20. Samples from integration tube (integr.) and three different depths: surface, 0.5 m and bottom

Limnological variables/Sites	JAC 18				JAC 20			
	Integr.	Surface	0.5 m	Bottom	Integr.	Surface	0.5 m	Bottom
WT (C°)	–	30.46 27.12–35.0	29.71 27.02–33.0	29.18 26.53–32.7	–	29.21 27.13–32.0	29.39 26.93–32.85	28.93 26.53–32.7
OD (mg L^{-1})	–	6.59 2.26–10.91	4.42 2.54–6.29	0.76 0.51–1.0	–	8.33 6.60–10.06	7.29 6.0–8.57	3.43 1.71–5.15
Zeu (m)	–	0.63 0.54–0.68	–	–	–	0.63 0.54–0.68	–	–
Zmax (m)	–	1.07 1.0–1.2	–	–	–	1.17 1.0–1.3	–	–
pH	–	9.61 9.08–10.52	9.39 8.78–10.25	8.98 8.55–9.78	–	9.28 7.70–10.52	9.21 7.63–10.52	9.01 7.52–10.27
Salinity (ppt)	–	5.67 5.21–6.21	5.68 5.21–6.23	5.77 5.19–6.33	–	5.04 4.47–5.49	5.05 4.48–5.50	4.90 4.63–5.12
Cond (mS cm^{-1})	–	10.14 9.35–11.08	10.14 9.35–11.1	10.27 9.31–11.25	–	9.05 8.11–9.81	9.09 8.11–9.88	9.16 8.37–9.93
Alkal (mEq L^{-1})	4.36 4.24–4.48	–	–	–	3.95 3.54–4.35	–	–	–
NNO_2 (mg L^{-1})	0.09 0.03–0.15	–	–	–	0.04 0.02–0.06	–	–	–
NNO_3 (mg L^{-1})	0.80 0.34–1.26	–	–	–	0.27 0.16–0.38	–	–	–
NNH_4 (mg L^{-1})	3.34 2.40–4.39	–	–	–	1.08 0.46–1.58	–	–	–
SRP (mg L^{-1})	0.76 0.71–0.83	–	–	–	0.84 0.78–0.96	–	–	–
TP (mg L^{-1})	1.22 1.19–1.25	–	–	–	1.23 1.20–1.27	–	–	–
Chl-*a* (μg L^{-1})	211.7 203.7–216.3	–	–	–	205.5 165.4–225.6	–	–	–
M. aeruginosa (%)	85 56–99	–	–	–	89 72–98	–	–	–
P. agardhii (%)	8 0–25	–	–	–	7 0–22	–	–	–

WT water temperature, *OD* dissolved oxygen, *Zeu* euphotic zone, *Zmax* maximum deep, *pH*, *Salinity*, *Cond* electrical conductivity, *Alkal* alkalinity, NNO_2^-; NNO_3^- and NNH_4^+ concentrations, *SRP* soluble reactive phosphorus concentration, *TP* total phosphorus, *Chl-a* chlorophyll-*a* concentration; percentage contribution of *Microcystis aeruginosa* and *Planktothrix agardhii* to total biovolume of phytoplankton

differences in temperature, dissolved oxygen varied from oxic (top and 0.5 m) to hypoxic in JAC 18 near the bottom (Table 1). Low salinity (averages <5.77 ppt) and high conductivity and alkalinity were found. Considering the high concentrations of TP, chlorophyll-*a* and the low water transparency, the lagoon can be classified as hypereutrophic (Nürnberg 1996). During the sampling period, *M. aeruginosa* and *P. agardhii* together represented on average more than 90 % of total phytoplankton biomass (Table 1). *M. aeruginosa* was always present and comprised 56 to 99 % of total biomass while *P. agardhii* contributions reached up to 25 and 22 % in JAC 18 and JAC 20, respectively.

Effects of PAC and Chitosan on the Vertical Position of the Cyanobacteria

The cyanobacteria collected in Jacarepaguá had a strong positive buoyancy as in the absence of PAC (0 mg Al L^{-1} in Fig. 2) or chitosan (0 mg L^{-1} in Fig. 4); the chlorophyll-*a* concentrations in the top of the test tubes after 1 h were, on average, respectively 11 times and 8 times higher than in the bottom. In the PAC series, at 1 and 2 mg Al L^{-1}, small flocks were formed that aggregated at the water surface, while at 4 and 8 mg L^{-1}, the flocks formed were dense enough to settle the cyanobacteria to the bottom of the tubes reaching a removal efficiency of 71 and 93 %, respectively; at higher PAC dose, large fluffy aggregates accumulated at the water surface in the tubes (Fig. 2). PSII efficiency was unaffected at all PAC doses and was on average 0.52 (±0.01) in the top of the tubes and 0.51 (±0.01) in the bottom of the tubes. The pH gradually decreased with higher PAC doses; from a pH value of 9.19 (±0.09) in 0–2 mg Al L^{-1}, pH 8.84 in 4 mg Al L^{-1}, pH 8.20 in 8 mg Al L^{-1}, pH 7.02, in 16 mg Al L^{-1} and pH 5.95 in a dose of 32 mg Al L^{-1} (Fig. 2).

The most dominant Al species in all treatments was the $Al(OH)_3$ precipitate (Fig. 3), while in the lower PAC doses,

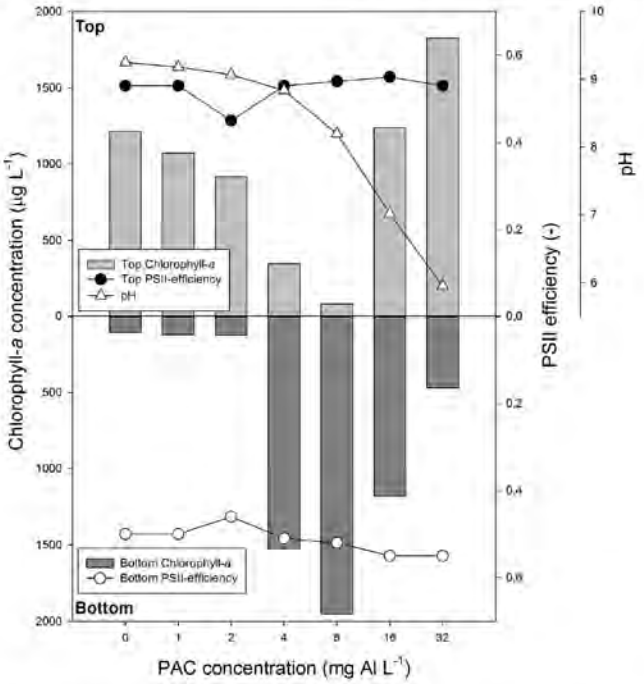

Fig. 2 Chlorophyll-*a* concentrations (µg L^{-1}) in the top 5 mL (*top light grey bars*) and bottom 5 mL (*lower dark grey bars*) of 60 mL cyanobacteria suspension from Jacarepaguá Lagoon incubated for 1 h in the absence or presence of different concentrations of the flocculent PAC (0–32 mg Al L^{-1}). Also included are the Photosystem II efficiencies (*PSII*) of the cyanobacteria collected at the water surface (*filled circles*) and at the bottom (*open circles*) as well as the pH values of the suspensions (*open triangles*)

some aluminate was present as a consequence of the higher pH. In none of the PAC treatments occurrence of Al^{3+} was predicted (Fig. 3).

In the chitosan series, no flocks were formed; not even at the highest dose of 32 mg L^{-1} which settled only 7 % of the cyanobacteria. In all treatments, most of the cyanobacteria aggregated at the water surface in the tubes (Fig. 4). PSII efficiency was unaffected at all chitosan doses and was on average 0.52 (±0.01) in the top of the tubes and 0.52 (±0.07) in the bottom of the tubes. The pH remained unaffected in the chitosan range 0 to 8 mg L^{-1} (pH 9.21 ± 0.03), it was slightly lower at 16 mg chitosan L^{-1} (pH 9.06) and pH was 8.58 at the highest chitosan dose (Fig. 4).

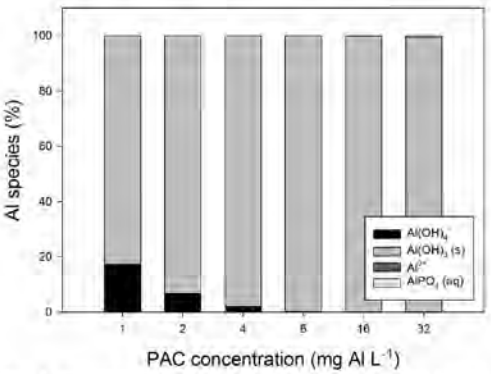

Fig. 3 Proportion of Al species in water from Jacarepaguá Lagoon treated with different PAC concentrations

Effect of Flocculants and Red Soil on the Vertical Position of the Cyanobacteria

In the experiment with different concentrations PAC in the presence of 320 mg L^{-1} RS, solely the RS (0 mg Al L^{-1} treatment) already caused a 33 % decrease in the top chlorophyll-*a* concentration and a 3.4 times increase at the bottom (Fig. 5). Adding PAC strongly improved the cyanobacteria removal from Jacarepaguá water; from 64 % removal from the top layer in 1 mg Al L^{-1} to 97 % at 8 mg Al L^{-1} or even 99 % removal at 32 mg Al L^{-1} (Fig. 5). PSII efficiency was unaffected at all PAC doses and was on average 0.52 (±0.01) in the top of the tubes and 0.52 (±0.03) in the bottom of the tubes. The pH gradually decreased with higher PAC doses; from a pH value of 9.30 in the control to pH 7.62 in the 8 mg Al L^{-1} dose and further down to pH 5.80 in the 32 mg Al L^{-1} dose (Fig. 5).

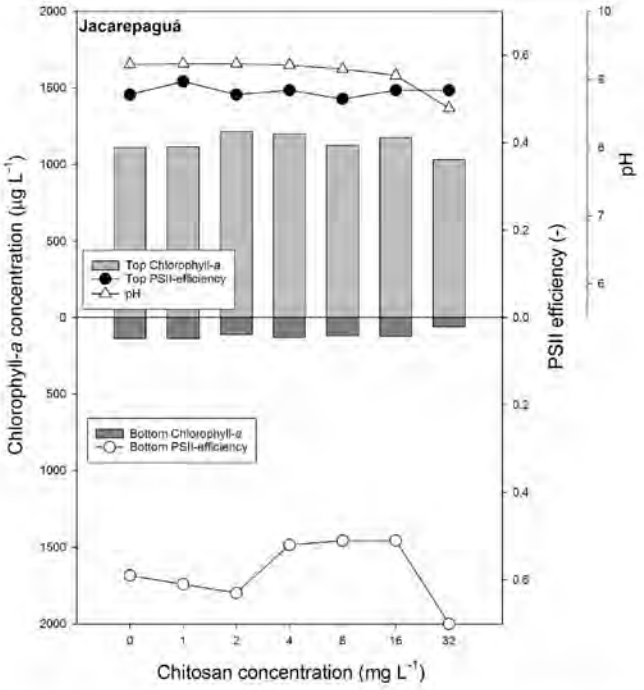

Fig. 4 Chlorophyll-*a* concentrations (µg L^{-1}) in the top 5 mL (*top light grey bars*) and bottom 5 mL (*lower dark grey bars*) of 60 mL cyanobacteria suspension from Jacarepaguá Lagoon incubated for 1 h in the absence or presence of different concentrations of the coagulant chitosan (0–32 mg L^{-1}). Also included are the Photosystem II efficiencies (*PSII*) of the cyanobacteria collected at the water surface (*filled circles*) and at the bottom (*open circles*) as well as the pH values of the suspensions (*open triangles*)

In the experiment with different concentrations of chitosan mixed with a fixed dose of 320 mg L^{-1} RS, solely the RS (0 mg L^{-1} treatment) resulted in a 47 % decrease in the top chlorophyll-*a* concentration and a 3.7 times increase at the bottom of the test tube (Fig. 6). However, adding chitosan did not improve this and, actually, in the range 1 to 16 mg chitosan L^{-1} the reduction in the top chlorophyll-*a* concentration was only 26 (±3) % compared to the control without anything added. Only in 32 mg chitosan L^{-1} the reduction in chlorophyll-*a* concentration in the top of the test tube (49 %) was comparable to the solely RS treatment (Fig. 6). The PSII efficiencies were similar in the top of the tubes 0.52 (±0.01) regardless of RS and RS plus chitosan additions; the same was observed in the bottom of the test tubes with a mean PSII efficiency of 0.52 (±0.03) (Fig. 5). The pH was on average 9.07 (±0.13) in the control and the treatments up to a chitosan concentration of 16 mg L^{-1}; only at 32 mg chitosan L^{-1}, the pH was slightly reduced to 8.38 (Fig. 6).

Based on the former experiments, a fixed PAC dose of 8 mg Al L^{-1} appeared most suitable in terms of removal efficiency through flocculation, influence on the pH and no toxic Al^{3+} formation, but solely the flocculating colloidal-sized $Al(OH)_3$ (s).

