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**Variação espacial e temporal da qualidade da água e do sedimento  
em uma lagoa costeira dominada por cianobactérias –  
Lagoa do Peri – Florianópolis/SC**

Tese submetida ao Programa de Pós-Graduação em Ecologia da Universidade Federal de Santa Catarina para a obtenção do título de doutor(a) em Ecologia.

Orientador: Dr. Mauricio Mello Petrucio

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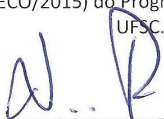
**“Variação espacial e temporal da qualidade da água e do sedimento em uma lagoa costeira dominada por cianobactérias – Lagoa do Peri – Florianópolis/SC”**

Por

**Mariana Coutinho Hennemann**

Tese julgada e aprovada em sua forma final pelos membros titulares da Banca Examinadora (034/PPGECO/2015) do Programa de Pós-Graduação em Ecologia -

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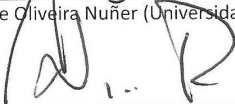
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*“Na natureza nada se cria, nada se perde, tudo se transforma.”*

Antoine Lavoisier

## RESUMO

Lagoas costeiras são controladas por parâmetros tróficos que influenciam a distribuição e abundância de organismos aquáticos, especialmente os produtores primários. Ambientes oligotróficos geralmente apresentam ausência ou baixa densidade de cianobactérias, sendo estes organismos normalmente encontrados em ambientes eutrofizados. Na Lagoa do Peri observa-se uma dominância de *Cylindrospermopsis raciborskii*, com esta cianobactéria apresentando importantes mecanismos de adaptação que determinam seu sucesso neste ecossistema oligo-mesotrófico. O presente estudo avaliou a dinâmica temporal de nutrientes, clorofila-a e variáveis abióticas na coluna d'água e sedimento de uma lagoa costeira subtropical rasa (Lagoa do Peri, ilha de Santa Catarina, sul do Brasil). Para isso, amostras de água foram coletadas mensalmente de março/2007 a fevereiro/2013 para avaliar variações em pequena e média escala em parâmetros físicos, químicos e biológicos da água. Tendências em longo prazo foram avaliadas por meio de dois testemunhos de sedimento coletados e analisados quanto a algumas características paleolimnológicas. Amostras mensais de sedimento também foram coletadas e analisadas quanto à granulometria, fauna bentônica, matéria orgânica e fósforo, de março/2007 a maio/2009. A Lagoa do Peri apresentou baixa concentração de nutrientes dissolvidos e altas concentrações de clorofila-a, com um padrão sazonal de variação para as concentrações de P e clorofila-a. Diferenças significativas foram observadas em diferentes anos para alguns parâmetros. A lagoa foi considerada potencialmente limitada por P durante a maior parte do período de estudo e uma correlação positiva foi encontrada entre as concentrações de clorofila-a e de P. A biomassa fitoplanctônica foi aparentemente controlada pela temperatura da água e pela disponibilidade de P (razões N:P e P dissolvido). Em relação aos dois testemunhos de sedimentos coletados, ambos mostraram tendências gerais similares, com quantidades crescentes de matéria orgânica (OM), carbono (TOC), nitrogênio total (TN) e fósforo total (TP) do fundo para as camadas superiores mais recentes. As razões TOC:TN indicaram uma mistura de contribuições alóctones e autóctones na OM. A razão TN:TP também indicou uma condição de potencial limitação por P, de forma geral. Tanto  $\delta^{13}\text{C}$  quanto  $\delta^{15}\text{N}$  mostraram um padrão de diminuição do

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**Palavras-chave:** parâmetros físico-químicos, qualidade da água, sedimento, paleolimnologia, nutrientes, razões N:P, cianobactérias, Florianópolis, clorofila, Parque Municipal da Lagoa do Peri.



## ABSTRACT

Coastal lakes are controlled by trophic parameters which influence in the distribution and abundance of aquatic organisms, especially primary producers. Oligotrophic environments usually show absence or low densities of cyanobacteria, organisms usually found in eutrophic systems. In Peri Lake, there is a dominance of *Cylindrospermopsis raciborskii*, a cyanobacteria that shows important adaptations that determine its success in this oligo-mesotrophic ecosystem. The present study assessed the dynamics of nutrients, chlorophyll-a and abiotic variables in the water column and sediments of a shallow subtropical coastal lake (Peri Lake, Santa Catarina island, Southern Brazil). Water samples were taken monthly from March 2007 to February 2013 to assess small and medium term variation in physical, chemical and biological parameters. Longer time trends were evaluated by two sediment cores sampled and analyzed for some paleolimnological characteristics. Monthly sediment samples were also taken and analyzed for grain size, benthic fauna, organic matter and phosphorus from March 2007 to May 2009. Peri Lake showed low dissolved nutrients and high chlorophyll-a concentration, with a seasonal pattern of variation concerning P and chlorophyll-a. Significant differences were observed in different years for some parameters. The lake was considered potentially P limited during the majority of the study period and a positive correlation was found between chlorophyll-a and P concentration. Phytoplankton biomass was apparently controlled by water temperature and N:P ratios (P availability). In relation to the two sediment cores sampled, both cores showed similar general tendencies, with increasing amounts of organic matter (OM), total organic carbon (TOC), total nitrogen (TN) and total phosphorus (TP) from the bottom toward the top more recent layers. TOC:TN ratios indicated a mixture of allochthonous and autochthonous contribution to the OM. TN:TP also indicated a condition of potential limitation by P in general. Both  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  showed a decreasing pattern toward the top of the cores. Differences in the depth variation pattern between the two cores were associated to the marginal location of one of the cores. For the monthly sediment sampling, the main results found were: 1) P forms and concentration varied seasonally, with OP and TP increasing in the sediments in warmer periods; 2) P forms and concentration also varied

among the sampling sites, associated with sediment grain size compositions and OM content; 3) quantities and qualities of P in the sediments were correlated with water characteristics, especially temperature, chlorophyll-a, nitrate, dissolved oxygen, pH and TP; 4) some benthic functional feeding groups showed significant relationships with temporal variation in sediment P, including gathering-collectors, shredders and filterers and filtering-collectors. The results suggest a strong importance of climatic factors, especially temperature, and of the P limited condition in the water quality dynamics of Peri Lake, through their influence in the phytoplankton biomass, P release from the sediments and changes in nutrients and primary production in the long term.

**Keywords:** physical-chemical parameters, water quality, sediments, paleolimnology, nutrients, N:P ratios, cyanobacteria, Florianópolis, chlorophyll, Lagoa do Peri Municipal Park.

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# 1. INTRODUÇÃO

## *Ecosistemas aquáticos costeiros e a qualidade da água*

As lagoas costeiras são ecossistemas lênticos distribuídos em todos os continentes, comumente dividindo espaço com uma intensa ocupação antrópica - característica de zonas costeiras. Localizadas em regiões de interface entre ecossistemas terrestres e oceânicos, a baixa profundidade e a suscetibilidade às alterações climáticas são características predominantes e difusas nestes ecossistemas. As lagoas costeiras são separadas do oceano por uma barreira ou conectados a este por um ou mais canais ou pequenas baías que permanecem abertos pelo menos intermitentemente; dessa forma, podem apresentar diferentes níveis de salinidade, desde águas permanentemente doces até hipersalinas (Esteves et al., 2008; Kennish e Paerl, 2010).

Diversos estudos mostram que as lagoas costeiras são sistemas fisiograficamente diversificados, abrigando uma proporção considerável de biodiversidade. Estão entre os ecossistemas mais produtivos do planeta, e fornecem uma ampla gama de recursos e serviços, sendo consideradas ambientes de grande importância ecológica e econômica (Esteves et al., 2008).

As lagoas costeiras são formadas e mantidas através de processos de transporte de sedimentos (Anthony et al., 2009). Devido à pouca profundidade, a penetração de luz na interface sedimento-água é geralmente alta. A hidrodinâmica é fortemente condicionada pela topografia do fundo, e o vento afeta toda a coluna d'água, promovendo a resuspensão de materiais, nutrientes e pequenos organismos das camadas superficiais do sedimento. Além disso, a forte dependência dos ecossistemas lagunares de suas bacias hidrográficas faz com que sejam especialmente vulneráveis a impactos humanos e aportes terrestres e de água doce (Perez-Ruzafa et al., 2005). A localização geralmente em terras baixas promove acumulação de materiais orgânicos e inorgânicos, que resulta em elevados graus de eutrofização natural (Chagas e Suzuki, 2005).

Outros fatores também são capazes de provocar alterações nos corpos d'água costeiros, podendo resultar em eutrofização desses ambientes, como por exemplo o clima, alterações antrópicas dos fluxos de água, alterações no uso e cobertura do solo, poluentes químicos,

espécies aquáticas invasoras, e a retirada de biota para uso humano (incluindo a aquicultura) (Carpenter et al., 2011).

Os fatores supracitados têm o potencial de alterar significativamente a qualidade da água de lagos e lagoas costeiras, especialmente as concentrações de nutrientes. Os dois principais nutrientes envolvidos no processo de eutrofização de corpos d'água são o nitrogênio (N) e o fósforo (P).

O nitrogênio, necessário para a síntese de proteínas, e o fósforo, necessário nas moléculas de DNA, RNA e nos processos de transferência de energia, são ambos essenciais para permitir o crescimento dos produtores primários, sendo os principais nutrientes limitantes na maioria dos ecossistemas aquáticos e terrestres (Conley et al., 2009). É importante estabelecer a importância relativa do N e do P no processo de eutrofização e, dessa forma, avaliar a disponibilidade e a qualidade de registros de longo prazo para estabelecer tendências e alterações (Heathwaite et al., 1996).

Nesse sentido, esforços consideráveis têm sido despendidos para determinar o papel do N e P na limitação da produção dos sistemas, especialmente qual nutriente limita a produção fitoplânctônica. Uma variedade de indicadores específicos tem sido utilizada para avaliar a limitação por nutrientes, incluindo a determinação do estado fisiológico do fitoplâncton, estequiometria e concentração de nutrientes inorgânicos, razões de composição, e várias medições de crescimento do fitoplâncton (Conley, 2000).

Elser et al. (2007) demonstraram que tanto a limitação por N, quanto por P, são fortes e muito difundidas nos principais habitats da biosfera. Observações das razões N:P na água, em relação aos requerimentos nutricionais do fitoplâncton, podem ser utilizadas para inferir se um lago/lagoa é suscetível de ser limitado por N ou P ou ambos (Abell et al., 2010). Uma razão molar N:P de 16:1 é frequentemente utilizada como referência de requerimentos de crescimento balanceados, de forma consistente com a “composição elementar do plâncton” de Redfield et al. (1963). Corpos d'água com razões significativamente menores sugerem limitação por N, enquanto razões substancialmente maiores sugerem limitação por P. A razão exata na qual cada nutriente torna-se limitante pode variar entre lagos e dentro dos lagos, dependendo da comunidade fitoplânctônica presente (Abell et al., 2010).



Diversos estudos já testaram razões N:P (e.g. Guildford e Hecky, 2000; Klausmeier et al., 2004; Loladze e Elser, 2011) e indicaram uma significância inerente para a razão N:P = 16:1, mas todos eles ressaltam que isso não significa que essa razão canônica seja um ótimo universal.

Assim, embora tanto os reservatórios de nitrogênio total (TN) e fósforo total (TP) incluam uma série complexa de frações químicas que variam em sua disponibilidade para absorção pelos organismos, a razão TN:TP é provavelmente um bom indicativo da disponibilidade relativa desses dois elementos para a biota em escalas temporais e espaciais ecologicamente significativas (Sterner, 2008).

Contudo, é importante destacar que a questão acerca do que limita a produção em lagos e lagoas é dependente da escala de análise. As evidências apontam para a visão de que o P geralmente controla a produção biológica em ambientes oligotróficos em escalas de tempo multi-anuais, mas a co-limitação por múltiplos nutrientes é a regra na maioria dos lagos em escalas de tempo menores (Sterner, 2008).