The effect of adding additional ballast (RS) to this fixed PAC dose showed that top chlorophyll-*a* concentrations were even further reduced than the 95 % reduction by solely PAC; at 40 mg RS L^{-1}, more than 98 % was removed, and at higher dose more than 99 % of the cyanobacteria were removed from the top water layer (Fig. 7). The one-way ANOVA indicated that the differences were significant ($F_{6,14} = 63.7$; $p < 0.001$), while the post hoc comparison revealed three homogenous groups that were significantly different from each other: (1) the controls, (2) the sole PAC treatment and (3) all PAC + RS treatments. Also for the chlorophyll-*a* concentrations measured at the bottom of the tubes, a one-way ANOVA indicated significant differences ($F_{6,14} = 560.6$; $p < 0.001$), while the post hoc comparison revealed three homogenous groups that were significantly different from each other: (1) the controls with the lowest chlorophyll-*a* concentrations, (2) the sole PAC treatment with the highest chlorophyll-*a* and (3) all PAC + RS treatments (Fig. 7).

The PSII efficiencies showed some variability in the top of the tube, but remained fairly high (0.41–0.71), while in the bottom they were similar (0.55 ± 0.01). The pH in the controls (9.04 ± 0.01) was significantly higher than the pH values (mean 7.35 ± 0.20) in all other treatments ($F_{6,14} = 50.2$;

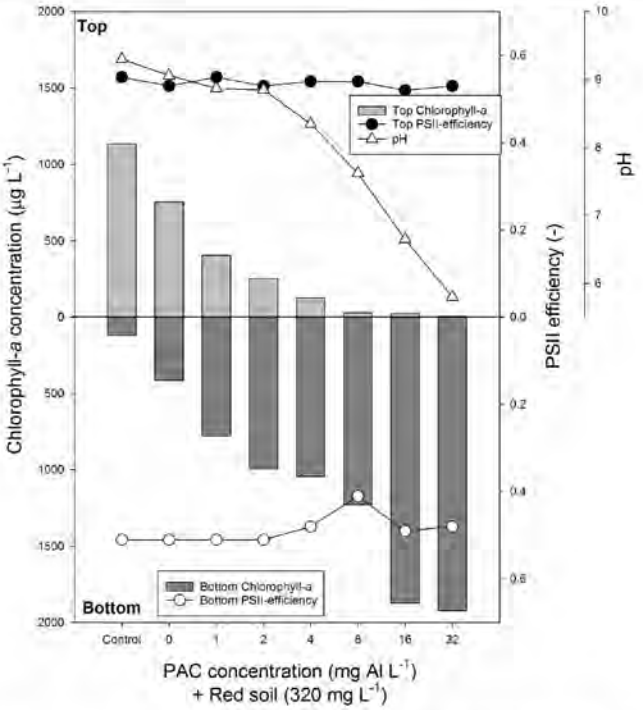

Fig. 5 Chlorophyll-*a* concentrations (µg L^{-1}) in the top 5 mL (*top light grey bars*) and bottom 5 mL (*lower dark grey bars*) of 60 mL cyanobacteria suspension from Jacarepaguá Lagoon incubated for 1 h in the absence or presence of different concentrations of the coagulant PAC (0–32 mg Al L^{-1}) combined with a fixed dose of red soil (320 mg L^{-1}) as ballast. Also included are the Photosystem II efficiencies (*PSII*) of the cyanobacteria collected at the water surface (*filled circles*) and at the bottom (*open circles*) as well as the pH values of the suspensions (*open triangles*)

$p < 0.001$), which was confirmed by the post hoc comparison (Fig. 7).

Effect of Sediment on the Vertical Position of the Cyanobacteria

Adding only sediment did not lead to removal of cyanobacteria from the water column in the test tubes in contrast to adding PAC at a dose of 8 mg Al L^{-1} (Fig. 8). The one-way ANOVA indicated significant differences in both the chlorophyll-*a* concentration in the top of the test tubes ($F_{3,8} = 2290$; $p < 0.001$) as in the bottom ($F_{3,8} = 853.7$; $p < 0.001$); in both cases, the post hoc comparison revealed three homogenous groups that were significantly different from each other: (1) the control and the solely sediment treatment, (2) the sole PAC treatment and (3) the PAC + sediment treatment. The PSII efficiency in the top of the control tubes was significantly lower ($F_{3,8} = 26.6$; $p < 0.001$) than in the treatments, while in the bottom PSII efficiency in the control and PAC treatment were significantly higher ($F_{3,8} = 28.5$; $p < 0.001$) than in the sediment and sediment + PAC treatments (Fig. 8). Finally, the pH was significantly different ($F_{3,8} = 4964$; $p < 0.001$) and clearly reduced in the two treatments with PAC added (pH 7.47 and 7.42) compared to the control (pH 9.13 ± 0.01) and the only sediment addition (pH 9.07 ± 0.01) (Fig. 8).

Discussion

Our field work confirmed the strong cyanobacterial proliferation of the water in Jacarepaguá Lagoon. Jacarepaguá is an oligo-mesohaline system suffering from strong anthropogenic pressure of which eutrophication is causing massive cyanobacterial blooms (Gomes et al. 2009) that also threaten humans consuming fish from the system which have accumulated cyanobacterial toxins (Magalhães et al. 2001). Hence, there is strong pressure to reduce the harmful cyanobacteria blooms. While nutrient input control may take quite some years, we hypothesized that the cyanobacteria flourishing in Jacarepaguá Lagoon could also be effectively removed from the water column using a combination of PAC or chitosan with a RS or local sediment as ballast. Our experimental data showed an efficient removal when these ballast compounds were joined with PAC, but not for chitosan, which did not form flocks in the Jacarepaguá Lagoon water.

Chitosan is widely used in water and waste water treatment, because it is a non-toxic, non-corrosive natural product.

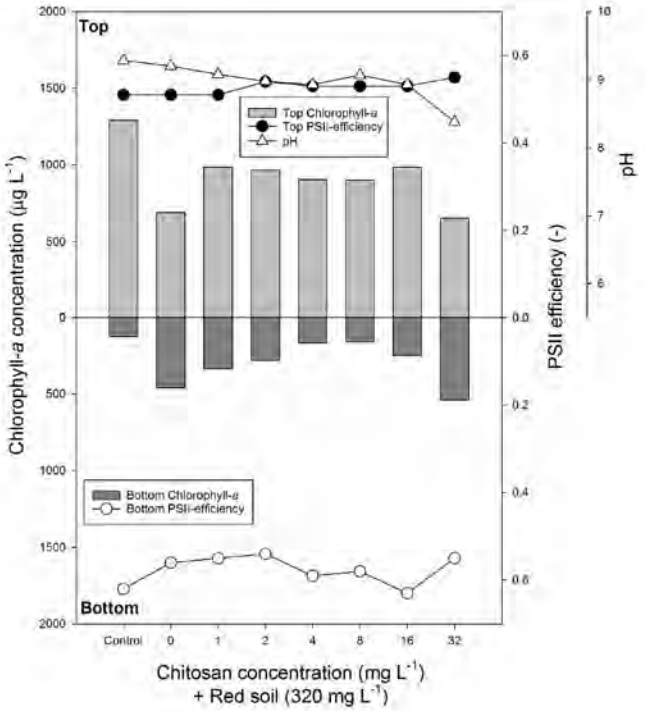

Fig. 6 Chlorophyll-*a* concentrations (µg L^{-1}) in the top 5 mL (*top light grey bars*) and bottom 5 mL (*lower dark grey bars*) of 60 mL cyanobacteria suspension from Jacarepaguá Lagoon incubated for 1 h in the absence or presence of different concentrations of the coagulant chitosan (0–32 mg L^{-1}) combined with a fixed dose of red soil (320 mg L^{-1}) as ballast. Also included are the Photosystem II efficiencies (*PSII*) of the cyanobacteria collected at the water surface (*filled circles*) and at the bottom (*open circles*) as well as the pH values of the suspensions (*open triangles*)

which is efficient in cold water without causing environmental pollution (Renault et al. 2009). Deacetylation of chitin—mostly derived from shrimps and crabs—produces chitosan, which is a linear copolymer of D-glucosamine and *N*-acetyl-D-glucosamine that due to its rigid structure is insoluble in water. The copolymer becomes fully soluble in dilute acids when the free amino groups of chitosan are protonated that enables electrostatic interactions between the protonated amino groups of chitosan and the negatively charged cyanobacteria (Renault et al. 2009). The long chain polymers, like chitosan, can attach onto particles forming "bridging" connections. These bridging connections between the particles can together form a "net" (Tripathy and De 2006; Chen et al. 2014). However, in conditions where large amounts of negative ions gather around the protonated groups, it becomes shielded, the molecule contracts and also hampers the netting and bridging properties (Pan et al. 2006b; Qun and Ajun 2006). Consequently, chitosan is not a very efficient coagulant at high pH (Morales et al. 1985; Vandamme et al. 2013) and at high ionic strength of the water (Pan et al. 2006a). Given the high pH and considerable ionic strength of the Jacarepaguá water (see Table 1), chitosan is not an appropriate coagulant to be applied in Jacarepaguá, or any other high ionic strength and high pH water. In addition, the price of chitosan is much higher than that of aluminium salts (Granados et al. 2012).

Contrary to chitosan, polyaluminium chloride (PAC) turned out an excellent coagulant in Jacarepaguá water. In general, aluminium salts are widely used in water treatment including cyanobacteria removal (Jančula and Maršálek 2011). PAC has several advantages over other aluminium salt coagulants, such as alum: less pH reduction, lower dose needed, less residual Al, less sulphate added and better flocs at low temperature (Gebbie 2001; de Julio et al. 2010). Use of aluminium formulations is sometimes met with scepticism related to presumed toxic effects (e.g. Renault et al. 2009). However, aluminium is the most abundant metal in the Earth's crust (>8 %) and application of aluminium formulations in waters with neutral pH can be considered safe (Jančula and Maršálek 2011). The toxicity of metals depends on speciation which is steered by pH (Stumm and Morgan 1996), where in the case of aluminium the trivalent Al^{3+} prevails at pH lower than 5.5 (Driscoll and Schecher 1990; Gensemer and Playle 1999). As the pH in Jacarepaguá Lagoon keep alkaline in the entire water column, low soluble aluminium will be free even near the bottom. In our experiments, no occurrence of this toxic Al species in the water was predicted.

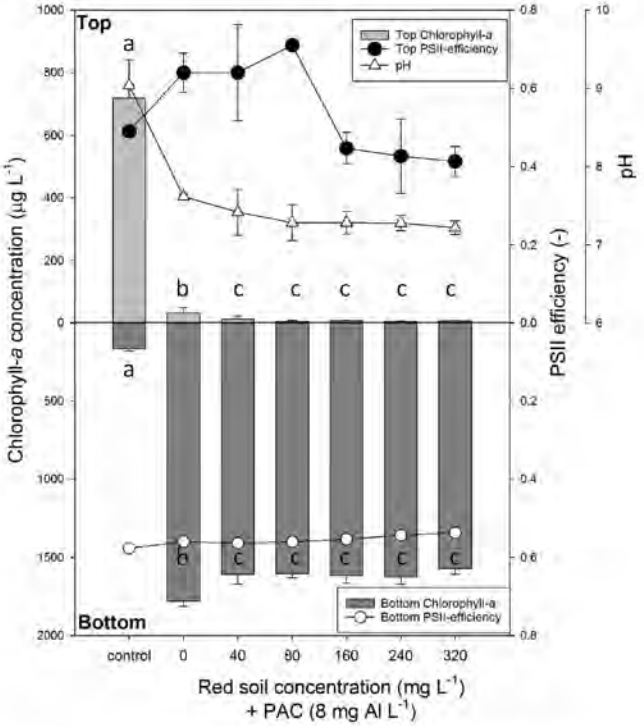

Fig. 7 Chlorophyll-*a* concentrations (µg L^{-1}) in the top 5 mL (*top light grey bars*) and bottom 5 mL (*lower dark grey bars*) of 60 mL cyanobacteria suspension from Jacarepaguá Lagoon incubated for 1 h in the absence and presence of the coagulant PAC (8 mg Al L^{-1}) combined with different concentration of red soil (0–320 mg L^{-1}) as ballast. Also included are the Photosystem II efficiencies (*PSII*) of the cyanobacteria collected at the water surface (*filled circles*) and at the bottom (*open circles*) as well as the pH values of suspensions (*open triangles*). *Error bars* indicate one standard deviation (n = 3). *Similar letters* indicate homogeneous groups according to the Holm-Sidak method

Nonetheless, it should be notified that aluminium toxicity in fish has also been ascribed to precipitation of $Al(OH)_3$ on the gills leading to suffocation of the fish (Wauer et al. 2004). Therefore, before applying PAC to Jacarepaguá, albeit in a relative low dose of 8 mg Al L^{-1}—field applications of Al salts are reported to be dosed at 2.6 to 45 mg L^{-1} (Cooke et al. 2005)—additional enclosure studies including the abundant fish *Tilapia rendalli* are recommended.

Red soil in itself removed 33–47 % of the cyanobacteria from the water, which may have been caused by some flocculating properties of the RS (Pan et al. 2006b). The RS is a typical laterite soil—rich in iron and aluminium—and predominantly composed of kaolinite, goethite, gibbsite and some anatase (Noyma et al. 2016). The main component, the clay kaolinite, removed 43 % of a *M. aeruginosa* populations when dosed at 200 mg L^{-1} and 88 % at 700 mg L^{-1} (Pan et al. 2006b), while 1000 mg L^{-1} removed almost 60 % of the red-tide dinoflagellate *Karenia brevis* (Sengco and Anderson 2004). The stickiness of *M. aeruginosa* may also cause attachment of clay particles resulting in sedimentation of buoyant *Microcystis* (Verspagen et al. 2006). However, given sediment from Jacarepaguá had no effect on settlement of *M. aeruginosa*, where RS did partly, stickiness seems not have been the main mechanisms operating. Hence, just RS or local sediment are not appropriate to sink the cyanobacteria out of the water column. Similarly, Li and Pan (2013) found that sand alone was ineffective to flock and sink two marine algae and also *M. aeruginosa*. When they added chitosan, however, removal was between 40 and 60 %, whereas *Moringa oleifera* (Moringaceae) extract led to more than 90 % removal (Li and Pan 2013). Also, Pan et al. (2012) recognised that soils by themselves hardly remove phytoplankton and flocculent addition was needed to facilitate removal.

Indeed, the combination of PAC and RS as ballast improved the settling efficiency at low PAC dose. At a sole PAC dose of 1 and 2 mg Al L^{-1}, although flocks were formed, no difference in settling with the control was observed (see Fig. 2). Adding RS, however, greatly improved sedimentation of cyanobacteria flocks at these PAC doses (see Fig. 5). The choice for 8 mg Al L^{-1} PAC as optimum dose in combination with RS was based on the efficient removal of cyanobacteria from the water column and acceptable lowering of pH.

The dose of RS could be lowered to 80 mg L^{-1} without losing any efficiency (see Fig. 7). This dose of ballast is quite comparable with the 100 mg L^{-1} of a local sand or soil found in other studies (Pan et al. 2011a; Li and Pan 2013, 2015). The

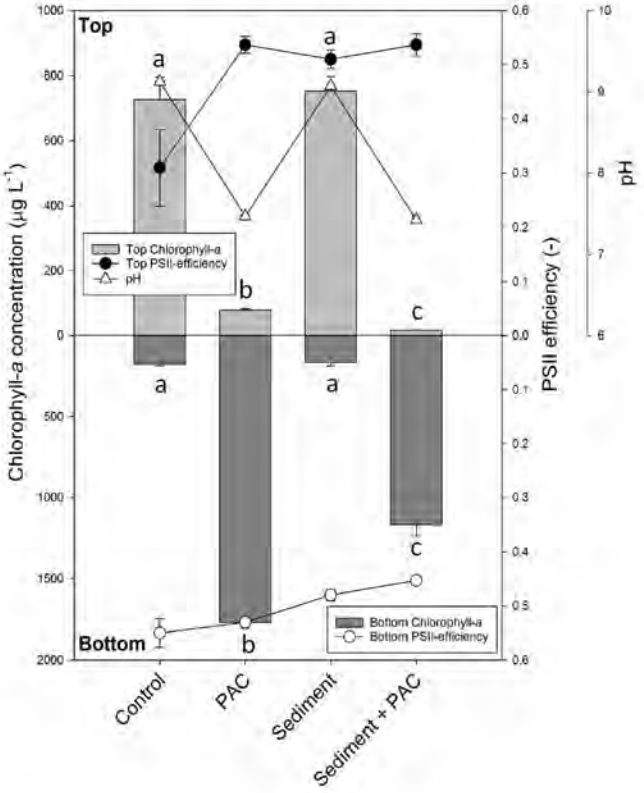

Fig. 8 Chlorophyll-*a* concentrations (µg L^{-1}) in the top 5 mL (*top light grey bars*) and bottom 5 mL (*lower dark grey bars*) of 60 mL cyanobacteria suspensions from Jacarepaguá Lagoon incubated for 1 h without addition (Control) or solely the coagulant PAC (8 mg Al L^{-1}) added (PAC), solely sediment from the Lagoon (320 mg L^{-1}) added (Sediment) or a combination of both PAC and sediment (Sediment + PAC). Also included are the Photosystem II efficiencies (*PSII*) of the cyanobacteria collected at the water surface (*filled circles*) and at the bottom (*open circles*) as well as the pH values of suspensions (*open triangles*). *Error bars* indicate one standard deviation ($n = 3$). *Similar letters* indicate homogeneous groups according to the Holm-Sidak method

combination of flocculent and soil has already been applied successfully in an isolated bay of Lake Taihu (China), where adding 25–31 mg L^{-1} (40–50 g m^{-2}) effectively cleared the water of cyanobacteria (Pan et al. 2011b). In Lake Rauwbraken (The Netherlands), PAC (0.83 mg L^{-1}) and a lanthanum-modified bentonite (84 mg L^{-1}) effectively removed cyanobacteria from the water column and resulted in water devoid of cyanobacteria nuisance for several years (Lürling and van Oosterhout 2013). As in this technique, entrapped cyanobacteria in flocks remain intact (Chow et al. 1999; Drikas et al. 2001)—the intactness of precipitated cells is also reflected in unaffected PSII efficiencies, no release of toxins and nutrients during treatment occurs, which is a major advantage over using algaecides in treating cyanobacterial blooms.

The experiments in laboratory scale are important to demonstrate, in rapid assays, the possible effects of the lagoon water chemistry on flocculation efficacy. Although physical factors, i.e. turbulence, can interfere in the flocculation processes, resuspending flocks, the wind-induced mixing might also be beneficial in facilitating formation of flocks. The flock and sink approach has been applied successfully to a shallow and small lake (Lake De Kuil, The Netherlands) (Waajen et al. 2016). Furthermore, this promising approach seems to be applicable for different water characteristic, although complementary studies are needed to evaluate the effectiveness of the compounds in larger scales.

Although it is widely recognised that preventing cyanobacterial and harmful algal bloom development through adequate nutrient control in the watershed is far better than eliminating existing blooms, costs and politics may delay such actions that make curative bloom control strategies inevitable (Heisler et al. 2008). Furthermore, synergistic effects of eutrophication and global change may promote an escalation in cyanobacterial and harmful algal blooms in estuarine and coastal waters (Paerl et al. 2014). Hence, efficient, cheap, fast and safe curative measures to lessen the cyanobacteria and harmful algal bloom nuisance will provide a welcome extension of the water managers' tool-box. Combined coagulant and ballast seems a very promising tool, and it may give

temporal relief from cyanobacteria or harmful algal nuisance in periods when particularly needed, such as around the 2016 Olympics in Jacarepaguá Lagoon.

Conclusions

- Polyaluminium chloride (PAC) flocculated cyanobacteria from a brackish tropical lagoon, while chitosan appeared ineffective as flocculent.
- Positively buoyant cyanobacteria from a brackish tropical lagoon could be flocked and effectively precipitated using a combination of PAC with red soil (RS) or local sediment as ballast.
- Sole use of RS or sediment as ballast was inefficient in removing cyanobacteria.
- Combined use of PAC and ballast seems a very efficient curative measure to lessen cyanobacterial bloom nuisance.

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ANEXO B – Manuscrito submetido referente ao capítulo 3

Estuaries and Coasts

Managing eutrophication in a tropical brackish water lagoon: testing lanthanum modified clay and coagulant for internal load reduction and cyanobacteria bloom removal

--Manuscript Draft--

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Full Title:	Managing eutrophication in a tropical brackish water lagoon: testing lanthanum modified clay and coagulant for internal load reduction and cyanobacteria bloom removal
Article Type:	Original Paper
Keywords:	Geo-engineering, Lake restoration, Phosphorus control, PAC, Phoslock, Sediment release
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Abstract: The release of phosphorus (P) stored in the sediment may cause long term delay in the recovery of lakes, ponds and lagoons from eutrophication. In this paper, we tested on a laboratory scale the efficacy of the flocculant polyaluminium chloride (PAC) and a strong P-binding agent (lanthanum modified bentonite, LMB) on their ability to flocculate a cyanobacterial bloom and hamper P-release from a hypertrophic, brackish lagoon sediment. In addition, critical P loading was estimated through PCIake. We showed that cyanobacteria could be effectively settled using a PAC dose of 2 mg Al L-1 combined with 400 mg L-1 LMB; PAC 8 mg Al L-1 alone could also remove cyanobacteria, although its performance was improved adding low concentrations of LMB. The efficacy of LMB to bind P released from the sediment was tested based on potentially available sediment P. A dose of 400 g LMB m-2 significantly reduced the P-release from sediment to over standing water (either deionized water or water from the lagoon with and without cyanobacteria). In sediment cores, LMB+PAC reduced sediment P flux from 9.9 (± 3.3) to - 4.6 (± 0.3) mg P m-2 d-1 for the experimental period of 3 months. The internal P load was 14 times higher than the estimated P critical load (0.7 mg P m-2 d-1), thus even if all the external P sources would be ceased the water quality will not improve promptly. Hence, the combined LMB+PAC treatment seems a promising in-lake intervention to diminish internal P load bellow the critical load. Such intervention is able to speed up recovery in the brackish lagoon once external loading has been tackled and at a cost of less than 5% of the estimated dredging costs.

Cover Letter

Dear editor,

Please find attached the manuscript entitled "Managing eutrophication in a tropical brackish water lagoon: testing lanthanum modified clay and coagulant for internal load reduction and cyanobacteria bloom removal", which I am submitting on behalf of the co-authors for exclusive consideration of publication as an article in Estuaries and Coasts.

The current submission elaborates on our previous work published in Estuaries and Coasts (de Magalhães et al. 2017, 40(1): 121–133) in which we explored the possibilities of flocking and sinking cyanobacteria out of the water in samples collected from the hypertrophic brackish coastal lagoon Jacarepaguá in Rio de Janeiro. This lagoon, located next to the Olympic village, suffers heavily from eutrophication and cyanobacteria blooms because of years of ongoing discharge of untreated domestic wastewater. Consequently, the sediments have become loaded with nutrients which means that even when catchment measures such as treatment in inflowing streams will be implemented and become effective, the internal loading will fuel blooms for a long time. In our current submission we studied the effect of a solid phase phosphate fixative (LMB) alone and in combination with a flocculent (PAC) on sediment phosphorus release. We determined the internal phosphorus loading from the sediment and compared it with estimated critical phosphorus loading for effective rehabilitation. The PAC dose used was not capable to block phosphate release from the sediment, but the LMB proved highly efficient in the brackish system. In all treatments with LMB and LMB+PAC negative phosphate fluxes were determined meaning even a net removal of P from the water column towards the sediment. Finally, in a three month sediment core experiment combined LMB+PAC treatment kept phosphate as low as 2% of the controls underpinning the strong and robust interception of P released from the heavily P enriched sediment of Jacarepaguá lagoon. It might offer a much cheaper alternative to sediment dredging in the rehabilitation of the lagoon. Given the underrepresentation of eutrophication research in tropical eutrophic lagoons, we believe that our manuscript might be of wide interest to readers of Estuaries and Coasts. Moreover, it is the first study that intensely investigated the performance of LMB in a brackish water and this might be of great interest to a wide audience of scientists, water managers and decision makers.

Experienced reviewers for this paper could be:

Gertrud Nurnberg, Ph.D., Freshwater Research, 3421 HWY #117, RR 1 Baysville, Ontario, P0B 1A0 Canada. Email: gertrud.nurnberg@gmail.com. Dr. Nurnberg is a great expert in eutrophication issues and has recently gained experience in using the lanthanum modified clay we've also used.

Prof. Hans W. Paerl, Institute of Marine Sciences, The University of North Carolina at Chapel Hill, 3431 Arendell Street, Morehead City, NC 28557, USA. Email: hpaerl@email.unc.edu. Prof. Paerl is the world leading expert on the causes and consequences of human-induced eutrophication of rivers, lakes, estuaries and coastal oceans.

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Email: spear@ceh.ac.uk. Dr. Spears is an expert in lake restoration using geo-engineering.

Dr. Diego Copetti, Consiglio Nazionale delle Ricerche, Istituto di Ricerca Sulle Acque, UOS Brugherio, Via del Mulino, 19, 20861 Brugherio, MB, Italy. Email: copetti@irsa.cnr.it. Dr Copetti has great knowledge and expertise in water quality issues, lake restoration and use of geo-engineering materials such as LMB.

Thank you for your consideration of our work.

Kind regards,

Leonardo de Magalhães

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Managing eutrophication in a tropical brackish water lagoon: testing lanthanum modified clay and coagulant for internal load reduction and cyanobacteria bloom removal

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Abstract

The release of phosphorus (P) stored in the sediment may cause long term delay in the recovery of lakes, ponds and lagoons from eutrophication. In this paper, we tested on a laboratory scale the efficacy of the flocculant polyaluminium chloride (PAC) and a strong P-binding agent (lanthanum modified bentonite, LMB) on their ability to flocculate a cyanobacterial bloom and hamper P-release from a hypertrophic, brackish lagoon sediment. In addition, critical P loading was estimated through PClake. We showed that cyanobacteria could be effectively settled using a PAC dose of 2 mg Al L^{-1} combined with 400 mg L^{-1} LMB; PAC 8 mg Al L^{-1} alone could also remove cyanobacteria, although its performance was improved adding low concentrations of LMB. The efficacy of LMB to bind P released from the sediment was tested based on potentially available sediment P. A dose of 400 g LMB m^{-2} significantly reduced the P-release from sediment to over standing water (either deionized water or water from the lagoon with and without cyanobacteria). In sediment cores, LMB+PAC reduced sediment P flux from 9.9 (± 3.3) to – 4.6 (± 0.3) mg P m^{-2} d^{-1} for the experimental period of 3 months. The internal P load was 14 times higher than the estimated P critical load (0.7 mg P m^{-2} d^{-1}), thus even if all the external P sources would be ceased the water quality will not improve promptly. Hence, the combined LMB+PAC treatment seems a promising in-lake intervention to diminish internal P load bellow the critical load. Such intervention is able to speed up recovery in the brackish lagoon once external loading has been tackled and at a cost of less than 5% of the estimated dredging costs.