Como foi possível observar, a variação espaço-temporal na disponibilidade de nutrientes tem um importante papel na determinação da distribuição e abundância do fitoplâncton (Pacheco et al., 2010). De forma semelhante, a produção primária tem um papel essencial na ciclagem dos elementos e na produção de alimento para os heterótrofos, formando a base da pirâmide ecológica. É um processo biológico de grande importância, capaz de influenciar em diversas reações químicas nos ecossistemas aquáticos e em todos os níveis tróficos.

Dentre os organismos fitoplantônicos, um grupo tem recebido especial atenção na literatura não só por possuir diversas espécies capazes de produzir toxinas, mas também por serem organismos com excelente capacidade de competição por recursos: as cianobactérias. Compreender a causa da dominância de cianobactérias tem sido um importante foco das pesquisas clássicas e contemporâneas em Limnologia (Havens et al., 2003). As mudanças climáticas são um forte catalisador para expansões adicionais da dominância e de florações de cianobactérias, através de alterações não só na temperatura, mas também nos padrões de precipitação e seca, capazes de alterar os ciclos hidrológicos em diferentes regiões (Paerl e Huisman, 2008).

Dentre as cianobactérias, *Cylindrospermopsis raciborskii* é uma espécie que tem sido amplamente estudada nos últimos anos, devido à alta competitividade dessa espécie em ambientes eutrofizados, aliada à

sua capacidade de formar florações e produzir toxinas (Tucci e Sant'Anna, 2003). A maior parte do conhecimento sobre as preferências ambientais de *C. raciborskii* é baseada em corpos d'água tropicais. Entretanto, a expansão da espécie para climas temperados sugere que diferentes padrões ecológicos estão emergindo (Vidal e Kruk, 2008).

De acordo com a revisão de Padisák (1997) sobre a espécie, o sucesso ecológico de *C. raciborskii* está diretamente relacionado aos seguintes fatores: capacidade de migração na coluna d'água, tolerância à baixa luminosidade, habilidade de armazenar P internamente, alta afinidade com P e amônio, capacidade de fixar N<sub>2</sub> atmosférico, resistência à herbivoria pelo zooplâncton, alta capacidade de dispersão (acinetos resistentes, dispersão por rios, aves etc.), sobrevivência em condições levemente salinas. Plasticidade ecofisiológica e a existência de ecotipos com diferentes preferências ambientais também tem sido consideradas importantes características que permitem à espécie ter um elevado sucesso em diferentes condições ambientais (Briand et al., 2004; Piccini et al., 2011; Bonilla et al., 2012).

Apesar de ser comumente dominante em ambientes mais eutróficos (Bonilla et al., 2011), algumas características de *C. raciborskii* favorecem a espécie em ambientes com baixa disponibilidade de P, tais como: alta capacidade de armazenar P dentro das células (grânulos de poli-fosfato) e um sistema de absorção de alta afinidade (Istvanovics, 2000); dominância favorecida em ambientes com suprimento de P variável (Posselt et al., 2009); e existência de diferentes ecotipos com diferentes afinidades por altas ou baixas concentrações de P (Dokulil, 2000; Piccini et al., 2011).

Essa capacidade superior de *C. raciborskii* para competir por P pode fazer com que as comunidades fitoplanctônicas de ecossistemas oligo e mesotróficos sejam susceptíveis de serem dominadas por esta espécie em situações de pequenos aumentos nas concentrações de nutrientes (Bonilla et al., 2011).

Compreender as características que permitem que espécies de cianobactérias tenham sucesso em ambientes contrastantes é fundamental para prever o comportamento das florações em futuros cenários de mudanças climáticas globais (Bonilla et al., 2011).

## *O papel do sedimento na dinâmica de nutrientes*

O sedimento pode ter um papel chave na dinâmica dos nutrientes em corpos d'água, especialmente em ecossistemas costeiros rasos e em relação ao ciclo do P.

O P no sedimento pode ser liberado para a coluna d'água por uma combinação de processos químicos, físicos e biológicos, de forma que os sedimentos desempenham um papel central especialmente na ciclagem de P atuando como fontes ou depósitos desse nutriente (Kaiserli et al. 2002; Torres et al., 2014).

Tradicionalmente, sedimentos aeróbicos de lagos oligotróficos têm sido considerados retentores de nutrientes, enquanto sedimentos anaeróbicos de lagos eutróficos têm sido considerados fontes de nutrientes para a coluna d'água (Doremus e Clesceri, 1982).

Em lagos rasos, a importância dos sedimentos como fontes de P é ainda maior devido a alta razão entre superfície do sedimento e coluna d'água (Søndergaard et al., 2001; Dong et al., 2011). A resuspensão de P dos sedimentos tem papel fundamental em lagos rasos, devido ao efeito estimulante no crescimento do fitoplâncton (Kleeberg e Herzog, 2014).

De acordo com a visão clássica do ciclo do P em lagos, o fosfato que chega ao lago por seus tributários ou é liberado dos sedimentos, é retirado da água por organismos vivos e partículas suspensas não-vivas, e perdido para o fundo do lago em proporção à velocidade de deposição das partículas. No sedimento, o P orgânico é liberado como fosfato solúvel para a solução durante a decomposição por bactérias, ou fica depositado como P orgânico refratário. O fosfato liberado, por sua vez, pode ser adsorvido a superfícies inorgânicas, complexado com materiais orgânicos refratários, ou precipitado como apatita ou vivianita. Parte do P pode permanecer em solução ou ser reciclado para a água do entorno. Em muitos casos, o fluxo de fosfato dos sedimentos para a água é grandemente controlado pelas condições de redox predominantes na interface sedimento-água (Gächter e Meyer, 1993).

O modelo clássico de Mortimer (1941) associa os fluxos de P no sedimento a condições redox na interface entre o sedimento e a água, que são efetivamente controladas pelas concentrações de oxigênio dissolvido no fundo da coluna d'água. Quando a superfície do sedimento está oxigenada, uma forte adsorção do fosfato dissolvido aos hidróxidos de ferro sólidos limita a liberação de P, impedindo que o

fosfato se difunda dos sedimentos reduzidos mais profundos para a coluna d'água. Sob condições anóxicas, os hidróxidos de ferro reduzidos se dissolvem e o fosfato é liberado para a coluna d'água.

Conforme já exposto, o fosfato pode ser encontrado na matriz sedimentar na forma de complexos de sais de cálcio, ferro ou alumínio e espécies orgânicas, ou adsorvido à superfície de minerais. A forma mais lábil de fosfato encontrada nos sedimentos é sem dúvida o fosfato adsorvido, envolvendo várias interações físicas e químicas fracas entre a superfície sólida e o composto (Aminot e Andrieux, 1996).

Assim sendo, a adsorção é um processo de grande importância na ciclagem do P entre os sedimentos e a coluna d'água, de forma que os sedimentos suspensos podem constituir um reservatório de P rapidamente disponível para os produtores primários, especialmente em ambientes oxigenados (Aminot e Andrieux, 1996).

Sedimentos com diferentes características apresentam diferentes características para adsorção de fosfato. O tamanho das partículas é um fator importante que afeta a troca de P entre a água e os sedimentos, sendo as maiores taxas de adsorção associadas a uma maior quantidade de partículas finas no sedimento (An e Li, 2009; Zhu et al., 2013).

Além da concentração do oxigênio dissolvido e do tamanho dos grãos do sedimento, temperatura e concentração de nitrato também têm um importante papel na liberação de P dos sedimentos (Jensen e Andersen, 1992). Outros fatores que potencialmente influenciam na retenção de P no sedimento incluem: o pH da água (que afeta a força da adsorção iônica do fosfato às superfícies sólidas do sedimento), quantidade e qualidade do aporte de carbono orgânico, aportes de minerais contendo P, bioturbação, fotossíntese epipélica, atividade de plantas aquáticas, concentrações de matéria orgânica no sedimento, ferro reativo, sulfato dissolvido, calcita e outras características do sedimento (Wetzel, 2001).

Estudos têm demonstrado a importância das bactérias no ciclo de P, especialmente na interface sedimento-água, e que esta contribuição não é apenas indireta por meio da influência em processos redox dependentes, mas também de forma direta devido à regeneração de diferentes compostos de P (Kleeberg e Dudel, 1997; Martins et al., 2011).

Os efeitos dos macroinvertebrados bentônicos no transporte de nutrientes dos sedimentos para a água também tem sido bastante

documentado em ambientes aquáticos. Esses efeitos incluem o transporte vertical de P associado ao sedimento e às águas intersticiais durante as atividades físicas de macroinvertebrados dentro de cavidades, excreção de P por organismos diretamente nos sedimentos do entorno ou cavidades, e excreção de P derivados dos sedimentos diretamente nas águas do entorno. As características dos organismos tais como tamanho, comportamento, e modo de alimentação são importantes determinantes de quais processos serão dominantes e sob quais condições ambientais (Caliman et al., 2007; Swan et al., 2007).

As atividades de organismos bentônicos alteram a matriz de sedimentos e a troca de solutos entre a interface sedimento-água. Esses animais bentônicos podem misturar partículas de sedimentos, alterar a estratificação do sedimento, aumentar a porosidade do sedimento, produzir heterogeneidade na distribuição de oxigênio, pH e microbiota através de seus movimentos. Também são capazes de alterar a degradação da matéria orgânica, a ciclagem de nutrientes, a dinâmica do oxigênio, e as concentrações de ferro (Caliman et al., 2007; Zhang et al., 2014).

Conforme anteriormente exposto, há muito tempo o papel dos sedimentos tem sido reconhecido na dinâmica dos ecossistemas lacustres, tanto como depósitos quanto como fontes de nutrientes, influenciando fortemente no estado trófico e biodiversidade dos lagos e lagoas (Trolle et al., 2009).

Parte da matéria orgânica que entra em um lago a partir da bacia hidrográfica (alóctone) ou é produzida dentro do próprio lago (autóctone) é depositada no fundo do lago e torna-se incorporada permanentemente no sedimento. Dessa forma, os sedimentos dos corpos d'água também funcionam como depósitos para matéria orgânica e macro-elementos associados (C, N e P). Como resultado, os sedimentos de lagos contêm um arquivo das condições ambientais e dos processos biogeoquímicos passados dentro e fora do corpo d'água, de forma que testemunhos de sedimento podem ser usados para documentar alterações no ecossistema através do tempo. As taxas de acumulação de macro-elementos e matéria orgânica nos sedimentos têm sido estudadas juntamente com isótopos estáveis ( $\delta^{13}\text{C}$  e  $\delta^{15}\text{N}$ ) para inferir mudanças ambientais passadas nos ecossistemas. Estes parâmetros são utilizados para identificar a origem da matéria orgânica, inferir produtividade

primária passada, documentar eutrofização histórica, elucidar ciclos biogeoquímicos (Torres et al., 2012).

Uma abordagem paleoecológica quantitativa multifatorial oferece uma história específica de um determinado local acerca da resposta de um sistema a distúrbios ambientais recentes, tais como a eutrofização, e é uma ferramenta poderosa por fornecer evidências de condições químicas e biológicas históricas de referência (Clarke et al., 2006). A abordagem é particularmente valiosa onde informações históricas são esparsas, descontínuas, incompletas e/ou não comparáveis, e tais dados podem ser essenciais para estabelecer a história ambiental de corpos d'água em relação ao desenvolvimento de suas bacias de drenagem (Haworth et al., 1996). Tal conhecimento é pré-requisito para uma gestão inteligente, para a definição de objetivos para restauração, utilização de modelos dinâmicos para avaliar diferentes cenários de gestão, e monitorar tendências de resultados (Battarbee, 1999).

De acordo com Meyers (2003), os dois tipos mais importantes de informações fornecidas pela matéria orgânica sedimentar são a origem da matéria orgânica e a abundância da biota que a produziu. A fonte dominante de matéria orgânica para os sedimentos de lagos e lagoas são os organismos fotossintetizantes que vivem dentro e ao redor do corpo d'água.