Keywords: Geo-engineering, Lake restoration, Phosphorus control, PAC, Phoslock, Sediment release

48 ## Introduction

49 Eutrophication is one of the main anthropogenic stressors leading to major degradation of
50 coastal waters worldwide (Kennish 2002). Water quality problems caused by eutrophication
51 include fish deaths due to anoxia, loss of biodiversity, bad smells and massive plant growth
52 (Paerl and Huisman 2008; Conley et al. 2009). Key symptom of eutrophication is a blooming
53 of harmful algae and cyanobacteria, which pose an additional risk to wildlife and humans
54 because of the toxins they may produce (Correl 1998; Huszar, et al. 2000; Paerl et al. 2012).
55 Hence, there is a great need to control these nuisance blooms.
56 Since blooms are fueled by nutrients, the first step in mitigation would be reducing the
57 nutrient discharge into the receiving waters (Cooke et al. 2005; Paerl et al. 2014). Although
58 some waters will clear up and recover rapidly from such lowered external nutrient loading,
59 many will show a considerable delay in recovery due to internal nutrient cycling (Jeppesen et
60 al. 1991; Søndergaard et al. 1999; 2001; Cooke et al. 2005). This legacy of nutrients created
61 from decades of uncontrolled excessive external nutrient loading will periodically be recycled
62 between sediment and water column and is viewed as one of the main reasons why many
63 restoration attempts have failed (Gulati and Van Donk 2002). Removal of polluted sediments
64 is then a straightforward restoration approach, but it may come with relatively high costs
65 compared to other techniques such as *in situ* fixation or capping (Cooke et al. 2005; Perelo
66 2010).
67 In recent years, the use of solid phase phosphorus (P)-adsorbing compounds has gained
68 interest to tackle the widespread internal loading issue (Spears et al. 2013a). The rationale to
69 target stored P lays in the fact that it is the only essential element that can be easily be made to
70 limit algal growth through the formation of insoluble precipitates (Golterman 1975). Internal
71 P loading is not only a major issue in inland freshwater systems (Søndergaard et al. 2001), but
72 also occurs in brackish coastal lagoons (Markou et al. 2007). While there is a growing number

of studies demonstrating efficacy and applicability of solid-phase P sorbents in freshwater systems, studies on brackish coastal waters are virtually lacking. Nonetheless, eutrophication is considered the most common problem affecting coastal lagoons (Esteves et al. 2008; Kennish et al. 2014). For instance, the coastal system Jacarepaguá lagoon in the western part of Rio de Janeiro city (Brazil) suffers heavily from eutrophication and perennial presence of cyanobacterial blooms (Gomes et al. 2009; De-Magalhães et al. 2017).

Recently, we have explored the possibility of removing cyanobacteria from Jacarepaguá lagoon water using a coagulant (poly-aluminiumchloride, PAC or chitosan) and red soil or local sediment as ballast (De-Magalhães et al. 2017). While PAC was effective, chitosan appeared ineffective to flock cells even when combined with ballast compounds (De-Magalhães et al. 2017). Elevated pH and high alkalinity were identified as factors that may hamper the coagulation of chitosan and impair its ability to effectively remove cyanobacteria from the water column (Lürling et al. 2017).

In the present study, we elaborated on these findings and first tested the combination of PAC and the solid phase P adsorbent Phoslock®, which is a lanthanum modified bentonite (LMB) with strong P binding capacity and widely used in freshwater systems (Copetti et al. 2016), on the ability to remove cyanobacteria from the brackish water of Jacarepaguá lagoon. In addition, we were particularly interested in the performance of LMB as Copetti et al. (2016) reported that even moderately saline environments of >0.5 ppt will render LMB ineffective. A thorough scientific underpinning of this statement is, however, lacking in that review paper (Copetti et al. 2016), and also finds no support in the few studies that included more saline environments (Haghseresht 2006; Reitzel et al. 2013). Given the current uncertainty on applicability of LMB in brackish environments, we tested the hypotheses that 1) LMB will block P-release from the sediment of the eutrophic coastal lagoon Jacarepaguá and 2) that a combination of PAC with LMB will clear the water and block the P release effectively.

98

99 Material and Methods

100 Study ecosystem

101 The Jacarepaguá Lagoon (43°17' - 43°30'W, 22°55' - 23°00'S) is part of a brackish water
102 lagoon complex located in the western part of Rio de Janeiro City (Fig. 1). The Jacarepaguá
103 lagoon is 3.7 km² in area; it has an average depth of 3.3 m; drainage area of 103 km^2; and the
104 freshwater inflow from the six tributaries is about 0.8 m^3 s^{-1} (Gomes et al. 2009). This system
105 has a direct communication with the sea water by the Joatinga channel, giving an average
106 salinity of 5.35 ppt (De-Magalhães et al, 2017). The lagoon usually presents high pH and
107 alkalinity with perennial relatively high chlorophyll-*a* concentrations (mostly exceeding 100
108 µg L^{-1}) and long periods of cyanobacteria dominance promoted by the constant sewage input
109 (Gomes et al. 2009; De-Magalhães et al. 2017).

110 Sediment and water sampling

111 On November 2014, 10 L of surface water was collected for experiments with coagulants and
112 ballast. The most important species in this moment was *Microcystis aeruginosa* and the
113 chlorophyll-*a* concentration was 225 µg L^{-1}. Jacarepaguá sediment was collected with a Kajak
114 sediment core sampler on January 19th 2015 at station JAC20 (Fig. 1). At this moment the
115 chlorophyll-*a* concentration, collected by an integration tube, was 226 µg L^{-1} composed
116 mainly by *Microcystis aeruginosa* with some undergrowth of *Planktothrix agardhii* (Fig 1).
117 The pH of the water was 9.04 (± 0.24); salinity was 5.49 ppt and the alkalinity 4.35 mEq L^{-1}.
118 On September 2015 more sediment was collected using the gravity Uwitec Corer sampler at
119 station JAC20 and at this moment the pH was 9.88, salinity 5.17 ppt and the alkalinity was

120 3.74 mEq L^{-1}. No cyanobacteria bloom was observed and the phytoplankton community was
121 composed mainly by Cryptophyceae and green algae.

122

123 **Chemicals and materials**

124 The lanthanum modified bentonite Phoslock® (LMB) was obtained from HydroScience (Porto
125 Alegre, Brazil). This LMB was developed by the Australian CSIRO, as dephosphatisation
126 technique aiming at removing soluble reactive phosphorus (SRP) from the water and blocking
127 the release of SRP from the sediment (Douglas 2002). The coagulant PAC-AP (polyalumnium
128 chloride; $Al_n(OH)_mCl_{3n-m}$, $\rho \approx 1.37$ kgL^{-1}, 8.9% Al, 21.0% Cl) was obtained from Pan-
129 Americana (Rio de Janeiro, Brazil).

130

131 **Effect of different concentrations of LMB and PAC on cyanobacteria removal**

132 The first experiment tested the efficacy of a combination of LMB with PAC to settle the
133 cyanobacteria from Jacarepaguá water. Different concentrations of LMB (0 to 400 mg L^{-1}) in
134 presence of two fixed doses of PAC were used. The low PAC dose (2 mg Al L^{-1}) was based
135 on the results from previous experiments in freshwaters (Lürling and van Oosterhout 2013;
136 Noyma et al. 2016); the higher PAC dose (8 mg Al L^{-1}) was based on the effective removal of
137 cyanobacteria from Jacarepaguá water with red soil as ballast (De-Magalhães et al. 2017). The
138 experiment was run in 75 mL glass tubes that were filled with 60 mL of unfiltered water from
139 Jacarepaguá. The water collected from Jacarepaguá contained cyanobacteria at a chlorophyll-
140 *a* concentration of 222 (± 2) µg L^{-1}; the cells were healthy as indicated by a photosystem II
141 (PSII) efficiency of 0.53 (± 0.03), both determined using a PHYTO-PAM phytoplankton
142 analyser (Heinz Walz GmbH, Effeltrich, Germany). The experiment included a control

143 without any compound added and was performed with three replicates per treatment.
144 Immediately after adding the designated amount of LMB, the PAC coagulant was added and
145 the content in the test tube mixed briefly using a glass rod. Tubes were placed in the
146 laboratory at 25 °C under stagnant conditions. After one hour 5 mL samples were taken from
147 both the top and the bottom of the tubes in which chlorophyll-*a* concentrations and PSII
148 efficiencies were measured. The 5 mL from the top and the bottom of the tubes were sampled,
149 since an accumulation at the top would indicate a scum formation in the field, which is an
150 unwanted effect, whereas the accumulation at the bottom is the intended effect from the
151 combined coagulant and ballast (De-Magalhães et al. 2017; Miranda et al. 2017). After the top
152 and bottom samples were taken, the pH was measured in the middle of the tubes. The
153 chlorophyll-*a* concentrations in the top of the tubes and those measured at the bottom of the
154 test tubes, as well as PSII-efficiencies and pH values were statistically evaluated running a
155 one-way ANOVA in the program SigmaPlot version 13. Homogeneity of variance was tested
156 by the Equal Variance Test (Brown-Forsythe) and normality, by the Shapiro-Wilk Normality
157 Test. In cases where normality failed data were log-transformed to fulfill this prerequisite. An
158 all pairwise multiple comparison was performed to distinguish means that were significantly
159 different at the 0.05 level (Holm-Sidak method; $p = 0.05$).

160

161 **LMB dose**

162 The manufacturers advice to dose the LMB in an LMB:P ratio 100:1, with P the "labile" P-
163 pool in the sediment. The ratio LMB:P 100:1 is based on the 1:1 molar La:P from the
164 precipitation reaction equaling a 4.485:1 La:P weight ratio and a 4.5% La in LMB. Based on
165 the 0.05 g P / kg (wet sediment) we estimated a dose of 400 and 507.5 g LMB m^{-2} assuming a

166 communicating sediment depth of 8 cm and 10 cm respectively, which are consistent with
167 LMB doses applied in the field (Dithmer et al., 2016b).

168

169 **Sediment P extraction**

170 To determine the dose of LMB needed in the experiments, an estimate of the potentially
171 releasable P in the sediment was required. Hereto, a sequential extraction protocol modified
172 from Paludan & Jensen (1995) and used by Cavalcante et al. (2018) to measure different P
173 forms in the sediment was adopted. One gram of wet sediment was brought into each of four
174 50 mL Falcon tubes to which, as a first step, 25 mL anoxic demineralized water was added to
175 extract the immediately available P. The tubes were shaken for 30 minutes (oxygen at the start
176 was 0.21 and at the end 0.44 mg L^{-1}). The tubes were centrifuged and the supernatant
177 collected. A second aliquot of 25 mL anoxic demineralized water was added to the pellets and
178 shaken for five minutes, where after the tubes were centrifuged and the supernatants joined,
179 filtered through 0.6 µm glass fiber filters (GF-3, Macherey-Nagel), acidified with 0.5 mL 2 M
180 H_2SO_4 and stored in the refrigerator until P analysis. In the second step, to the pellets 25 mL
181 of anoxic Bicarbonate/Dithionite (BD: 0.11 M $NaHCO_3$ and 0.11 M $Na_2S_2O_4$) was added to
182 extract P bound to Fe-hydroxides and Mn-compounds from the sediment pellets. The tubes
183 were shaken for 30 minutes, subsequently centrifuged and the supernatant collected. To the
184 pellets, another 22 mL anoxic BD was added and tubes were shaken for 5 minutes,
185 centrifuged and supernatants joined. The joined 47 mL supernatants were aerated for half an
186 hour, filtered through 0.6 µm glass fibre filters, acidified with 3 mL 2 M H_2SO_4 and stored in
187 the refrigerator for P analysis. In the third and last step, to the pellets 25 mL 0.1 M NaOH was
188 added aiming to extract P bound to metal oxides of Al. The tubes were shaken for 30 minutes,
189 centrifuged, and supernatants collected, followed by a second extraction with 25 mL 0.1 M

NaOH for five minutes and a washing step for five minutes with 23.5 mL demineralized water. The three joined supernatants (73.5 mL) were filtered as before, acidified with 1.5 mL 2 M H_2SO_4 and stored in the refrigerator. The filtrates were analysed on their SRP and total phosphorus (TP) concentrations using a Flow Injection Analysis System (model 2500, FIAlab, USA). The dry weight of the sediment was determined by weighing triplicate samples of 10 mL sediment before and after drying at 105 °C.

Effect of different over-standing water on sediment phosphate release

Fifty gram wet sediment from Jacarepaguá, corresponding to a 2.43 mg of releasable P in the sediment, considering the P content determined as described above, was transferred into 250 mL Schott glass bottles. To six bottles 100 mL demineralized water was added, to nine bottles 100 mL filtered Jacarepaguá water (0.6 µm glass fiber filters; GF-3, Macherey-Nagel) was added, while to nine other bottles 100 mL unfiltered Jacarepaguá water was added, which was collected on January 19th 2015. Three bottles of each series were left untreated (control) and three were treated with 400 g m^{-2} LMB, while the two series with filtered and unfiltered Jacarepaguá water also included a treatment with PAC (8 mg Al L^{-1}) and LMB (400 g m^{-2}) in triplicates. This dose of PAC was found effective in flocculating the cyanobacteria out of the water column without strong effects on the pH of Jacarepaguá water (De-Magalhães et al. 2017). PAC was not included in the demineralized water series, because of strong effects on pH (Gebbie, 2001). We calculated a dose of 400 g LMB m^{-2} assuming a communicating sediment depth of 8 cm which is consistent to the La profile in 10 LMB treated lakes where La was mixed in the sediment from ~5 cm to more than 10 cm (Dithmer et al., 2016b). The experimental bottles were placed at 25°C at low light (≅ 1 µmol photon m^{-2} s^{-1}) in day-night regime (13 hours light:11 hours dark). Initially and after 7, 14 and 21 days samples were

214 taken, filtered through 0.6 µm glass fibre filters (GF-3, Macherey-Nagel), and analysed on
215 their SRP concentrations using a Flow Injection Analysis System (model 2500, FIAlab,
216 USA). Differences in SRP concentrations between start and one week incubations were used
217 to derive an estimate of SRP fluxes using the known water volume (100 mL) and the surface
218 area of the sediment at the Schott glass bottles (28.27 cm^2).

219

220 **Treating sediment cores with PAC or LMB + PAC- short term experiment**

221 On January 19th 2015, seven sediment cores were drilled from Jacarepaguá using a Kajak core
222 sampler. The cores contained between 18 and 30 cm length of black sediment and 9 to 21 cm
223 over-standing, cyanobacteria dominated water. Hereto, considering a communicating
224 sediment depth of 8 cm, and the results of the extraction described above, the cores contain an
225 estimated amount of 10.15 mg of P releasable to the water column. Two cores were treated
226 with sole PAC (8 mg Al L^{-1}), two cores with LMB (400 g m^{-2}) plus PAC (8 mg Al L^{-1}), while
227 three cores remained untreated (controls). The cores were incubated in the laboratory at 25°C
228 at low light (≅ 1 µmol photon m^{-2} s^{-1}) in day-night regime (13 hours light: 11 hours dark).
229 Initially and after 1.5, 3.5, 18, 42, 90, 138, 186 and 306 hours water samples were taken and
230 analysed on their chlorophyll-*a* concentrations. Additional samples taken before, just after
231 application and after 138 and 306 hours incubation, were filtered through 0.6 µm glass fiber
232 filters (GF-3, Macherey-Nagel) and analysed on their SRP concentration as previously
233 described. The differences between SRP concentrations from the start and after incubation of
234 306 hours were used to estimate the SRP fluxes using the formula: $\{(P_{final} - P_{start}) \times$ water
235 height$\}/\Delta t$, with P in mg m^{-3}, water height in m and Δt in days (d).

236

237 **Treating sediment cores with LMB + PAC- long term experiment**

238 On September 29th 2015, additional sediment cores were taken from Jacarepaguá using a
239 gravity Uwitec Corer sampler. The tubes contained between 18 and 28 cm length of black
240 sediment and 32 to 43 cm of over-standing water. The potential available P was determined as
241 outlined above and the SRP concentration in the water was determined. Both were used to
242 estimate the dose of LMB required assuming a 10 cm communicating sediment depth. The 10
243 cm communicating sediment depth contain a calculated amount of 12.68 mg of P releasable
244 yielding a dose of 507.5 g m^{-2} to be added together with PAC (8 mg Al L^{-1}) to each of four
245 replicate cores (treatment), while four other cores remained untreated (controls). The
246 chlorophyll-*a* concentration of the over-standing water was 86 (± 1) µg L^{-1}. The cores were
247 closed with a rubber stopper and placed in the laboratory at 25°C in the dark. The experiment
248 lasted 96 days to give insight in the durability and efficacy of the treatment. The experiment
249 was conducted under anoxia 0.20 (± 0.45) mg L^{-1} at a circumneutral pH 7.01 (± 0.54). 10 ml
250 of water from the middle of the core tubes were sampled initially and after 1, 3, 15, 22, 29, 35,
251 64 and 96 days and filtrated before been analysed using a Flow Injection Analysis System
252 (model 2500, FIAlab, USA) for SRP measurements. The treatment took place on October 1st,
253 i.e. two days after collection, because the sediment P had to be determined prior to
254 application. Consequently, the course of SRP concentrations was statistically evaluated
255 running a rmANOVA in the toolpack SPSS (version 22) using the whole period as well as
256 using only the data obtained after application (days 3,.... 96). The differences between SRP
257 concentrations from start and after 96 days of incubation were used to estimate the SRP fluxes
258 using the formula: $\{(P_{final} - P_{start}) \times \text{water height}\}/\Delta t$, with P in mg m^{-3}, water height in m and
259 Δt in days (d).

260

Comparison of SRP fluxes with estimated critical P loadings

The PClake metamodel is used to estimate the critical P load sufficient to cause a shift between a clear water state (P load below its critical value) and a turbid water state (P load above its critical value) (Mooij et al. 2010, PBL 2015), available at http://themasites.pbl.nl/modellen/pclake/index.php. In the clear water state blooms of cyanobacteria are not expected as they are P-limited. PCLake simulates the influence of phosphate on lakes based on water and sediment P, transparency, amount of water plants, phytoplankton concentration, fish stock and swamp and bank vegetation, whilst taking into consideration soil type, size and depth of a lake. PCLake simulations have been run by the model builders using a whole range of P loads for a number of lake types and both starting conditions. In these 100.000 simulations depth, lake surface, retention time, soil type, swamp area defined the lake types. All results are stored in a database and the critical transitions determined for each combination. The critical transition is the P-load yielding a transparency of half the water column depth. In case of new combinations, the critical P loads are estimated using a neural network (http://www.pbl.nl/dossiers/water/modellen/WerkingModelPCLake). PClake was run with the following parameters based on previous Jacarepaguá Lagoon studies (Barbosa and Almeida 2001; Ferrão-Filho et al., 2002; Gomes et al., 2009). The input parameters were: average depth of 3.3m, swamp area 0.1, fetch 4000m, discharge (19 mm d^{-1} = residence time of 176 days), average depth = 3.3 m, background extinction = 0.5 m^{-1}, and sand as soil type. We compare the SRP-fluxes derived from our current experiments to the PClake critical P loadings. An additional critical P load estimate was made, targeting a TP concentration of 30 µg L^{-1}, which correspond to a decrease of 98% of TP in Jacarepaguá Lagoon (De-Magalhães et al 2017), using the Vollenweider (1976) model: $P_{critical} = P_{target} \times (1 + \sqrt{\tau}) \times z_m \times \tau^{-1}$, where $P_{critical}$ is the critical P load (g m^{-2} $year^{-1}$), P_{target} is the target in-lagoon P concentration (g m^{-3}), τ is the water retention time (year) and z_m is mean water depth (m).

286 The same model was used to derive an estimate of the actual load based on the current in-
287 lagoon P concentration.

288

289 ## Results

290 **Effect of different concentrations of LMB and PAC on cyanobacteria removal**

291 With the PAC dose fixed at 2 mg Al L^{-1} the chlorophyll-*a* concentrations in the top of the test
292 tubes declined with increasing LMB dose. The F-test revealed a significant difference among
293 the treatments ($F_{5,12}$ = 135.0; p< 0.001). The pairwise multiple comparison revealed no
294 difference between the control and the sole PAC treatment (0 mg LMB L^{-1}) while with higher
295 LMB dose all chlorophyll-*a* concentrations in the top were significantly different and
296 decreased with higher concentrations of LMB as ballast (Fig. 2). Also, in the bottom of the
297 test tubes significantly different ($F_{5,12}$ = 495.4; p< 0.001) chlorophyll-*a* concentrations were
298 found. The *post-hoc* comparison, considering the top of the bottles revealed four homogenous
299 groups that were significantly different from each other: 1) the lowest chlorophyll-*a*
300 concentrations were in the control and the 0 mg LMB L^{-1} treatment; 2) significantly higher
301 chlorophyll-*a* concentrations were measured in the bottom of the tubes treated with
302 concentrations 50 mg LMB L^{-1} treatment; 3) even higher chlorophyll-*a* concentrations were
303 measured in the bottom of the tubes treated with concentrations 100 mg LMB L^{-1} treatment;
304 4) the highest chlorophyll-*a* concentrations were measured in the bottom of the tubes treated
305 with 200 and 400 mg LMB L^{-1} (Fig. 2). PSII-efficiencies in the top of the tubes were also
306 statistically different ($F_{5,12}$ = 6.19; p = 0.005), the *post-hoc* comparison revealed that the PSII
307 in the 200 mg LMB L^{-1} treatment was lower than in the 100 and 400 mg LMB L^{-1}.
308 Nonetheless, values varied on average between 0.49 and 0.55. PSII efficiency was also
309 statistically different in the bottom of the tubes (H_5 = 13.8; p = 0.017). The pairwise multiple

310 comparison test revealed that PSII in the control (0.59) was significantly higher than in the
311 400 mg LMB L^{-1} treatment (0.42) (Fig. 2). Although pH in the control was significantly
312 higher than the treatments ($F_{5,12} = 94.1$; $p < 0.001$), the differences were relatively small
313 varying from 9.1 (control) to 8.7 (400 mg LMB L^{-1}; Fig. 2).

314 In the series with PAC dosed at 8 mg Al L^{-1} and concentration range of LMB, chlorophyll-*a*
315 concentrations in the top of the test tubes were significantly different among treatments ($F_{5,12}$
316 = 66.7; $p < 0.001$). The *post-hoc* comparison revealed four homogeneous groups: 1) the
317 control; 2) the 0 mg LMB L^{-1} treatment, i.e. the sole PAC treatment; 3) the combined PAC
318 and 50, 100 and 400 mg LMB L^{-1} treatments and 4) the 100, 200 and 400 mg LMB L^{-1}
319 treatments combined with PAC (Fig. 3). The bottom chlorophyll-*a* concentrations were also
320 significantly different ($F_{5,12} = 217.7$; $p < 0.001$). Three significantly different groups were
321 detected: 1) the control 2) the 0, 50, 100 and 200 mg LMB L^{-1} treatments combined with
322 PAC, and 3) the 400 mg LMB L^{-1} treatment also combined with PAC (Fig. 3). PSII-
323 efficiencies in the top of the test tubes were similar ($F_{5,12} = 2.78$; $p = 0.068$) and on average
324 0.55 (± 0.05). In the bottom, the ANOVA indicated significant differences ($F_{5,12} = 6.50$; $p =$
325 0.004), where the *post-hoc* comparison indicated PSII in the 400 mg LMB L^{-1} treatment was
326 significantly lower than those in the 0, 50 and 100 mg LMB L^{-1} treatments. However,
327 differences were very small, as were within group variations. The mean PSII-efficiency at the
328 bottom was 0.53 (± 0.02) (Fig. 3). The pH was significantly different ($F_{5,12} = 288.3$; $p <$
329 0.001) and three different groups were found: 1) the control; 2) the 0 mg LMB L^{-1} treatment,
330 i.e. the sole PAC treatment; and 3) all PAC + LMB treatments (Fig. 3).

331

332 **Effect of different over-standing water on sediment phosphate release**

333 The initial SRP concentration in the Jacarepaguá lagoon was 786 µg L^{-1} in the filtered water
334 and 783 µg L^{-1} in the unfiltered water, while it was below the detection limit (3 µg L^{-1}) in the
335 demineralized water. The SRP concentrations in the filtered and unfiltered lagoon water
336 standing over Jacarepaguá sediment were reduced by treatments with LMB or PAC+LMB,
337 while it was the same in the controls (Fig. 4). Contrary, in over standing demineralized water
338 SRP concentrations seems to increase in treatments with LMB and control (Fig. 4), however
339 the rmANOVA indicated no time effect ($F_{1.5,6.0}$= 2.12; p = 0.200), no treatment effect ($F_{1,4}$=
340 1.60; p = 0.274) and no time x treatment interaction ($F_{1.5,6.0}$= 0.36; p = 0.655), (Fig. 4A). The
341 SRP fluxes, from demineralized water, determined after one-week incubation were not
342 significantly different (t_4 = 2.25; p = 0.065), despite they were on average 4.0 (± 2.5) mg P m^{-2}
343 d^{-1} in the control and 0.4 (± 0.2) mg P m^{-2} d^{-1} in the LMB treatment (Fig. 5).