A matéria orgânica de algas, que é rica em proteínas e pobre em celulose, tem razões molares de C/N normalmente entre 4 e 10, enquanto plantas terrestres vasculares, que são pobres em proteínas e ricas em celulose, geram matéria orgânica com razões C/N usualmente iguais ou maiores que 20 (Meyers, 1994). Essas diferenças fundamentais na composição da matéria orgânica geralmente sobrevivem à deposição e sedimentação (Meyers, 2003).

A análise de isótopos estáveis também tem se mostrado uma excelente ferramenta para estudar os ciclos biogeoquímicos de C e N em sistemas lacustres e lagunares (Gu et al., 2006), bem como para compreender a origem e ciclagem da matéria orgânica (Lehmann et al., 2004). A razão isotópica de C e N da matéria orgânica nos sedimentos resultam de diversos processos complexos, incluindo biossíntese na zona fótica, degradação da matéria orgânica e crescimento bacteriano na coluna d'água e no sedimento, e aporte de fontes alóctones (Lehmann et al., 2002).

Os valores de  $\delta^{13}\text{C}$  da matéria orgânica sedimentar são afetados pelas taxas de produção algal em lagos, as quais são controladas pela disponibilidade de nutrientes dissolvidos. A lixiviação de nitratos e fosfatos de origem terrestre aumenta a produtividade, que remove seletivamente C inorgânico dissolvido rico em  $^{12}\text{C}$  e leva a valores mais elevados de  $\delta^{13}\text{C}$  na matéria orgânica produzida pelo carbono inorgânico remanescente (Meyers, 2003).

Os valores de  $\delta^{13}\text{C}$  da matéria orgânica sedimentar também aumentam com o aumento do estado trófico, de forma que a assinatura isotópica do carbono na matéria orgânica pode servir como uma evidência para inferir o estado trófico passado dos lagos (Brenner et al., 1999).

A razão isotópica de  $\delta^{15}\text{N}$  também tem sido amplamente utilizada como parâmetro para determinar as fontes de matéria orgânica e processos internos ao corpo d'água. O nitrato é a forma mais comum de N inorgânico dissolvido utilizada por algas não fixadoras de  $\text{N}_2$ , enquanto as plantas terrestres utilizam o  $\text{N}_2$  fixado por bactérias simbiontes no solo (Meyers, 2003). Os valores mais elevados de  $\delta^{15}\text{N}$  típicos (7 – 10%) do nitrato dissolvido, em comparação com o  $\text{N}_2$  atmosférico (0%), auxiliam na investigação das fontes de nitrogênio, e assim, das fontes de matéria orgânica (Das et al., 2008).

## 2. ÁREA DE ESTUDO

### *Localização e características gerais*

A lagoa do Peri está localizada a sudeste da ilha de Santa Catarina (Figura 1), entre as latitudes Sul de  $27^{\circ}42'59''$  e  $27^{\circ}46'45''$  e as longitudes Oeste  $48^{\circ}30'33''$  e  $48^{\circ}31'59''$  (Oliveira, 2002), inserida em um dos últimos remanescentes de Mata Atlântica da ilha. Apresenta um espelho d'água de  $5,7 \text{ km}^2$ , sendo rodeada por morros cobertos por Mata Atlântica e uma restinga típica de vegetação litorânea, a qual a mantém separada do Oceano Atlântico (Silva, 2000).

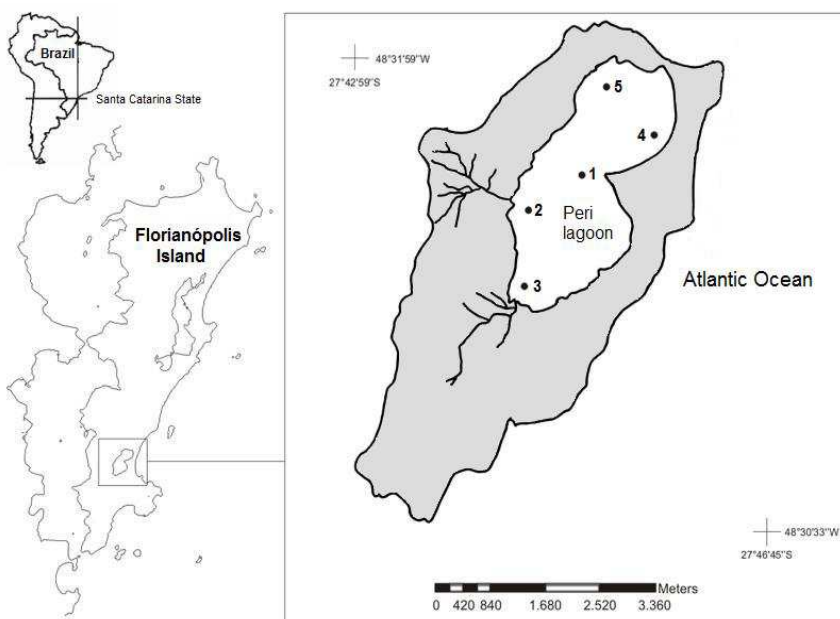


Figura 1. Mapa da bacia hidrográfica (área destacada em cinza) da lagoa do Peri, sul do Brasil, e localização dos cinco pontos amostrais.



A lagoa apresenta um perímetro de 11.064 m, comprimento máximo efetivo de 4 km, largura máxima efetiva de 1,54 km para o setor norte e 1,87 km para o setor sul (Oliveira, 2002), uma profundidade máxima de 11 m na sua porção central e profundidade média de 4,2 m.

### ***O Parque Municipal da Lagoa do Peri***

Em 1976, a lagoa do Peri foi tombada como Patrimônio Natural do Município de Florianópolis e, desde 1981, a lagoa e seus arredores constituem o Parque Municipal da Lagoa do Peri (Lei 1.828/81; Decreto 091/82), com área total de 20,1 km<sup>2</sup>, criado com o intuito de preservar os atributos excepcionais da natureza a fim de conciliar a proteção dos ecossistemas com práticas educacionais, científicas e recreativas que envolvam a comunidade local, sendo proibida qualquer atividade de exploração dos recursos naturais (CECCA, 1997).

O Parque é dividido em três áreas (FLORAM – PMF, 2009):

Áreas de Reserva Biológica - destinadas à preservação integral e permanente do ecossistema e de seus recursos, tendo apenas seu uso permitido para fins científicos; abrange áreas cobertas pela Floresta Pluvial da Encosta Atlântica e pela vegetação litorânea.

Área de Paisagem Cultural - onde se localizam os assentamentos e atividades tradicionais (engenhos de farinha e de cana-de-açúcar) dos descendentes dos antigos colonizadores de origem açoriana.

Área de Lazer - destinada a fins educacionais e científicos através do desenvolvimento de atividades de recreação e lazer compatíveis com a preservação do meio ambiente. Dentro desta área encontra-se a sede administrativa do parque.

Segundo estudo realizado por Dechoum e Arellano (2012), o Parque Municipal da Lagoa do Peri fornece 16 tipos de serviços ecossistêmicos, sendo: quatro de suporte (formação e fertilidade de solos, manutenção da biodiversidade, produção primária, ciclos biogeoquímicos); cinco culturais (valor culturais, valor turístico/recreativo, valor educativo e científico, valor estético, valor espiritual e religioso); três de provisão (recursos pesqueiros, água para abastecimento, plantas medicinais); e quatro de regulação (quantidade e qualidade de água, controle da erosão/sedimentação, regulação da qualidade do ar, regulação do clima local).

### *Características físicas: clima, solo, relevo e geologia*

O clima da região de Florianópolis é considerado do tipo Cfa: mesotérmico úmido sem estação seca definida e com verão quente, típico da região litoral sul do Brasil, com distribuição de chuvas mais ou menos regular ao longo do ano, porém com uma concentração relativamente maior nos meses de verão e um pouco menor no inverno. A média anual das precipitações fica em torno de 1.500 mm.

Em um levantamento realizado por Oliveira (2002) com dados de 1947 a 2001 obtidos junto à CIRAM, os ventos predominantes na região de Florianópolis são o vento Norte ( $\approx 37\%$ ), seguido pelos ventos Sudeste ( $\approx 17\%$ ), Sul ( $\approx 16\%$ ) e Nordeste ( $\approx 10\%$ ). Os demais 20% são pertencentes às demais direções ou referentes a períodos de calmaria. Ainda de acordo com Oliveira (2002), apesar dos ventos predominantes na região serem originários do quadrante Norte, os mais atuantes como agentes modificadores de relevo, com maiores velocidades e com maior capacidade de transporte são os ventos do quadrante Sul.

A região é caracterizada por uma topografia acidentada nas porções sul, oeste e norte, com altitudes inferiores a 500 metros, e uma faixa de restinga situada na porção leste. As maiores altitudes estão situadas ao longo da crista que contorna a bacia de captação da lagoa, representada pelo Morro da Chapada (440 m), Morro da Tapera (383 m), Morro da Boa Vista (367 m) e Morro do Peri (334 m). Na maioria das encostas, predominam declividades acentuadas, entre 20 e 45% (Penteado, 2002).

De acordo com Oliveira (2002), a lagoa do Peri teve sua origem a partir da “transgressão marinha no Holoceno, estando separada do oceano no seu setor leste, por um proeminente cordão arenoso, enquanto que no setor oeste limita-se com o embasamento cristalino”.

Quanto à granulometria, Oliveira (2002) constatou que a maior parte do sedimento de fundo da lagoa é composta por silte muito fino, o qual está presente em quase toda a porção sul e oeste da lagoa, bem como boa parte das porções noroeste e central. As areias finas e médias estão presentes principalmente nas porções norte e leste.

### ***Características biológicas: flora***

De acordo com Oliveira (2002), a cobertura vegetal da bacia da lagoa do Peri segue o padrão apresentado para a ilha de Santa Catarina, obedecendo à estrutura geológica local em dois domínios principais: Floresta Pluvial Atlântica (Mata Atlântica) no embasamento cristalino, ocupando a maior parte do entorno da lagoa (porções sul, oeste e norte), apresentando um bom estado de preservação; e Vegetação Litorânea na planície costeira, associada ao substrato arenoso recente de origem flúvio-marinha e eólica, pobre em nutrientes, onde se desenvolveu uma vegetação típica de restinga. Além dessas duas formações, pequenos reflorestamentos de espécies exóticas e plantações podem ser observados na bacia.

### ***Bacia hidrográfica***

A lagoa do Peri encontra-se a aproximadamente três metros acima do nível do mar, o que a classifica como “lagoa suspensa” (Poli et al., 1978) e de água doce, e mantém contato permanente com o mesmo através de um canal de despejo (canal Sangrador) com fluxo unidirecional lagoa → mar. É alimentada por dois cursos d’água: o rio Cachoeira Grande e o rio Ribeirão Grande, e secundariamente por pequenos córregos (IPUF, 1978).

O rio Cachoeira Grande possui uma extensão de 1,7 km, nasce a uma altitude de 280 m e apresenta uma declividade média de 20 cm/m, drenando uma área de 1,66 km<sup>2</sup>. O rio Ribeirão Grande, por sua vez, nasce a 285 m de altitude, possui uma extensão de 4,6 km e declividade média de 12 cm/m e drena uma área de 6,98 km<sup>2</sup> (IPUF, 1978; Lapolli et al., 1990).

A retificação do rio Sangradouro, em 1975, acarretou no rebaixamento do nível da água na lagoa em cerca de dois metros, ao passo que a construção de uma barragem na entrada do canal da lagoa em 1988, elevou o nível da água em cerca de um metro. A construção da estação de tratamento da CASAN levou a uma nova elevação de quase um metro no final da década de 1990.