344 In the series where Jacarepaguá sediment was incubated with filtered lagoon water, the
345 rmANOVA indicated no time effect ($F_{2,12}$ = 1.15; p = 0.351), a significant treatment effect
346 ($F_{2,6}$ = 107.5; p < 0.001) and no time x treatment interaction ($F_{4,12}$ = 0.79; p = 0.552). Tukey's
347 *post-hoc* comparison revealed that SRP concentrations in the LMB and LMB+PAC
348 treatments were significantly lower than in the controls (Fig. 4B). Likewise, the SRP fluxes
349 were significantly different ($F_{2,8}$ = 22.8; p = 0.002). Tukey's test showed that controls differed
350 from treatments with values of 2.3 (± 1.2) mg P m^{-2} d^{-1} in the control, -2.7 (± 0.9) mg P m^{-2} d^{-1}
351 in LMB treatment and -2.4 (± 0.9) mg P m^{-2} d^{-1} in LMB+PAC treatment. The negative
352 values indicate a net removal of SRP from the over-standing water and thus a flux towards the
353 sediment (Fig. 5).

354 The treatment effects in the series with sediment and unfiltered water were comparable to
355 those obtained with filtered water (Fig. 4B and C). The rmANOVA indicated no time effect
356 ($F_{2,12}$ = 1.90; p = 0.192), a significant treatment effect ($F_{2,6}$ = 13.1; p = 0.006) and no time x
357 treatment interaction ($F_{4,12}$ = 1.37; p = 0.301). Tukey's *post-hoc* comparison revealed that

358 SRP in the LMB and LMB+PAC treatments were significantly lower than in the controls
359 (Fig. 4). The SRP fluxes were significantly different ($F_{2,8} = 8.87$; $p = 0.016$) and Tukey's test
360 showed that the control differed from treatments with values of 6.1 (± 4.8) mg P m^{-2} d^{-1} in the
361 control, -2.5 (± 1.0) mg P m^{-2} d^{-1} in LMB treatment and -2.3 (± 0.9) mg P m^{-2} d^{-1} in
362 LMB+PAC treatments. Again, the negative values indicate a net removal of SRP from the
363 over-standing water and thus a flux towards the sediment (Fig. 5).

364

365 **"Labile" P-pool in Jacarepaguá Lagoon sediment**
366
367 The average value from the phosphate concentration sum, for all three extraction steps was
368 362.5 µg P/g DW. The major part of the phosphorus was extracted in step 2, with BD (167.1
369 ±27.1 µg P/g DW). The P sorbed by clay minerals and oxides of Al extracted using NaO
370 contributed with 131.8 (±20.5) µg P/g DW. Lower contribution of loosely adsorbed P
371 (extracted with anoxic demineralized water) was observed in a concentration of 63.5 (±12.1)
372 µg P/g DW (Fig 6). Considering 14% of dry weight in each ml of sediment it yields a
373 concentration of 51.5 µg P/ml.

374

375 **Treating sediment cores with PAC or LMB + PAC - short term experiment**

376 The sediment cores treated with PAC+LMB or only PAC caused a rapid decline in both the
377 chlorophyll-*a* and the SRP concentrations in the water column (Fig. 7A and B). Already after
378 1.5 hours chlorophyll-*a* concentrations in the sole PAC treatment were 59% lower than in the
379 control, while in the LMB + PAC treatment it was more than 90% lower. The rmANOVA
380 indicated a significant time effect ($F_{3.5,14.3} = 34.3$; $p < 0.001$), a significant treatment effect
381 ($F_{2,4} = 11.1$; $p = 0.023$) and a significant time x treatment interaction ($F_{7.1,\ 14.3} = 3.84$; $p =$
382 0.015). The chlorophyll-*a* concentrations in the control also gradually decreased to values

383 similar as in the treatments (Fig. 7A). Tukey's test revealed that only the control and the
384 LMB+PAC treatments were significantly different from each other. The SRP concentrations
385 were strongly influenced by the treatments where PAC reduced the SRP concentrations by
386 72% within 1.5 hours, while LMB+PAC caused a 92% reduction (Fig. 7B). However, SRP
387 concentrations in PAC treatments started to increase again and after 306 hours they were
388 similar to the control (t_3 = 1.25; p = 0.299), while SRP in the PAC + LMB treatments were
389 still significantly lower (Tukey's test following one-way ANOVA; $F_{2,6}$ = 49.2; p = 0.002).
390 The SRP fluxes were on average 9.2 (± 6.7) mg P m^{-2} d^{-1} in the control, 3.6 (± 1.7) mg P m^{-2}
391 d^{-1} in PAC treatment and -10.4 (± 5.5) mg P m^{-2} d^{-1} in LMB+PAC treatment. The ANOVA
392 indicated that SRP fluxes were significantly different ($F_{2,6}$ = 7.70; p = 0.043), (Fig 5), but this
393 was not confirmed by the Tukey *post-hoc* comparison yielding a marginal difference between
394 the control and LMB+PAC treatment (p = 0.052).

395

396 **Treating sediment cores with LMB + PAC-long term experiment**

397 When sediment cores from Jacarepaguá were treated with PAC+LMB a strong reduction in
398 SRP concentrations could be observed (Fig. 8). The rmANOVA on SRP data over the whole
399 period indicated a significant time effect ($F_{3.4,16.8}$ = 7.29; p = 0.002), a significant treatment
400 effect ($F_{1,5}$ = 136.0; p < 0.001) and a significant time x treatment interaction ($F_{3.4,16.8}$ = 16.4; p
401 < 0.001). To check whether the interaction effect was caused by the initial data obtained prior
402 to the treatment (days 0 and 1), an additional rmANOVA was run on data after the application
403 (days 3,...,96). This rmANOVA yielded similar results; a significant time effect ($F_{3.3,16.7}$ =
404 7.22; p = 0.002), a significant treatment effect ($F_{1,5}$ = 146.7; p < 0.001) and a significant time x
405 treatment interaction ($F_{3.3,16.7}$ = 7.62; p = 0.002). The time x treatment interaction effect was
406 caused by the gradual increase in SRP in the controls, while SRP in the treatments remained

407 equally low over the course of the experiment (Fig. 8). SRP in the treatments was on average
408 only 2% of the values in the control. The SRP fluxes were 9.9 (± 3.3) mg P m^{-2} d^{-1} for the
409 control and -4.6 (± 0.3) mg P m^{-2} d^{-1} for the PAC+LMB treatments (Fig.5).

410

411 **Comparison of SRP fluxes with estimated critical P loadings**

412 Based on the output from the PCLake Metamodel, a critical SRP flux of 0.7 mg P m^{-2} d^{-1}
413 indicates the shift from a clear to turbid stable state in Jacarepaguá lagoon. While after the
414 turbid stable state is stablished only decreasing the SRP flux to values lower than 0.2 mg P m^{-2}
415 d^{-1} would shift the water from the turbid to clear. The Vollenweider (1976) model yielded -
416 for a target in-lagoon P concentration of 30 µg L^{-1}- a critical P load of 0.95 mg P m^{-2} d^{-1}
417 (Table 1). These values are considerably lower than the fluxes that have been estimated in the
418 controls of the different experiments conducted and higher than the LMB treatments in this
419 study (Fig. 5).

420

421 **Discussion**

422 The results of this study are in agreement with our hypotheses that LMB will block P-release
423 from the sediment of the eutrophic coastal lagoon Jacarepaguá and that a combination of PAC
424 with LMB also clears the water effectively from cyanobacteria. The LMB strongly reduced
425 the internal loading from the nutrient rich sediment from Jacarepaguá lagoon. These results
426 add to the growing body of evidence that LMB is an effective eutrophication management
427 agent. Meanwhile, LMB has been used in dozens of freshwater systems where it in general
428 led to an improved water quality (e.g., Copetti et al. 2016; Spears et al. 2013; 2016; Epe et al
429 2017). In freshwater lakes with cyanobacterial blooms, the combination of LMB with a

coagulant clearly improved water quality through effective control of the bloom and internal SRP loading (Lürling and Van Oosterhout 2013; Waajen et al. 2016a). A growing number of studies show that LMB is effective in reducing the SRP efflux from freshwater sediments (e.g., Waajen et al., 2016a,b), but reports on its efficacy in eutrophic coastal lagoons is still limited. Few studies have reported that LMB could adsorb SRP effectively in saline water (Haghseresht 2006; Zamparas et al. 2012) and brackish water (Reitzel et al. 2013), while reports on effective SRP efflux reduction from brackish and saline sediments are even more rare (Douglas et al. 1999). Hence, our study is one of the few that demonstrates the effectiveness of LMB in hampering the SRP efflux from a brackish sediment and the first that shows that combined with PAC and LMB can control the sediment SRP release for at least three months. In our short term experiment, we could see that PAC alone (at 8 mg Al L^{-1}) was ineffective in hampering sediment P efflux as within two weeks SRP was as high as in the control, but when combined with LMB, the SRP remained at 2% of the control for the entire experimental period of three months.

Our results also refute the claim that even moderately saline environments of >0.5 ppt will render LMB ineffective, because La would be freed from the clay matrix and therewith prohibit formation of a reactive layer for the absorption of labile P species at the sediment-water interface (Copetti et al. 2016). Liberation of some of the La from the clay matrix is likely in more ion rich environments, but formation of "soluble La species" (Copetti et al. 2016) is less likely, since any La will immediately react with oxyanions in the water to form complexes (Byrne and Kim 1993), including precipitates with phosphate (Firsching and Kell 1993). High pH and elevated alkalinity as in Jacarepaguá lagoon imply a higher proportion of hydroxyl- and carbonate ions in the water that could interfere with La-phosphate precipitation (Byrne and Kim 1993; Johannesson and Lyons 1994). Nonetheless, our results show that such interference in the water of Jacarepaguá is insufficient to render LMB ineffective and that

455 sufficient La remained to effectively reduce the SRP efflux from the brackish sediment of
456 Jacarepaguá lagoon. Effective blocking of sediment P release has also been found in a short-
457 term (4 d) experiment, where 0.1 g of LMB and 1.0 g of bottom sediment from Swan River
458 were incubated with 30 mL autoclaved water of 0.5 and 30 ppt salinity (Haghseresht 2006). It
459 would be advisable to conduct additional research with LMB under more saline conditions to
460 test the claim that "soluble La species" are released into the saline water and to evaluate the
461 efficacy of LMB in more saline conditions.

462 The main reason for including PAC is the year round presence of a relatively high biomass of
463 phytoplankton in Jacarepaguá lagoon (Gomes et al. 2009) and the incapacity of solely ballast
464 to precipitate cyanobacteria, whilst their combination is highly effective (Noyma et al. 2017).
465 The effectiveness of ballast compounds and a low dose coagulant is, however, inversely
466 related to cyanobacterial biomass – more biomass requires more ballast to effective settling
467 (Noyma et al. 2017). Our results showed that 2 mg Al L^{-1} PAC in itself was insufficient to
468 settle the cyanobacteria, but with a dose of 400 mg LMB L^{-1} effective removal could be
469 achieved. It should be noted, however, that such LMB dose comes down to 4884 tons for the
470 entire lagoon. Increasing the PAC dose to 8 mg L^{-1}, which proved to be the best concentration
471 in our previous studies with red soil as ballast (De-Magalhães et al. 2017), showed that
472 comparable results could be achieved with 100 mg LMB L^{-1}, which is 1221 tons for the entire
473 lagoon.

474 Of course the main reason for applying LMB is not the needed ballast weight, but the
475 effectiveness in reducing the sediment SRP-efflux. In the first trials we used 400 g m^{-2}, but
476 this was increased to 507.5 g m^{-2} in the last sediment core experiment as we increased the
477 communicating sediment depth to 10 cm and included the water column P in the calculations.
478 This dose is in close vicinity with the average dose of 388 g LMB m^{-2} (range 159-530) given
479 in Copetti et al. (2016) and the 348 g LMB m^{-2} (range 6-667) listed in Spears et al. (2013).

480 Considering the total sediment area of the lagoon (3.7 km^2) a 507.5 g m^{-2} dose implies 1878
481 tons of LMB would be needed, which with an average water depth of 3.3 m yields a dose of
482 154 mg LMB L^{-1} in the lagoon. Common application of LMB is as a slurry from the water
483 surface - LMB granules are mixed with surface water just before spraying on the water
484 (Copetti et al. 2016). Since this LMB dose is between suboptimal and optimal when combined
485 with 2 mg Al L^{-1} of PAC (see Fig. 2), a dose of 8 mg Al L^{-1} of PAC seems better suited (see
486 Fig. 3). Although, 8 mg Al L^{-1} of PAC by itself was already sufficient to precipitate the
487 cyanobacteria, the short term sediment core experiment clearly evidenced it was ineffective in
488 hampering the sediment P-efflux (see Fig. 7B). Using a higher dose of PAC to counteract the
489 sediment P release is not recommended for several reasons despite the cost of PAC is only
490 about 15-20% that of LMB. First, the minimum dose needed, based on an Al:P ratio of
491 minimally 10:1 (cf. De Vicente et al. 2008; Egemose et al. 2010), would boil down to at least
492 16 mg Al L^{-1}. At such PAC dose, the pH in Jacarepaguá water will drop and depending on the
493 pH at application could drop to pH values below 6 (De-Magalhães et al. 2017). Second, the Al
494 polymerization seems to be the most important factor for acute hypoxic death in fish (Poléo
495 1995) and thus negative effects of a relatively high Al dose are likely on the abundant fish,
496 such as *Tilapia rendalli*, which is an important feed and source of income to fishermen living
497 adjacent to the lagoon. Finally, Al-flocks are easily resuspended and hence distributed, while
498 LMB is not (Egemose et al. 2010). In fact, LMB strongly increased sediment
499 stability/consolidation and the resuspension data obtained by Egemose et al. (2010) drove
500 them to conclude that wind driven events will most probably not cause any resuspension of
501 LMB in contrast to Al flocks. Nonetheless, the influence of wind driven resuspension on
502 flocks and P-binding capacity in a large shallow system like Jacarepaguá lagoon needs to be
503 determined.