## *Histórico de estudos limnológicos na Lagoa do Peri*

A profundidade máxima observada na lagoa do Peri foi de 11 metros, com média de 5 metros, o que a distingue da maioria das lagoas costeiras que apresentam profundidades médias de 1-3 metros e raramente ultrapassam os cinco metros (Kjerfve, 1994), tornando-a um ambiente ainda mais singular.

Silva e Senna (1997) constataram que a lagoa apresenta ausência de anoxia e um relativo grau de homogeneidade espacial em suas características limnológicas, classificando-a como do tipo polimítico. Também afirmaram, através da medição de indicadores do grau de trofia, que a lagoa do Peri apresenta boas condições de preservação.

Laudares-Silva (1999) encontrou as menores e maiores temperaturas da água até agora registradas para a lagoa do Peri: 15°C e 30°C, assim como constatou a ocorrência de pequenas estratificações térmicas, com variações de até 2°C entre superfície e fundo, em estudo realizado entre março/1996 e fevereiro/1997. A mesma autora registrou condições relativamente boas de oxigenação da água, variando entre 5,6 e 8,3 mg/L e também ausência de anoxia.

Os dados de pH existentes para a lagoa do Peri indicam que suas águas são geralmente neutras, mas variam entre levemente ácidas (pH=6,0; Laudares-Silva, 1999) e levemente básicas (pH=8,1; Simonassi, 2001).

Estudos que registraram a variação mensal nas concentrações de nutrientes da lagoa mostram que estas são consideradas de baixas a moderadas comparadas a outras lagoas costeiras, com concentração média de nitrogênio total de 547 µg/L e de fósforo total de 15 µg/L (Laudares-Silva, 1999).

Quanto às concentrações de clorofila-a, Simonassi (2001) obteve valores médios entre 15,5 e 38,4 µg/L em 1998, enquanto Laudares-Silva (1999) encontrou médias variando entre 7,44 µg/L e 18,74 µg/L, em 1996.

A comunidade fitoplanctônica é típica de águas continentais, com dominância de poucas espécies. Laudares-Silva (1999) no período de março/1996 – fevereiro/1997 encontrou uma riqueza mensal variando entre 10 e 29 taxa, e Grellmann (2006), no período de novembro/2004 – setembro/2005, obteve resultado semelhante (11 a 21 taxa). Quanto à densidade mensal, um aumento significativo foi observado de 1996 para

2004: de 3.079 a 41.246 indivíduos.mL<sup>-1</sup> (Laudares-Silva, 1999) para de 40.305 a 116.961 indivíduos.mL<sup>-1</sup> (Grellmann, 2006).

Ainda em relação à comunidade fitoplanctônica, Laudares-Silva (1999) encontrou dominância da cianobactéria *Cylindrospermopsis raciborskii* em apenas dois meses de coleta e considerou a espécie abundante em seis outros meses. As espécies *Microcystis irregularis* e *Pseudoanabaena galeata* também mostraram dominância em ao menos uma coleta. No total, 16 taxa foram considerados abundantes no período de 1996-97. Uma mudança significativa pôde ser observada na comunidade fitoplanctônica em 2004-05 (Grellmann, 2006), quando *C. raciborskii* foi a única espécie dominante durante os 12 meses de coleta, exceto no mês de setembro/2005, quando foi abundante juntamente com *Limnothrix planctonica* e *Monoraphidium irregulare*. Somente quatro espécies foram consideradas abundantes em 2004-05: *C. raciborskii*, *L. planctonica*, *M. irregulare* e *Chlorella* sp.

Um estudo mais recente envolvendo a qualidade da água da Lagoa do Peri foi por Hennemann e Petrucio (2011). A lagoa apresenta água doce o ano inteiro, com baixa condutividade, pH próximo à neutralidade e uma coluna d'água relativamente bem oxigenada. É classificada como oligotrófica para as concentrações de nutrientes e meso-eutrófica para transparência e clorofila-a. Apresenta homogeneidade espacial e heterogeneidade sazonal nos parâmetros de qualidade da água (Hennemann e Petrucio, 2011).

Outro estudo recente na Lagoa do Peri quantificou as taxas de produção primária, respiração e metabolismo em 2009/2010 (Tonetta, 2012), observando ausência de variação vertical e presença de variação sazonal significativa nas taxas de produção primária e respiração, e alternância sazonal entre autotrofia (verão e primavera) e heterotrofia (outono e inverno) no metabolismo. Condições limitantes de luz e nutrientes, para o crescimento fitoplanctônico, foram os fatores atribuídos as menores taxas de produção primária encontradas neste ambiente em relação a outros ambientes tropicais e subtropicais. Cyanobacteria e Chlorophyta foram os grupos mais importantes da comunidade fitoplanctônica, em termos de densidade e diversidade, com destaque para *Cylindrospermopsis raciborskii* que dominou na maior parte do período de estudo.

A comunidade zooplanctônica foi examinada pela primeira vez durante 12 meses na Lagoa do Peri, em quatro regiões no período de

abril de 2011 a março de 2012. A comunidade zooplancônica foi composta por alta densidade de rotíferos, cladóceros de pequeno porte e copépodos ciclopoídes. A riqueza da comunidade foi de 16 táxons sendo os rotíferos dominaram em todos os pontos de amostragem e praticamente em todos os períodos do ano em riqueza de espécies e densidade. A comunidade mostrou homogeneidade espacial, porém com variabilidade temporal. A presença e dominância de cianobactérias filamentosas é o principal fator que tem regulado a comunidade, tornando-a dominada por rotíferos, característica de ambiente eutrofizado. A temperatura da água foi o fator abiótico que mais contribuiu para a variação da comunidade ao longo do tempo. A modificação da composição do zooplâncton, com presença de espécies indicadoras de eutrofização como *Brachionus calyciflorus*, *Brachionus angularis* e *Asplanchna* sp, podem confirmar que a água da lagoa Peri está passando um processo negativo que pode causar um aumento do estado trófico, causando grande impacto na qualidade da água e alterando a comunidade biológica (Gerzson, 2013).

O trabalho mais recente envolvendo a comunidade fitoplanctônica da Lagoa do Peri (Silveira, 2013), mostrou que, de maneira geral, a diversidade de espécies foi baixa, devido principalmente à dominância por poucas espécies de cianobactérias. Os grupos funcionais selecionados pelo ambiente foram constituídos predominantemente de cianobactérias adaptadas à baixa luminosidade, intensa mistura e temperaturas elevadas. A presença eminente da espécie fixadora de nitrogênio *Cylindrospermopsis raciborskii* foi observada em alta proporção em toda a série temporal, com elevada densidade de heterocitos. Assim, a fixação de nitrogênio parece estar exercendo papel crucial para o sucesso da espécie. As análises realizadas indicaram que os fatores físicos da água foram os principais condutores da dominância das populações de cianobactérias no sistema. De maneira geral, a estrutura e dinâmica do fitoplâncton da lagoa do Peri demonstraram estar relacionadas à limitação por luz e nutrientes dissolvidos - direcionados pelos padrões de mistura - somados a um amplo gradiente temporal de temperatura, promovendo o sucesso de espécies adaptadas a este cenário.

### 3. HIPÓTESES

A partir das informações anteriormente apresentadas, as seguintes hipóteses foram testadas pelo presente estudo:

- Os parâmetros de qualidade da água apresentarão um padrão sazonal de variação associada à subtropicalidade, mas não apresentarão diferenças significativas entre os anos amostrados, tendo em vista a condição de proteção da bacia hidrográfica;
- O fósforo (P) será o nutriente limitante ao crescimento do fitoplâncton em uma escala de tempo maior, e a concentração de clorofila-a estará associada à temperatura e disponibilidade de P, sendo maior nas estações mais quentes e quando as concentrações de P na água forem maiores;
- Os registros paleolimnológicos nos testemunhos de sedimento indicarão uma melhora na qualidade da água (redução nos nutrientes) da Lagoa do Peri em longo prazo, bem como aumento da contribuição da matéria orgânica de origem autóctone, tendo em vista a recuperação da vegetação do entorno e as altas concentrações de clorofila observadas na lagoa;
- Haverá ausência de diferenças entre os dois pontos onde os testemunhos de sedimento serão coletados, tendo em vista as profundidades semelhantes, o espelho d'água relativamente pequeno de lagoa e ausência de heterogeneidade espacial na qualidade da água;
- Haverá variação sazonal nas concentrações e formas de P no sedimento, em função da temperatura e seus efeitos sobre os produtores primários e decompositores, bem como diferenças significativas entre os diferentes pontos amostrados, associadas à granulometria e ao conteúdo de matéria orgânica;
- Encontrar-se-á correlações significativas entre as concentrações de P no sedimento e parâmetros de qualidade na coluna d'água e a densidade dos principais grupos tróficos bentônicos existentes na lagoa.

#### 4. OBJETIVOS E JUSTIFICATIVA

Somente através de dados de longo prazo da qualidade da água é possível compreender as causas e efeitos das variações nas concentrações de nutrientes e do processo de eutrofização de um corpo d'água, afim de definir estratégias de gestão sustentáveis e com o maior custo-benefício possível (Heathwaite et al., 1996).

Dessa forma, compreender como variam os principais parâmetros de qualidade da água no curto e longo prazo, bem como de que forma eles se relacionam com o sedimento, são conhecimentos fundamentais para buscar entender o funcionamento dos ecossistemas aquáticos e compreender a dominância de cianobactérias, assim como determinar as melhores estratégias de gestão para ambientes frágeis e de grande importância ecológica, econômica e social como as lagoas costeiras.

Assim sendo, o presente estudo teve como objetivo compreender como parâmetros de qualidade da água variam na coluna d'água e no sedimento em diferentes escalas temporais e espaciais na Lagoa do Peri, por meio do monitoramento mensal, bem como através de estudos paleolimnológicos que são capazes de registrar décadas de informações sobre o corpo d'água no sedimento. As informações obtidas também tinham como objetivo fornecer subsídios para explicar as altas concentrações de clorofila-a encontradas na água, apesar das baixas concentrações de nutrientes dissolvidos.

Os objetivos específicos foram:

- Compreender como parâmetros de qualidade da água e a limitação por nutrientes variam no tempo em uma lagoa costeira subtropical e quais seriam os fatores que determinam ou influenciam nessa variação;
- Determinar quais características da água podem estar contribuindo para as altas concentrações de clorofila-a encontradas em baixas concentrações de nutrientes dissolvidos observadas na Lagoa do Peri;
- Estimar variações temporais e espaciais em longo prazo nas fontes, no histórico de deposição e na preservação da matéria orgânica nos sedimentos, por meio de parâmetros paleolimnológicos;



- Compreender como as diferentes formas de fósforo (orgânico e inorgânico) variam espacial e temporalmente nos sedimentos de uma lagoa costeira;
- Avaliar quais características da água e da comunidade bentônica podem estar influenciando na ciclagem do fósforo entre os compartimentos pelágico e sedimentar da Lagoa do Peri.

## 5. Capítulo 1

High chlorophyll *a* concentration in a low nutrient context:  
discussions in a subtropical lake dominated by Cyanobacteria

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High chlorophyll *a* concentration in a low nutrient context:  
discussions in a subtropical lake dominated by Cyanobacteria

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Running head: “High chlorophyll and low nutrients in a subtropical lake.”

Number of tables: 02  
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## Abstract

Temporal variability in some water quality parameters can play an important role in determining the presence and abundance of primary producers, and consequently in the trophic state and other characteristics and uses of lake ecosystems. In this sense, the present study aimed at understanding temporal dynamics of some trophic relevant water quality parameters in different time scales and their correlation and influence in phytoplankton biomass (chlorophyll *a*) in a shallow subtropical coastal lake. Peri Lake is located in Florianópolis island in Southern Brazil and samples were taken monthly between March 2007 and February 2013. The lake showed low dissolved nutrients concentration, especially phosphorus (P) (median dissolved P:  $2.0 \mu\text{g}\cdot\text{l}^{-1}$ ) and high chlorophyll *a* (median:  $20.8 \mu\text{g}\cdot\text{l}^{-1}$ ) concentration. Total nitrogen (TN) concentration varied broadly, with a median of  $672.8 \mu\text{g L}^{-1}$ , and total P (TP) concentration was low (median:  $13.5 \mu\text{g L}^{-1}$ ). A seasonal pattern of variation concerning dissolved and total P and chlorophyll *a* concentration was observed, associated mainly with temperature and wind speeds, but no clear pattern was observed for nitrogen (N) fractions. Significant differences were observed in different years for some parameters, with higher chlorophyll *a* and lower N concentration in the last three years sampled. The lake was considered potentially P limited during the majority of the study period and a positive correlation was found between chlorophyll *a* and total and dissolved P concentration. Phytoplankton biomass (as chlorophyll *a*) was apparently controlled by water temperature and P availability (TN:TP ratio and dissolved P). Water transparency (as Secchi depth) was strongly and negatively influenced by chlorophyll *a* concentration. *Cylindrospermopsis raciborskii* abilities to compete for P and light seem to be important factors determining its success and dominance in this low P coastal ecosystem. The fluctuating P supply, probably associated to sediment resuspension by wind in this shallow waterbody, is an advantageous factor for cyanobacteria and has an important role in chlorophyll *a* dynamics. Thus, high chlorophyll *a* concentration in this subtropical lake seems to be related to the P-limited condition, shallowness and low water column transparency, which are probably favouring the dominance of *C. raciborskii*, especially in higher summer temperatures, and leading to high chlorophyll *a* concentration even in a low dissolved nutrient environment.

## 1. INTRODUCTION

The most important chemical elements affecting trophic state are nitrogen (N) and phosphorus (P), what makes the evaluation of the availability and quality of long-term records of these nutrients to establish trends and rates of change very important (Heathwaite *et al.*, 1996). Total N (TN) and total P (TP) pools in freshwaters can include a complex set of chemical fractions that may vary in their availability for biological uptake. In spite of that, the TN:TP ratio can be a good proxy for the relative availability of these two important elements to the biota over ecologically meaningful time and space scales (Stern, 2008).

TN:TP ratios have been commonly used to infer phytoplankton nutrient limitation in experimental and field studies (e.g. Chislock *et al.*, 2014; Figueredo *et al.*, 2014). The exact ratio at which either nutrient becomes limiting may vary among lakes as well as within lakes, depending on the phytoplankton community that is present, and therefore, a range of N:P ratios have been proposed to classify the nutrient limitation status of lakes (Abell *et al.*, 2010). On the other hand, reviews and studies indicate that the molar Redfield ratio of 16:1 can be used for inferring potential nutrient limitation (Klausmeier *et al.*, 2004; Abell *et al.*, 2010; Loladze and Elser, 2011). Klausmeier *et al.* (2004) suggested that field surveys should focus less on average values and more on the variation in particulate and dissolved nutrient ratios, by using higher spatial and temporal resolution and presenting the range of values observed rather than just averages. That is what we attempted in the present study.

Concerning the discussion of which nutrient is predominantly limiting in freshwater ecosystems, 'The Phosphorus Limitation Paradigm' states that P generally controls biological primary production in oligotrophic lakes over multi-annual time scales, but co-limitation by multiple factors would be the rule in most lakes over shorter time scales (Stern, 2008). In a review concerning global nutrient cycles, Arrigo (2005) highlighted that co-limitation of primary producers by multiple resources can occur in some parts of the world's ocean, and that this phenomenon is most commonly observed in oligotrophic systems.

Cyanobacteria can be an important component of the primary producers in freshwater ecosystems. *Cylindrospermopsis raciborskii* (Woloszynska) Seenayya and Subba-Raju is a highly adaptive bloom

forming cyanobacteria capable of producing toxins and commonly observed over a wide range of ecological conditions, that has been expanding its global distribution from the tropics toward temperate climates (Padisák, 1997; Hamilton *et al.*, 2005; Stuken *et al.*, 2006; Vidal and Kruk, 2008). The migration of *C. raciborskii* toward more southern latitudes in South America is relatively recent, and demonstrates the wide tolerance, plasticity and success of the species in subtropical climates (Piccini *et al.*, 2011).

In this context, Peri Lake is a freshwater subtropical system with low P concentration and dominance of *C. raciborskii*. Understanding the characteristics that allow high chlorophyll *a* concentration and cyanobacteria dominance in this low nutrient fragile ecosystem is important before more intensive *C. raciborskii* blooms occur and, more importantly, before the occurrence of toxin release, which would affect the entire biota and ecological equilibrium in the lake, as well as the water supply to thousands of people. Moreover, understanding the processes underlying nutrient cycles in freshwater ecosystems are particularly important in the face of increasing anthropogenic nutrient release and climate change (Arrigo, 2005).

In this sense, the present study aimed at understanding temporal dynamics of some trophic relevant water quality parameters in different time scales and their correlation and influence in phytoplankton biomass (chlorophyll *a*) in a subtropical coastal lake ecosystem (Peri Lake) over a 6-years period. Our hypotheses were: a) water quality parameters will show a seasonal pattern of variation because of the subtropical location of the lake, but no significant variation among years, since the watershed is inside a protected/preserved area; b) phytoplankton biomass (as chlorophyll *a*) will be constantly limited by P, reflecting in high N:P ratios; c) chlorophyll *a* will be controlled by P availability and water temperature.

## **2. METHODS**

### **2.1. Study Area**

Peri Lake is located Santa Catarina State, Southern Brazil (27°44'S and 48°31'W). It has a surface area of 5.07 km<sup>2</sup> surrounded by mountains covered by Atlantic Rain Forest and sandy Restinga (forest

formation typical of sandy coastal plains and dunes), and almost the entire drainage basin is within a conservation area (Municipal Park) with relatively low human influence since 1981. Peri Lake is considered a coastal lagoon due to the geographic location and geological origin, but presents some features that are quite different from other coastal lagoons worldwide, such as a maximum depth of 11.0 m, an average depth of approximately 4.2 m, and no sea water influence (freshwater). It is a polymictic water body, the water column is well oxygenated, and presents a relative spatial homogeneity (vertically and horizontally) concerning water quality features (Hennemann and Petrucio, 2011). Since 2000, the lake supplies potable water for approximately 100,000 people. The climate in the area is characteristically subtropical (Köppen-Geiger *cf.* – Kottek *et al.*, 2006), with rainfall and winds well distributed along the year, but relatively more frequent and stronger in spring and summer months (September-February).

Studies developed intermittently in the last 18 years have shown that phytoplankton in Peri Lake is dominated most of the year by the potentially toxic cyanobacterium *Cylindrospermopsis raciborskii*, and that its density and dominance are increasing (Laudares-Silva, 1999; Tonetta *et al.*, 2013). In monthly samplings in 2009-2010, Tonetta *et al.* (2013) found *C. raciborskii* densities between 11,074 and 231,886 ind.mL<sup>-1</sup> (mean: 86,734 ind.mL<sup>-1</sup>), with dominance ranging between 33% and 96% (mean: 73%).

## **2.2. Sampling and analysis**

The present study consisted of monthly sampling of physical, chemical and biological parameters in four depths in one central site ( $\approx 9.0$  m depth): surface ( $\approx 0.1$  m), Secchi depth ( $\approx 1.0$  m), photic zone limit ( $\approx 3.0$  m) and aphotic zone ( $\approx 6.0$  m). Samples were taken during 72 months (March 2007 to February 2013), using a 3 L van Dorn bottle. A map of Peri Lake watershed and the location of the central site sampled in the present study can be seen in Hennemann *et al.* (2015).

Transparency (with a Secchi disk), pH, dissolved oxygen (DO) and water temperature (WTemp) were measured *in situ* with specific probes (YSI and WTW). Climate data (air temperature, wind speed and rainfall) was provided by ICEA (“*Instituto de Controle do Espaço*

*Aéreo*”) from the Defence Ministry, Brazilian Federal government, taken from the Florianópolis airport station (5.5 km from Peri Lake).

Dissolved inorganic nitrogen (DIN) was determined as the sum of nitrite ( $N-NO_2^-$  - Golterman *et al.*, 1978), nitrate ( $N-NO_3^-$  - Mackereth *et al.*, 1978) and ammonium ( $N-NH_4^+$  - Koroleff, 1976); inorganic phosphorus was measured as soluble reactive phosphorus (*SRP* - Strickland and Parsons, 1960); total phosphorus and nitrogen (*TP* and *TN* – Valderrama, 1981) were also determined. Detection limit was around  $1.0 \mu\text{g.L}^{-1}$  for all methods. Nutrients were measured in laboratory from filtered and unfiltered frozen water samples kept in polyethylene bottles at  $-20^\circ\text{C}$ . Chlorophyll *a* (Chl-*a*) concentration was obtained by filtering 500 mL water samples through glass fibre filters Millipore AP40 followed by extraction with 90% acetone according to the method and equations described by Lorenzen (1967).

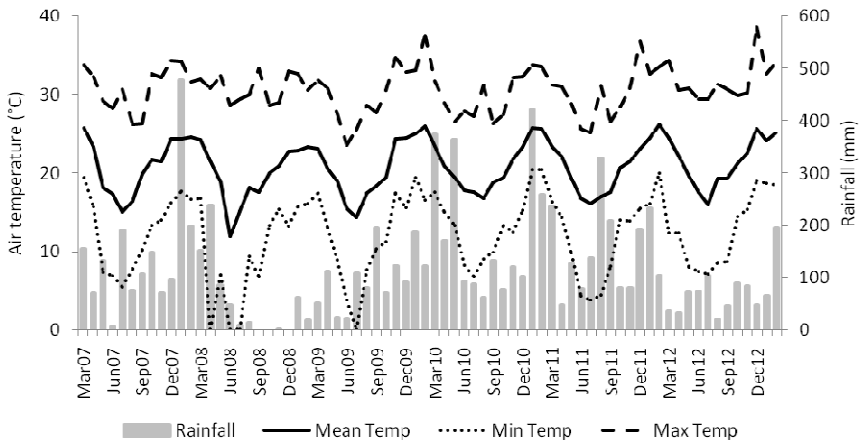
In order to work with six complete datasets of 12 months to compare among years variation, we considered December 2007, January 2008 and February 2008 as summer 2007; December 2008, January 2009 and February 2009 as summer 2008, and so on. Differences among seasons and years were tested by Kruskal-Wallis analysis of variation, followed by multiple comparisons. Spearman's correlation was also applied between all variables, including climate data of the seven days previous to sampling dates. General Linear Model (GLM) was applied with Chl-*a* concentration as dependent variable, and physical, chemical and climate parameters as continuous predictors. Statistical analyses and graphs were made in the software Statistica 7<sup>®</sup> (StatSoft) and Microsoft Excel 2007<sup>®</sup>.