504 The combination of a higher dose of PAC (8 mg L^{-1}) with dose of LMB targeting both water
505 column and sediment P, not only ensures a stripping of the water column of cyanobacteria and
506 phosphate, which is around 0.8 mg SRP L^{-1} despite cyanobacteria flourishing (De-Magalhães
507 et al. 2017), but also sufficient SRP binding capacity to counteract any P that might diffuse
508 from a bit deeper than 10 cm sediment as the PAC brings an additional SRP binding capacity
509 equal to about 5 cm of sediment.

510 The negative P-flux and the low SRP concentration in the long term experiment (-4.6 ± 0.3mg
511 P m^{-2} d^{-1}) showed the strong P binding capacity of LMB + PAC. This P binding occurred in
512 cores that had very low oxygen concentrations, which is common for Jacarepaguá lagoon, and
513 is in line with other studies that also found good P adsorption by LMB under anoxia (Robb et
514 al. 2003; Akhurst et al. 2004; Ross et al. 2008). The combination of a low dose PAC with a
515 sediment P target dose of LMB has been applied in a whole lake application in 2008 (Lürling
516 and Van Oosterhout 2013). The hypertrophic water with dominance of cyanobacteria in Lake
517 Rauwbraken (The Netherlands) was changed to a mesotrophic clear water state with total P
518 concentrations for more than four years being less than 10% pre-application concentrations
519 (Lürling and Van Oosterhout 2013). It should be noted, however, that Lake Rauwbraken,
520 unlike Jacarepaguá lagoon, has no major inflows of nutrient rich water, but rather diffuse
521 sources via ground water, litter fall and birds (Lürling and Van Oosterhout 2013). In
522 Jacarepaguá the external load is overwhelming with an average discharge of 0.8 m^3 s^{-1}
523 (Gomes et al. 2009) from the tributaries and an average total P concentration of 1477 mg m^{-3},
524 the external load comes to 27.6 mg P m^{-2} d^{-1} (~10 g P m^{-2} $year^{-1}$). Given such ongoing
525 external P loading in Jacarepaguá lagoon it is beyond doubt that first these external sources
526 should be tackled before massive in-lake rehabilitation actions are undertaken.

527 External load reductions could reduce the eutrophication symptoms within several years
528 depending on efficacy of P load reduction and retention time (Fastener et al. 2016). Although

529 the retention time in Jacarepaguá is around 0.5 years. suboptimal mixing and particular the
530 high internal P load could hamper delay in recovery for many years (Fastener et al. 2016). In
531 Jacarepaguá lagoon the internal P flux of ~10 mg P m^{-2} d^{-1} (or ~3.6 g P m^{-2} $year^{-1}$) is ~ 14
532 times higher than the critical load, here calculated. Although the model has not been
533 developed for brackish water, and estimated critical loadings come with some uncertainties
534 (Janse et al. 2010), the internal P loading was substantially larger than the critical loading.
535 Reducing the P loading to below the critical P load is the only option for rehabilitation
536 (Vollenweider 1976; Janse et al. 2008). Thus, even when external loadings are completely
537 stopped, the water quality in Jacarepaguá lagoon will not improve rapidly unless internal
538 loading is tackled adequately. Consequently, additional in-lake actions seem inevitable in this
539 system. Treatments with only LMB or LMB+PAC could bring the internal P load below the
540 critical load, but as emphasized the external load should also be strongly controlled by
541 implementing efficient waste water treatment in the catchment. Furthermore, those catchment
542 treatments should keep the P load below the critical load to ensure enduring improved water
543 quality.

544 The effective control of the sediment P release from Jacarepaguá sediment becomes
545 important in view of the planned but not yet executed dredging plans for the lagoon.
546 According to media reports the dredging project will cost $250 million
547 (http://www.dailymail.co.uk/wires/ap/article-2947878/Rio-official-visits-filthy-lagoon-near-
548 Olympic-Park.html). Of course, as mentioned before, such actions should only be undertaken
549 once external loading has been reduced drastically, but then LMB, or LMB+PAC might prove
550 a much cheaper option, or could be considered as addition to dredging. The effective dose
551 used here (507.5 g m^{-2}) will boil down to around 1878 tons of LMB for the entire lagoon.
552 With a pricing between $2500 and $3000 per ton of LMB, the total material costs to tackle the
553 internal load would be between $4.7- and $5.6 million. Assuming that also the entire water

554 column needs to be stripped of 1 mg P L^{-1}, which requires an additional 1000 tons ($2.5 – 3.0
555 million) and including operational costs a total budget of around $10 million would suffice.
556 This is only 4-5% of the estimated dredging costs. Moreover, it remains to be seen if the
557 planned dredging and storage of sediment in geotextiles in a newly to create island in the
558 lagoon will sufficiently reduce in-lake nutrients to improve water quality. The in-lagoon P
559 concentrations need to be pushed below the threshold concentration needed to minimize the
560 risk on cyanobacterial blooms (Fastner et al. 2016). The here tested combination of PAC and
561 LMB proved an efficient method to settle cyanobacteria out of the water column and to block
562 the sediment P release. Hence, the combination seems promising to test at a larger scale *in-*
563 *situ* using enclosures.

564

565 **Conclusions**

566 • Positively buoyant cyanobacteria could be precipitated using low dosage PAC (2 mg Al L^{-1})
567 combined with higher LMB dose and solely with a higher dose of PAC (8 mg Al L^{-1}) or also
568 combined with lower LMB dose.
569 • The determined internal P loading from the sediment exceeded estimated critical P loading
570 for rehabilitation meaning that only external load reduction will not improve water quality in
571 the lagoon and that both internal and external P load should be tackled.
572 • The PAC dose used (8 mg Al L^{-1}) was not capable to block P release from the sediment, but
573 the LMB proved highly efficient in a brackish system.
574 • In all treatments with LMB and LMB+PAC negative SRP fluxes were determined meaning
575 a net removal of P from the water column towards the sediment.

576 • In a three month sediment core experiment combined LMB+PAC treatment kept SRP as
577 low as 2% of the controls underpinning the strong and robust interception of P released from
578 the heavily P enriched sediment of Jacarepaguá lagoon.

579

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782 Table 1. Critical P loadings from the transitions from clear to turbid water and vice versa derived using the
783 PCLake Metamodel with the following input data: residence time = 173.7 days, discharge 19 mm d^{-1}; average
784 depth of 3.3 m; background extinction of 0.5 m^{-1}; maximum fetch of 4000 m; relative surface swamp area of
785 0.1; and sand as the soil type, as well as the critical P load based on the Vollenweider (1976) model with a target
786 in-lagoon P concentration of 30 µg L^{-1}

Model	Critical P load per day (mg P m^{-2} d^{-1})	Critical P load per year (g P m^{-2} $year^{-1}$)
PCLake - clear to turbid	0.66	0.24
PCLake - turbid to clear	0.17	0.06
Vollenweider	0.95	0.35

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802 Fig 1 Panel A: Location of the Jacarepaguá lagoon near to the Olympic 2016 venues and the
803 sediment sampling station (JAC 20). Panel B shows the green water of the lagoon (January
804 19th 2015) and panel C the main phytoplankton species (*M. aeruginosa* colonies and *P.*
805 *agardhii* filaments).

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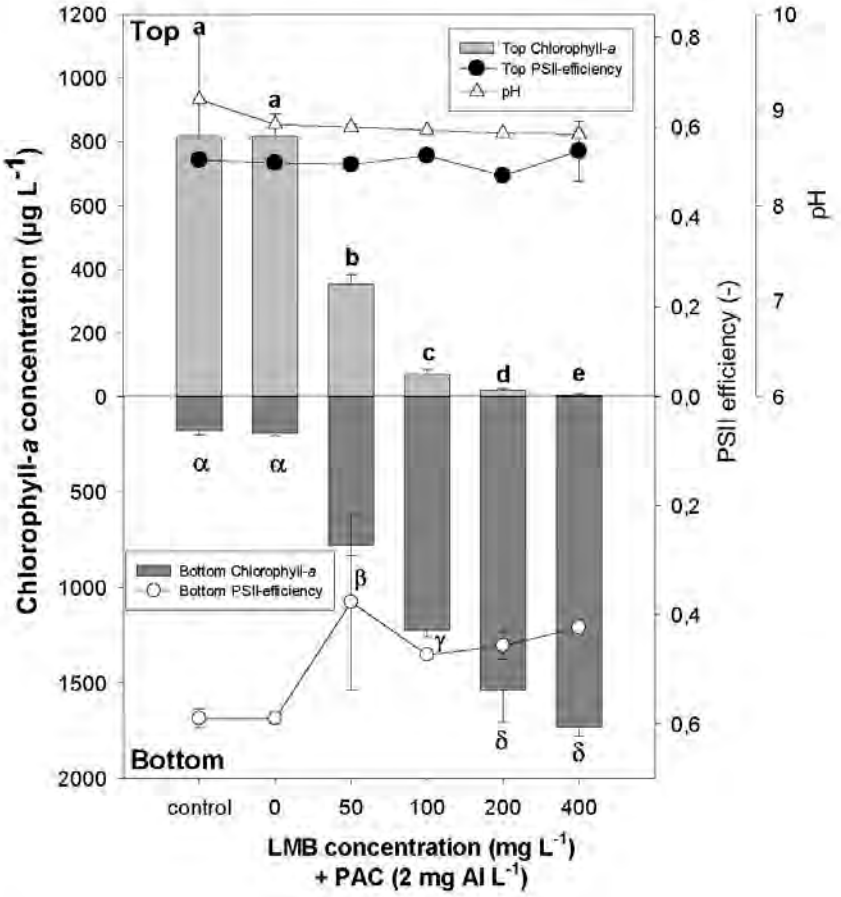


Fig 2 Chlorophyll-a concentrations (µg L^{-1}) in the top 5 mL (top light grey bars) and bottom 5 mL (lower dark grey bars) of 60 mL cyanobacteria suspensions from Jacarepaguá Lagoon incubated for one hour in the absence (control) or presence of the coagulant PAC (2 mg Al L^{-1}) and different concentrations of lanthanum-modified bentonite, LMB (0 - 400 mg L^{-1}). Also included the Photosystem II efficiency (PSII) of the cyanobacteria collected at the water surface (filled circles) and at the bottom (open circles). Error bars indicate one standard deviation (n = 3). Similar symbols (a,..,δ) above/below the bars indicate homogeneous groups that are not different at the 95% level (Holm-Sidak test).