### 3. RESULTS

#### 3.1. Dynamics of Trophic Relevant Parameters

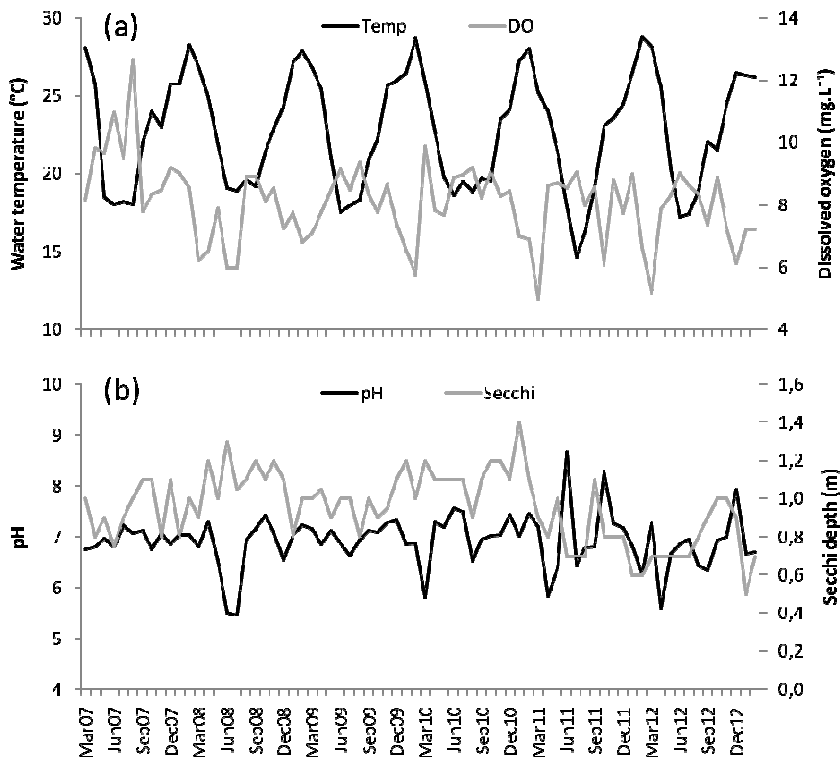
Monthly rainfall varied between 0 mm and 478 mm, with a mean of 112 mm/month in the 2007-2012 period, and accumulated year precipitation ranged between less than 1000 mm in 2008 and 2012, and around 2000 mm in 2010 and 2011. Air temperature varied according to the subtropical climate between  $0.0^\circ\text{C}$  and  $38.6^\circ\text{C}$  during the study period, and mean annual temperature gradually increased from 2008 ( $19.8^\circ\text{C}$ ) to 2012 ( $21.4^\circ\text{C}$ ) (Fig. 1).





**Fig. 1** Monthly climatic variables (rainfall and minimum, maximum and mean air temperature) in Peri Lake along the study period (March 2007 – February 2013). Data provided by ICEA – Ministry of Defense – Brazilian Government.

The four sampled depths did not show clear significant differences concerning the parameters analyzed (water column was well mixed), so the four depths were grouped in monthly means for the statistical analysis. Water temperature (Fig. 2a) varied seasonally (summer > fall > spring > winter), with all seasons significantly differing from each other ( $p < 0.01$ ). Dissolved oxygen (DO) was significantly higher in winter (Fig. 2a), and water temperature and DO varied inversely to each other, as expected because of lower  $O_2$  solubility in water with increasing WTemp. Water column was always well oxygenized. Water pH (Fig. 2b) remained close to neutrality and did not varied among years, but it was significantly higher in spring when compared to fall and winter ( $p < 0.01$ ). Secchi depth (Fig. 2b) remained around 1.0 m most of the time and showed a decrease in 2011 and 2012 ( $\approx 0.8\text{m}$ ) ( $p < 0.01$ ).

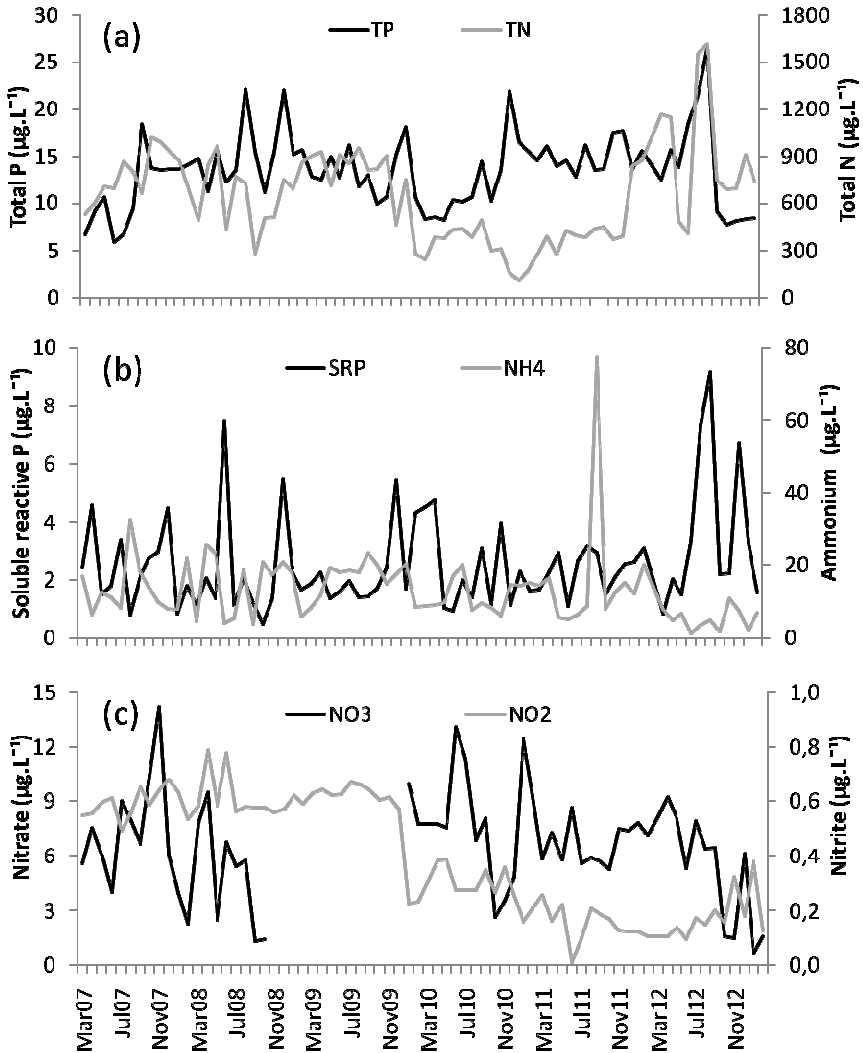


**Fig. 2** Monthly mean of water temperature and dissolved oxygen (a), and Secchi depth and pH (b) in the study period (March 2007 - February 2013).

Total P (Fig. 3a) varied from 4.0 to 39.1  $\mu\text{g L}^{-1}$  (median: 13.5  $\mu\text{g L}^{-1}$ ) and showed higher concentration in summer months when compared to fall ( $p < 0.01$ ). In spite of the ten times difference between minimum and maximum values, TP remained around the median in most months sampled in 2007-2012. Total P was positively correlated with Chl-*a* and negatively with rainfall (Tab. 1). Median TN (Fig. 3a) was 672.8  $\mu\text{g L}^{-1}$ , ranging from 90.6 and 1752.6  $\mu\text{g L}^{-1}$ . No clear seasonal pattern of variation was observed for TN, but it varied significantly among years ( $p < 0.01$ ), with lower concentration in 2010-2011 than in 2007-2009 and 2012.

Dissolved nutrients concentration were very low in general, and showed no clear seasonal pattern of variation, except for SRP, which showed a tendency of higher concentration in summer months. SRP (Fig. 3b) varied between undetectable and  $10.8 \mu\text{g L}^{-1}$  (median:  $2.0 \mu\text{g L}^{-1}$ ), with considerable variation among months and years. A positive correlation was observed between SRP and Chl-*a* concentration, wind speeds and Wtemp, but a negative correlation was found with  $\text{N-NH}_4^+$  (Tab. 1).

Concerning dissolved N fractions, the broad monthly variation in the  $\text{N-NH}_4^+$  (Fig. 3b) concentration (from undetectable to  $96.5 \mu\text{g L}^{-1}$ ; median:  $11.1 \mu\text{g L}^{-1}$ ), resulted in non-significant variation among years and seasons, except for lower values in 2012 ( $p < 0.01$ ). Nitrate (Fig. 3c) varied from undetectable to  $26.7 \mu\text{g L}^{-1}$  (median:  $6.4 \mu\text{g L}^{-1}$ ) and showed lower concentration in 2008 and 2012 in comparison to 2009 and 2010 ( $p < 0.05$ ). Nitrate varied considerably among months, but spring concentration was significantly lower than other seasons ( $p < 0.01$ ). Nitrate was negatively correlated with wind (Tab. 1). Nitrite (Fig. 3c) had very low concentration (median:  $0.4 \mu\text{g L}^{-1}$ , range: undetectable to  $1.3 \mu\text{g L}^{-1}$ ) and can be considered negligible in the N cycle in Peri Lake for the biota.

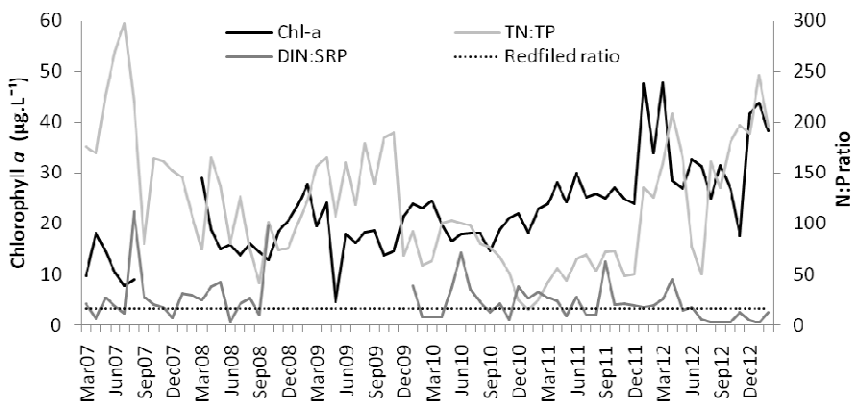


**Fig. 3** Monthly mean of TP and TN (a), SRP and  $\text{N-NH}_4^+$  (b),  $\text{N-NO}_3^-$  and  $\text{N-NO}_2^-$  (c) concentration ( $\mu\text{g L}^{-1}$ ) for the period of March 2007 - February 2013 in Peri Lake.

**Table 1.** Spearman's correlation between chlorophyll-a, nutrients and climate data in Peri Lake during the study period (March 2007 – February 2013). Marked correlations (bold) are significant at  $p < 0.01$ .

	Chl	TP	TN	SRP	NO <sub>2</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	TN:TP	DIN:SRP	Temp	pH	DO	Secchi	Wind	Rain
Chl	1.00														
TP	<b>0.26</b>	1.00													
TN	0.02	0.04	1.00												
SRP	<b>0.24</b>	0.10	0.05	1.00											
NO <sub>2</sub> <sup>-</sup>	<b>-0.64</b>	<b>-0.11</b>	<b>0.29</b>	<b>-0.05</b>	1.00										
NO <sub>3</sub> <sup>-</sup>	0.07	<b>0.16</b>	0.04	0.15	<b>-0.03</b>	1.00									
NH <sub>4</sub> <sup>+</sup>	<b>-0.32</b>	0.09	0.07	<b>-0.15</b>	<b>0.29</b>	<b>0.17</b>	1.00								
TN:TP	-0.14	<b>-0.51</b>	<b>0.80</b>	0.00	<b>0.26</b>	<b>-0.07</b>	0.03	1.00							
DIN:SRP	<b>-0.25</b>	0.03	<b>-0.06</b>	<b>-0.73</b>	0.14	<b>0.22</b>	<b>0.70</b>	<b>-0.07</b>	1.00						
Wtemp	<b>0.32</b>	0.02	0.07	<b>0.18</b>	<b>-0.05</b>	0.04	0.07	0.05	0.02	1.00					
pH	-0.11	-0.11	<b>-0.21</b>	<b>-0.24</b>	0.06	0.06	<b>0.20</b>	<b>-0.09</b>	<b>0.30</b>	0.09	1.00				
DO	<b>-0.27</b>	<b>-0.19</b>	<b>-0.03</b>	<b>-0.13</b>	<b>0.08</b>	<b>-0.04</b>	0.03	0.08	0.05	<b>-0.48</b>	<b>-0.07</b>	1.00			
Secchi	<b>-0.43</b>	<b>-0.07</b>	<b>-0.36</b>	<b>-0.01</b>	<b>0.40</b>	0.05	<b>0.19</b>	<b>-0.31</b>	<b>0.16</b>	0.05	<b>0.18</b>	<b>-0.16</b>	1.00		
Wind	0.08	0.03	0.07	<b>0.34</b>	0.11	<b>-0.16</b>	<b>-0.08</b>	0.07	<b>-0.25</b>	<b>-0.04</b>	0.03	<b>-0.02</b>	0.04	1.00	
Rain	0.13	<b>-0.24</b>	<b>-0.13</b>	<b>-0.04</b>	<b>-0.26</b>	0.07	<b>-0.18</b>	0.02	<b>-0.05</b>	0.09	0.11	0.03	<b>-0.09</b>	<b>-0.21</b>	1.00

In spite of the low dissolved nutrients and TP amounts, Chl-*a* concentration (Fig. 4) was high, varying from 4.3  $\mu\text{g L}^{-1}$  to almost 60.0  $\mu\text{g L}^{-1}$  (median: 20.8  $\mu\text{g L}^{-1}$ ), and showed the expected pattern of higher concentration in summer when compared to the other seasons ( $p < 0.01$ ). The last years sampled (2011 and 2012) had higher concentration ( $p < 0.01$ ) than previous years, and 2007 was significantly lower than all sampled years. Additionally, Chl-*a* was negatively correlated to  $\text{N-NH}_4^+$ , Secchi depth and DIN:SRP.