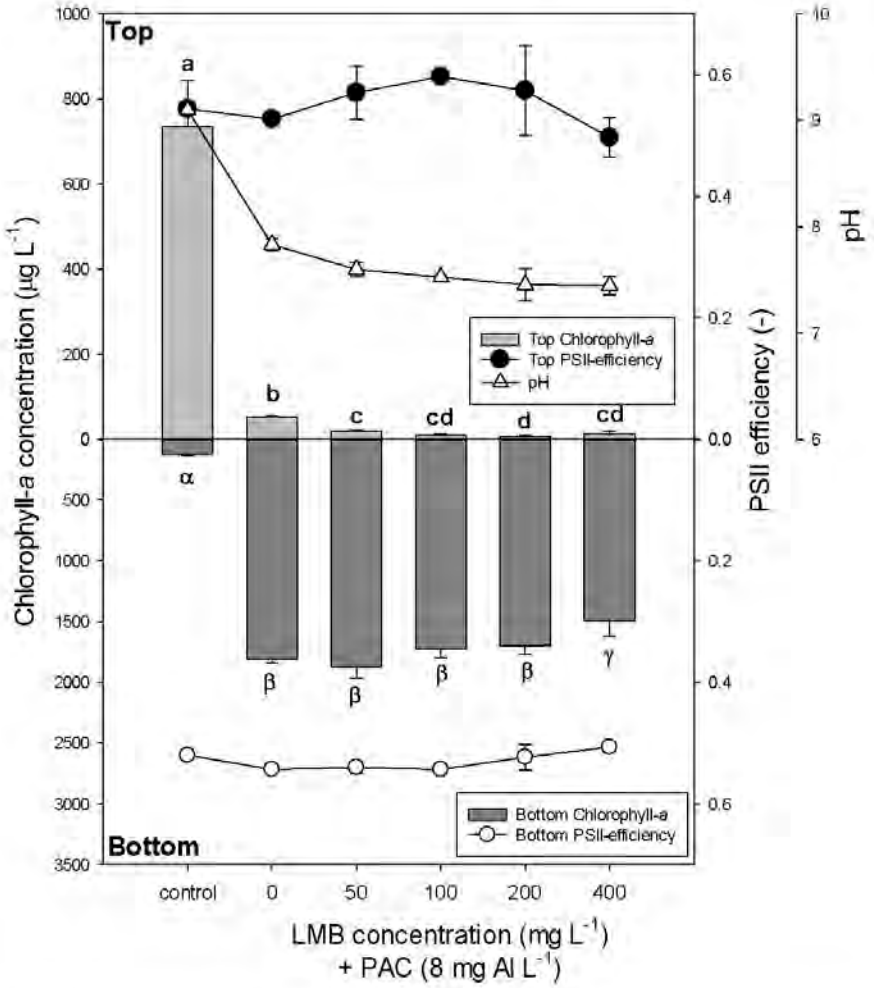
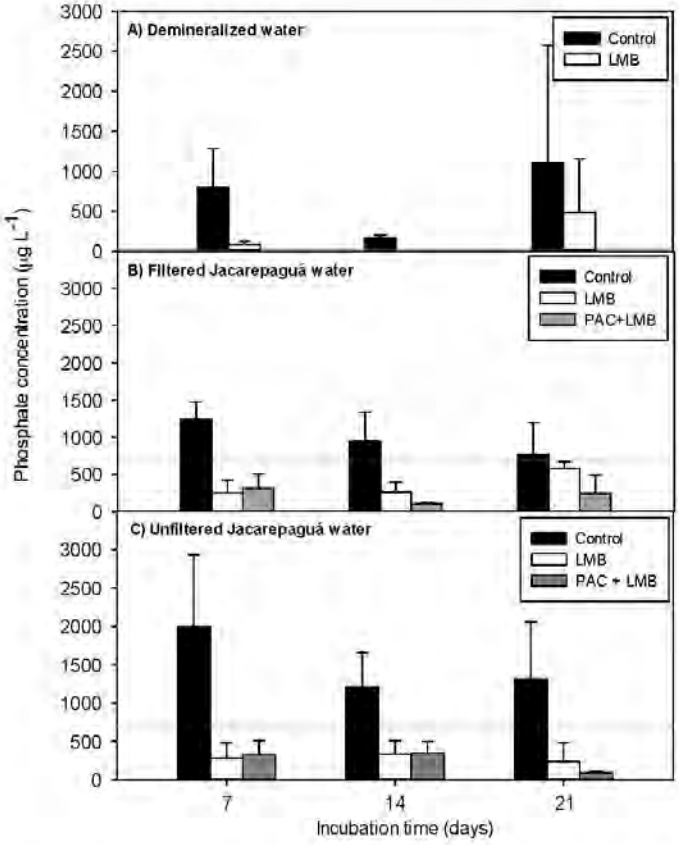


Fig 3 Chlorophyll-a concentrations (µg L^{-1}) in the top 5 mL (top light grey bars) and bottom 5 mL (lower dark grey bars) of 60 mL cyanobacteria suspension from Jacarepaguá Lagoon incubated for one hour in the absence (control) or presence of the coagulant PAC (8 mg Al L^{-1}) and different concentration of lanthanum-modified bentonite, LMB (0 - 400 mg L^{-1}). Also included are the Photosystem II efficiencies (PSII) of the cyanobacteria collected at the water surface (filled circles) and at the bottom (open circles) as well as the pH of the water (open triangles). Error bars indicate one standard deviation (n = 3). Similar symbols (a,.., γ) above/below the bars indicate homogeneous groups that are not different at the 95% level (Holm-Sidak test).



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846 **Fig 4** Phosphate (SRP) concentrations (µg L^{-1}) after 7, 14 and 21 days in 100 mL
847 demineralised water (A), filtered (B) and unfiltered (C) Jacarepaguá water standing above 50
848 g Jacarepaguá sediment that was untreated (controls) or treated with either LMB (400 g m^{-2})
849 or PAC + LMB (PAC at 8 mg Al L^{-1}). Error bars indicate one standard deviation (n = 3). The
850 grey line represents the initial SRP values at day '0" in each type of water used.

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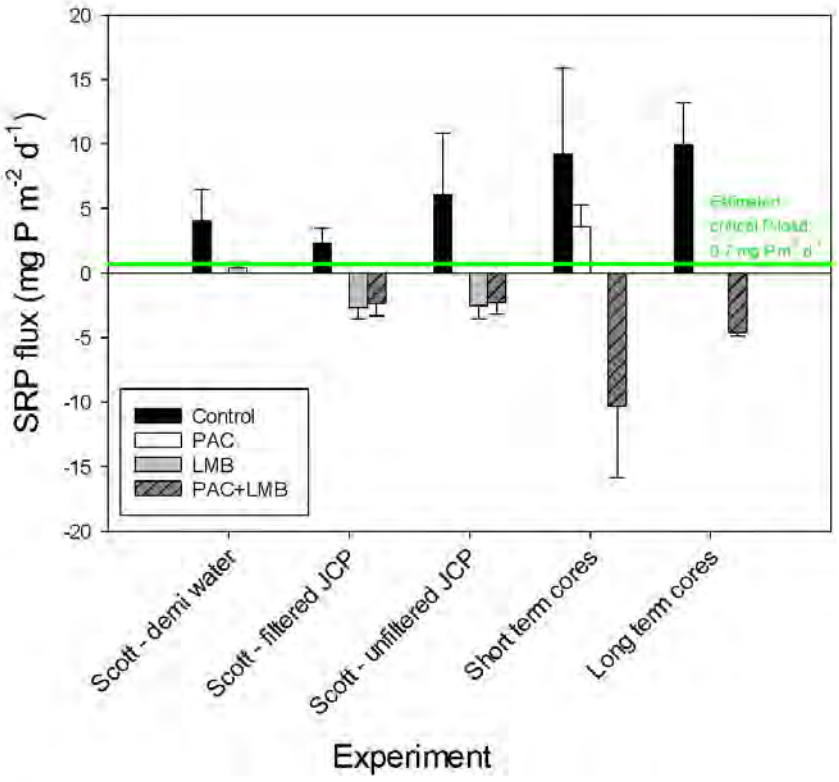

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855 **Fig 5** Estimated SRP fluxes in the different experiments and treatments performed in this
856 study. Negative values indicate a net SRP removal from over-standing water and thus an
857 accumulation in the sediment, whereas positive values indicate a net release from the
858 sediment (internal loading). The green line represents the estimated critical transition from
859 clear to turbid water, while the grey line represents the critical transition from turbid to clear
860 based on the PCLake Metamodel.

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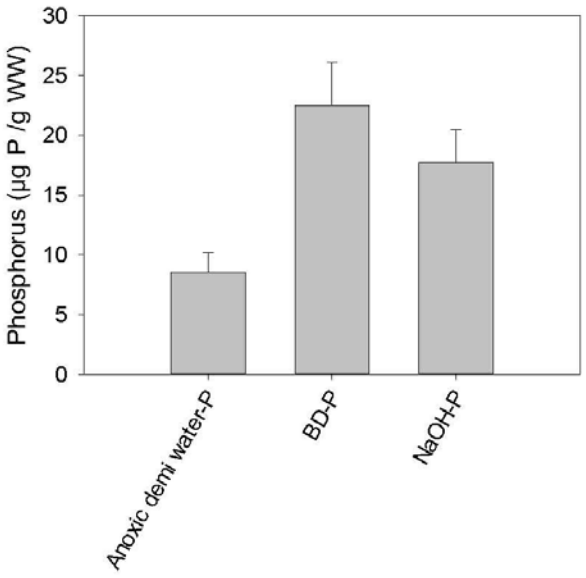

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863 Fig 6 average concentrations of P-fractions (µg P/g DW) in Jacarepaguá Lagoon sediment
864 core. Error bars indicate one standard deviation (n = 3). BD= strongly reducing reagent
865 (anoxic Bicarbonate/Dithionite).

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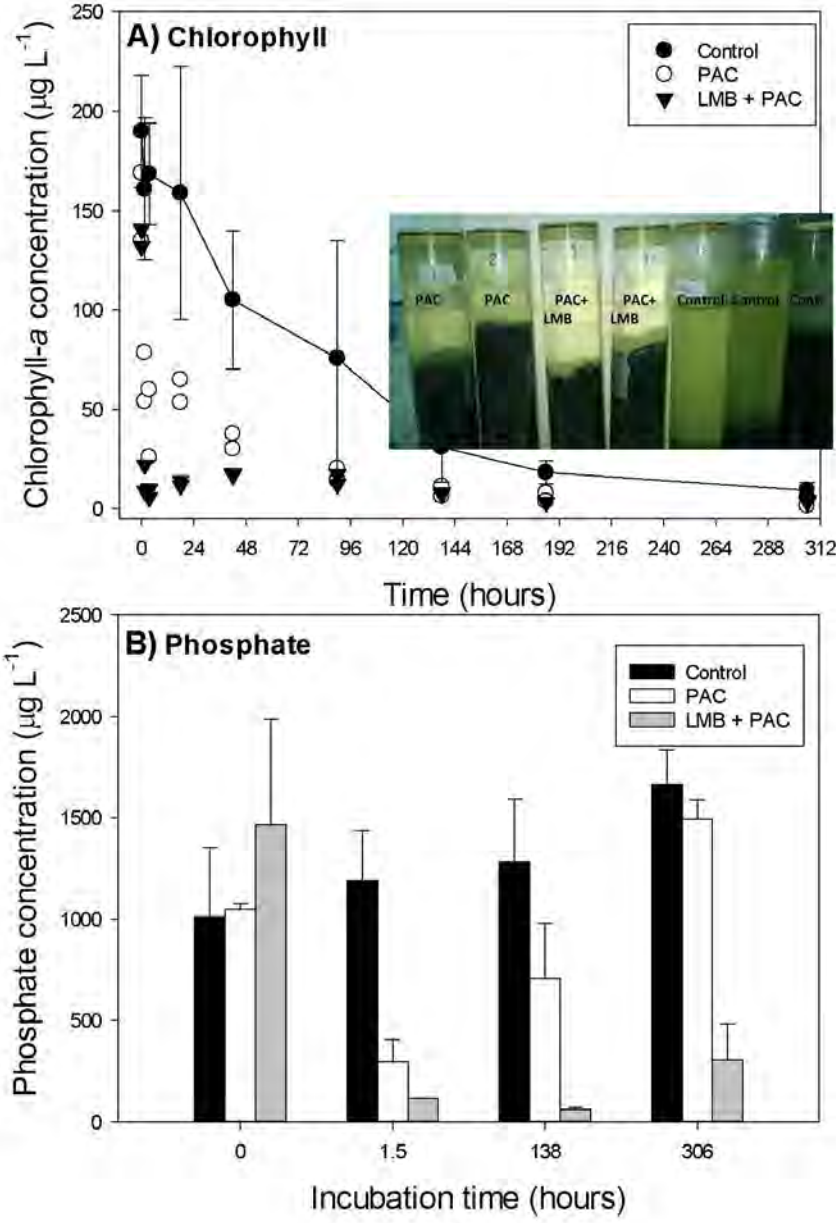
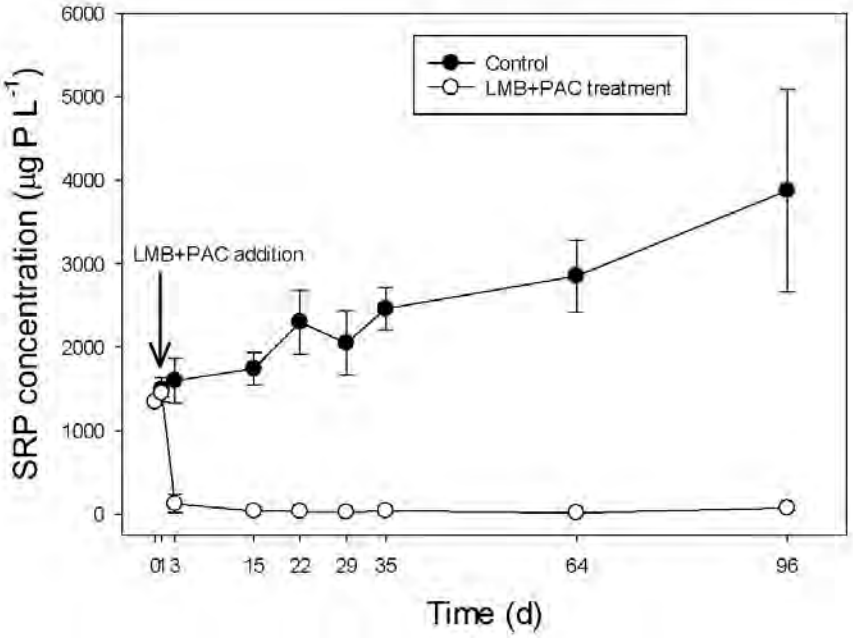


Fig 7 Course of the chlorophyll-*a* concentrations (upper panel A) and of SRP concentrations (lower panel B) in a short term experiment in which sediment cores from Jacarepaguá lagoon

893 (collected January 19th 2015) were left untreated (Control; $n = 3$) or were treated with either
894 PAC (8 mg L^{-1}; $n = 2$), or with PAC (8 mg L^{-1}) and LMB (400 g m^{-2}; $n = 2$).



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897 **Fig 8** Course of the SRP concentrations in sediment cores collected on September 29th 2015
898 in Jacarepaguá lagoon that were left untreated (Control; $n = 4$) or were treated with PAC (8
899 mg L^{-1}) and LMB (507.5 g m^{-2}; $n = 4$).

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