**Fig. 4** Monthly mean of Chl-*a* concentration ( $\mu\text{g L}^{-1}$ ) and TN:TP and DIN:SRP ratios for the period of March 2007 - February 2013 in Peri Lake. The dashed line is the Redfield mass ratio (7.2:1).

### 3.2. Nutrient Limitation and Chlorophyll-*a* Relationships

TN:TP molar ratio in Peri Lake (Fig. 4) varied from 9 to 451 (median: 105). Higher values were observed in 2007, 2009 and 2012 ( $p < 0.05$ ), decreasing in 2008 and especially in 2010 and 2011. A tendency of lower TN:TP ratios could be observed in summer months. On the other hand, when the ratio for dissolved nutrients DIN:SRP is considered (Fig. 4), the median ratio decreases considerably to 20, ranging from 1 to 482. The year of 2012 showed significantly lower DIN:SRP than the previous years ( $p < 0.01$ ).

Results from the GLM were significant ( $F = 7.237$ ;  $R^2 = 0.60$ ; adjusted  $R^2 = 0.51$ ;  $p = 0.000$ ) with transparency (Secchi depth), Wtemp and TN:TP ratio as the stronger most significant predictors of Chl-*a* variation (Tab. 2).

**Table 2.** General Linear Model (GLM) results, with Chl-*a* as dependent variable. Multiple  $R^2 = 0.596$ ; adjusted  $R^2 = 0.513$ ;  $p = 0.00000$ .

	<i>beta</i>	F	<i>p</i>
<i>Intercept</i>		4.946	0.030
TN:TP ratio	-0.570	4.868	0.031
Water Temp	0.279	6.785	0.012
Secchi depth	-0.617	37.211	0.000

## 4. DISCUSSION

The results found in the present study show that water quality parameters show considerable temporal variation, some of them showing clear seasonal patterns and others showing yearly variation. The importance of Wtemp and P in directly controlling Chl-*a* concentration in Peri Lake was demonstrated. High Chl-*a* concentration causes low transparency in the water column. N:P ratios showed considerable temporal fluctuations, but TN:TP were higher than 50 the majority of the sampling period, indicating a prevailing condition of P limitation of primary producers.

### 4.1. Dynamics of Trophic Relevant Parameters

Water temperature, DO and pH were influenced by seasonal air temperature variation, with Wtemp closely following air temperature, lower DO concentration in higher temperatures, and higher pH in the warmer most active growing season (spring), probably associated to higher CO<sub>2</sub> production. Lower DO was observed in periods of high Chl-*a*, what can also be a consequence of higher consumption by respiration processes. Previous studies in Peri Lake showed that the seston is predominantly composed by organic particles and living cells (Laudares-Silva, 1999), which explains the negative correlation found

between Secchi depth and Chl-*a*, and the lower transparency values observed in the last years sampled, when higher Chl-*a* concentration was also detected.

Concerning total nutrients, high and low TP concentrations observed in some occasions could be related to winds and rainfall previously to sampling dates (Tonetta *et al.*, 2013). The tendency of higher TP concentration in summer is probably also related to higher wind speed and frequency usually observed in this season, as well as to the higher phytoplankton biomass and P storage inside the cells; this explanation is reinforced by the positive correlation between TP and Chl-*a*. Negative correlation between TP and rainfall can be a consequence of the dilution effect of rainfall water over the already low TP concentration, since the preserved watershed would not significantly contribute to P-inputs to the lake.

Concentration of TP similar to the observed in Peri Lake is usually found in relatively protected tropical and subtropical lakes, considered oligotrophic and showing low Chl-*a* concentration, such as Cabiúnas Lagoon (Marotta *et al.*, 2010), Lake Annie (Torres *et al.*, 2012) and some reservoirs in Australia (Burford *et al.*, 2007). This becomes clearer when we observe datasets with several lakes around the world, such as the one provided by Solomon *et al.* (2013). Most subtropical shallow lakes show much higher TP concentration (e.g. James *et al.*, 2009; Fabre *et al.*, 2010; Andrade *et al.*, 2012).

In relation to TN concentration, the years of 2010 and 2011 showed periods of high rainfall, what could have had a diluting effect in TN concentration, leading to lower concentration of this nutrient in the water. A low rainfall period followed in 2012, which lowered lake water level, could also have influenced in the higher TN concentration observed in the lake this year. The lack of seasonal pattern for TN is probably associated to high variance among months and decoupling with temperature and Chl-*a*, differently from TP. Total N concentration similar to Peri Lake is usually found in more eutrophic lakes, with higher TP concentration, but with similar Chl-*a* amounts (Solomon *et al.*, 2013).

Low dissolved nutrients concentration and lack of a clear seasonal pattern of variation in general (except for SRP) could be associated to the relatively well distributed rainfall along the year. However, rainfall can vary broadly among months and even years,



which could be also a factor influencing in temporal variation in dissolved nutrients concentration in the water column. The low dissolved nutrients concentration observed in the lake may be related to high recycling rates, the well oxygenated water column and high assimilation by the phytoplankton and bacterial communities, which result especially in low nitrate and SRP concentrations (Hennemann and Petrucio, 2011). Lack of significant point and non-point sources of pollution associated with the preserved watershed also contribute with this low dissolved nutrients condition.

The tendency of higher SRP observed in summer months can be related to stronger and more constant winds in this season, what is corroborated by the positive correlation ( $p < 0.01$ ) found between SRP and wind. A positive correlation was also observed between SRP and Chl-*a* concentration in Peri Lake along the present long term study, what is expected in water bodies limited by P. The positive correlation between total and dissolved P fractions and Chl-*a* means that when there is a higher availability of dissolved P (increasing SRP in the water column), part of it is rapidly assimilated by phytoplankton, increasing both Chl-*a* and TP.

Variation in  $\text{N-NH}_4^+$  could not be directly related to any other parameter, except in the last seasons sampled, in which  $\text{N-NH}_4^+$  low concentration was followed by high Chl-*a* and though may be associated to consumption of  $\text{N-NH}_4^+$  by primary producers. This hypothesis is reinforced by the negative correlation found between Chl-*a* and  $\text{N-NH}_4^+$ . Concerning  $\text{N-NO}_3^-$  variation, spring is typically a high activity growing season for phytoplankton, after the cold temperatures and lower light availability in winter, and could have led to higher  $\text{N-NO}_3^-$  consumption and its depletion in the water column.

Chlorophyll *a* demonstrated the expected seasonal pattern, positively correlated with water temperature and showed a gradual increase from 2007 to 2012. Since this pattern was not observed for nutrients and no important alteration was observed in the lake watershed in the last two decades, especially due to the fact that almost the entire lake watershed is preserved and within a conservation area (Municipal Park) with limited human influence, the increasing Chl-*a* concentration, especially in 2012, could be related to higher temperatures (mean annual temperature gradually increased from 2008 to 2012, from 19.8 to 21.4°C) and/or lower rainfall (a significant drop in the lake water level

could be observed in its margins throughout 2012). Chl-*a* was also negatively correlated with DIN:SRP, which means that when there is a higher proportion of SRP, phytoplankton primary production is stimulated.

Chlorophyll-*a* concentration higher than 20  $\mu\text{g L}^{-1}$  is usually observed in eutrophic and highly human influenced ecosystems (e.g. Huszar *et al.*, 2000; Torres *et al.*, 2012). Water bodies with Chl-*a* concentration similar to Peri Lake usually have much higher P concentration. In a study in five subtropical shallow lakes in Uruguay (characteristics similar to Peri Lake), TP concentration were considerably higher than Chl-*a* (Pacheco *et al.* 2010) in comparison with concentration observed in Peri Lake. Fragoso *et al.* (2011) also found Chl-*a* values similar to our study lake, but in much higher dissolved P concentration in a subtropical shallow lake in southern Brazil. Large subtropical shallow lakes in USA and China also show considerably higher TP concentration than Peri Lake, but similar Chl-*a* content (James *et al.*, 2009).

These high levels of Chl-*a* in low-P Peri Lake are difficult to explain, but can be associated to the dominance of *C. raciborskii* in the phytoplankton community, which is a superior competitor for nutrients and light, as will be further discussed in the next section, and to a low predation pressure, since the zooplankton community presents only 16 taxa and is dominated by rotifers, which was also attributed to the presence and dominance of filamentous Cyanobacteria (N.D. Gerzson, unpublished data).

Results from Hennemann *et al.* (2015) show increasing nutrient accumulation in the sediments of Peri Lake in more recent times, which can mean that the system is becoming more eutrophicated, but these nutrients are being buried in the unsaturated sediments, especially P, because of the well oxygenated water column. This explanation also contributes in the understanding of high N:P ratios in the lake, which are discussed below.

#### ***4.2. Nutrient Limitation and Chlorophyll a Relationships***

TN:TP molar ratio in Peri Lake showed a condition of potential P limitation during almost the entire period of study, considering the Redfield molar ratio of 16:1 (Redfield, 1958). This is in agreement with

studies that say that freshwater oligotrophic ecosystems not subjected to pollution sources are usually P-limited (Downing and McCauley, 1992; Sterner, 2008).

In the present study, periods of lower TN:TP ratios, especially in summer, can be associated to P inputs from sediments resuspension, which are more intense in spring and summer, as previously discussed, and are the most likely explanation for the lower TN:TP ratios in warmer more windy periods.

The dissolved nutrients ratio DIN:SRP showed a condition of potential light P limitation and probably co-limitation by N and P during most of the studied period. Significantly lower DIN:SRP in 2012 was a consequence of both an increase in SRP and a decrease in  $\text{N-NH}_4^+$ , and was accompanied by high Chl-*a*. Higher availability of SRP probably promoted phytoplankton growth and depletion of  $\text{N-NH}_4^+$ . Dissolved nutrients concentration (of both N and P) are so low in Peri Lake that both nutrients can be considered limiting most of the time indeed, although the positive correlation between Chl-*a* and P indicates that P-limitation is more intense and more important in the long term.

Variations in nutrient stoichiometry can be associated not only with different species composition in the phytoplankton community, but also with different cellular components, which have their own unique stoichiometric properties (Arrigo, 2005). In the case of Peri Lake, the great time variability in N:P ratios may also reflect periods of resource acquisition (high N:P) and periods of exponential growth with cellular assembly (low N:P). The high TN:TP ratios observed in the majority of the sampling period can mean that primary producers contain high proportion of resource-acquisition machinery inside their cells and that the community has achieved a state of competitive equilibrium (Klausmeyer *et al.*, 2004).

Another possible explanation for the high TN:TP ratios found in Peri Lake comes from Elser *et al.* (2009), that suggested that enhanced N inputs from the atmosphere during the past several decades of human industrialization and population expansion appear to have produced regional phytoplankton P limitation, and are favouring those relatively few species that are best able to compete for the limiting P. Indeed, Hennemann *et al.* (2015) showed that paleolimnological records indicate increased N deposition in Peri Lake in recent decades, which could be

influencing in the dominance and high densities of *C. raciborskii* observed in the system.

The success of *C. raciborskii* has been attributed to several intrinsic competitive factors, including a high P storage capacity and a high-affinity cellular P uptake system (Istvánovics *et al.*, 2000). Additionally, it has been demonstrated that the species has the ability to grow under conditions of P-limitation that are already limiting to other Cyanobacteria (Jensen *et al.*, 1994; Padisák, 1997). Posselt *et al.* (2009) showed that dominance of this cyanobacterium can be favoured in lakes with fluctuating P supply, and Amaral *et al.* (2014) recently demonstrated growth optimization of phosphate-deficient *C. raciborskii* to short-term nutrient fluctuations in P supply, which was attributed to its physiological flexibility.

*Cylindrospermopsis raciborskii* tolerance to low light levels (Briand *et al.*, 2004), the capacity to fix atmospheric N<sub>2</sub> (Moisander *et al.*, 2012), phenotypic plasticity concerning pigments, size and growth rates (Bonilla *et al.*, 2012), together with the competitive advantages concerning P mentioned above, probably have contributed to the success of this species, maintaining high Chl-*a* concentration in the low nutrient context (specially P) of Peri Lake. According to Amaral *et al.* (2014), the adaptive behavior of this species may help to explain its invasive success in a wide range of aquatic ecosystems where P is frequently the limiting resource. Presence and dominance of *C. raciborskii* could even be contributing to the ongoing state of P limitation observed in Peri Lake. A more detailed discussion on *C. raciborskii* dominance in low light and low-P conditions in Peri Lake can be found in Tonetta *et al.* (2015).

Similarly to Peri Lake, subtropical Lakes Javier and Leandro in Uruguay are coastal shallow lakes limited by light and P, showing co-dominance by *C. raciborskii* and other colonial Cyanobacteria (Fabre *et al.*, 2010). In a review in temperate German lakes, Dolman *et al.* (2012) also found that *C. raciborskii* reached higher bio-volumes in lakes with high N relative to P concentrations. In tropical lake of Lagoa Santa (Brazil), a persistent bloom of *C. raciborskii* also occurs under low P availability (Figueredo and Gianì 2009).

Concerning GLM results, the negative influence of TN:TP ratio on Chl-*a* concentration corroborates the discussion above, since lower N:P ratios indicate a higher P availability and lead to higher

phytoplankton biomass, especially in a P limited environment such as Peri Lake. The negative relationship with Secchi depth (transparency) is probably a consequence of the fact that high Chl-*a* concentration in the lake causes low water transparency, and not the opposite. Additionally, lower transparency was observed in periods of lower rainfall (e.g. 2012), which resulted in lower water levels in the lake and higher concentration of phytoplankton biomass. Lower light availability could also be favouring dominance of *C. raciborskii* as previously mentioned. Temperature showed a positive influence in Chl-*a* concentration; in fact, cyanobacteria usually grow better at higher temperatures (Huszar *et al.*, 2000; Paerl and Huisman, 2008), such as the ones observed in Peri Lake during summer. Although Lürling *et al.* (2012) showed that chlorophytes growth rates are similar or even higher than cyanobacteria in temperature experiments, their results also showed that *C. raciborskii* had higher growth rates in water temperature of 27.5°C, which is the mean water temperature observed in the hottest month in Peri Lake.

As already pointed-out, P may generally control biological production in oligotrophic lakes over multi-annual time scales but co-limitation of multiple nutrients is probably the rule in most lakes over shorter time scales (Sterner, 2008). This seems to be the case in the oligotrophic Peri Lake ecosystem, since TN:TP over a longer time scale indicated P-limitation, while an analysis in shorter time periods and considering the dissolved nutrient fraction showed that co-limitation can occur relatively frequently. Time fluctuations observed in DIN:SRP ratio in Peri Lake are advantageous to *C. raciborskii*, since the species shows several adaptations to fluctuations in P supply, including tolerance to low nutrients concentration and capacity of rapid assimilation of available nutrients, as discussed above.

It is quite clear in the literature that several aspects can influence nutrient cycling, dynamics and availability in aquatic ecosystems, including sediment characteristics, bacterial community, land-use patterns in the watershed, food web structure, oxygen concentration, physical characteristics of the lake, among others (Heathwaite *et al.*, 1996; Elser *et al.*, 2007). According to Heathwaite *et al.* (1996), even in the absence of a land-use change, nutrient transport and transformation can be affected by a combination of internal and external factors. The author showed an example according to which increasing inputs of atmospheric N from increased emissions from fossil fuel combustion

combined with the decreasing nutrient requirement of forests in a more steady state could result in N leaching, even though major land-use change had not occurred. This could be the case in Peri Lake and together with the N<sub>2</sub>-fixing capacity of Cyanobacteria could be contributing to the P-limited condition observed in the present study.

## 5. CONCLUSIONS

Peri Lake showed a seasonal pattern of variation concerning dissolved and total P and Chl-*a* concentration, associated mainly with temperature and wind speeds, but no clear pattern was observed for N fractions, partially confirming hypothesis “a”. On the other hand, significant variations were observed among the years sampled, with the last three years (2010-2012) showing significant differences in comparison to the 2007-2009 period, especially in relation to Chl-*a* and N concentration. Climate differences among years, especially rainfall and air temperature, seem to be important factors influencing in this yearly variation.

The lake showed a condition of potential P limitation during most of the study period (hypothesis “b”) and a positive correlation between Chl-*a* and P. GLM showed that Chl-*a* seems to be controlled mainly by temperature and P availability, confirming hypothesis “c”. Sediment resuspension by wind is probably an important P source, influencing in Chl-*a* patterns. *C. raciborskii* abilities to compete for the limiting P seem to be an important factor determining its success and dominance in the lake.

These conclusions have very important management consequences for coastal ecosystems such as Peri Lake, especially in the context of future global climatic changes involving temperature elevation and alteration in rainfall and wind patterns, as well as increase in cultural eutrophication. Additional nutrient and temperature variation experiments with the phytoplankton community and research concerning sediment influence in the water quality dynamics of this shallow lake are important future studies to be conducted in order to better understand the dynamics of trophic relevant parameters and Cyanobacteria dominance and behaviour in low-P subtropical water bodies.

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## 6. Capítulo 2

### Paleolimnological record as an indication of incipient eutrophication in an oligotrophic subtropical coastal lake in Southern Brazil

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# Paleolimnological record as an indication of incipient eutrophication in an oligotrophic subtropical coastal lake in Southern Brazil

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**Abstract** Paleolimnology of lake sediments can be a powerful tool to assess various aspects of lake history and catchment change through elemental, isotopic and molecular analysis of the sedimented organic matter (OM). In this sense, the objective of the present study was to investigate the source, depositional history and preservation of OM in the sediments of two different sites in Peri Lake (southern Brazil) to better understand the nature and direction of environmental changes. Therefore, two sediment cores were sampled and analysed for total organic carbon (TOC), total nitrogen (TN) and total phosphorus (TP) concentrations and elemental ratios, and stable isotope ratios of C and N ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ). Both cores showed similar general tendencies, with increasing amounts of OM (range 1–35 %), TOC (2.55–258.40  $\text{mg g}^{-1}$ ), TN (0.30–25.97  $\text{mg g}^{-1}$ ) and TP (0.03–4.72  $\text{mg g}^{-1}$ ) from the bottom toward the top more recent layers. TOC:TN ratios (range 8.1–14.7) showed a slight decrease in recent times and indicated a mixture of allochthonous and autochthonous contribution to the OM, with predominance of the last source. TN:TP (range 0.2–51.3) indicated a condition of

potential limitation by P in general. Both  $\delta^{13}\text{C}$  (range –25.58 to –20.85) and  $\delta^{15}\text{N}$  (range 2.6 to 7.1) showed a decreasing pattern toward the top of the cores, in opposition to macronutrient concentration. Differences in the depth variation pattern between the two cores were associated to the marginal location of one of the cores. The results suggest that nutrients and primary production are increasing in the lake.

**Keywords** Paleolimnology · Santa Catarina · Stable isotope ratio · Sediment core · C:N ratio

## Introduction

It has long been recognized that bottom sediments play an important role in lake ecosystem dynamics, both as sinks and sources of nutrients, thereby strongly influencing lake trophic status and biodiversity (Trolle et al. 2010). Paleolimnology of lake sediments can be an important tool to assess various aspects of lake history and catchment change, as the organic matter (OM) content of sediments includes a variety of elemental, isotopic and molecular indicators that can be used to reconstruct paleoenvironments of lakes and their surrounding land areas (Meyers 2003). Paleolimnological studies have much to contribute to freshwater conservation, since they can provide essential information that is otherwise unavailable or of limited quality, relating to questions associated with the definition of pre-pollution baselines and natural variability and the evaluation of

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the magnitude, direction and causes of change (Battarbee 1999).

Despite evidence for substantial alteration during its sedimentation, the OM that is preserved in the sediment retains its original source signature and reflects the environmental conditions prevailing in the watershed at the time of deposition (Meyers 1997; Das et al. 2008). Organic matter can enter a lake from the watershed (allochthonous) or be produced within the lake itself (autochthonous). The study of carbon (C), nitrogen (N) and phosphorus (P) ratios and concentrations and C and N stable isotope ratios ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ , respectively) of preserved OM has been successfully used as a proxy to understand these OM sources and paleoenvironmental information (Lehmann et al. 2004; Vreca and Muri 2006; Das et al. 2008; Torres et al. 2012).

Increased primary production stimulated by nutrient loadings to the basin results in increased sediment deposition of organic C. Sediment deposition of N and P has also been shown to increase with primary production (Wolfin and Stoermer 2005). Atomic C:N ratio has been widely used to identify the different sources of OM (algal versus land-plant) in lake sediments (Meyers 2003; Das et al. 2008; Torres et al. 2012). Alterations in the N:P ratio in the sediments may have also important effects on community composition of phytoplankton, especially on the cyanobacteria (Eilers et al. 2004).

Carbon and N stable isotope ratios can offer an excellent mean to trace different biogeochemical processes and may allow for a detailed understanding of the origin and cycling of OM in modern lacustrine environments (Lehmann et al. 2004). The C isotopic composition of OM in lake sediments is important for assessing OM sources, for reconstructing past productivity rates and for identifying changes in the availability of nutrients in surface waters (Meyers 2003; Torres et al. 2012). Nitrogen isotopic ratios can similarly help to identify sources of OM to lakes and to reconstruct past productivity rates (Terranes and Bernasconi 2000; Gu 2009; Torres et al. 2012). Both  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  may also serve as an additional, qualitative line of evidence for inferring past lake trophic status (Brenner et al. 1999).

The main objective of our study was to assess the source, depositional history and preservation of OM in the sediments of a subtropical lake by using macronutrient concentrations and elemental ratios (C:N and N:P), and stable isotope ratios ( $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ ). Specific aims were to establish baseline conditions, compare

depositional patterns in different sites and describe the nature and direction of environmental changes in the lake.

## Materials and methods

### Study site

Peri Lake is located in southern Brazil, in the southeastern portion of Santa Catarina island (27° 44' S and 48° 31' W), in the city of Florianópolis. Its surface area of 5.07 km<sup>2</sup> is surrounded by mountains covered by Atlantic Rain Forest in the north, west and south portions, and by sandy restinga in the east (Fig. 1). Peri Lake is considered a coastal lagoon due to the geographic location and geological origin (Holocene marine transgression), but presents some features that are quite different from those of coastal lagoons in general, such as a maximum depth of 11.0 m, an average depth of 4.2 m and no direct seawater influence (freshwater). The bottom of the lake is composed mainly by silt and clay (~70 %), which predominate in the northwest, west and southern portions of the lake, and fine and medium sands (~25 %), which can be observed in higher proportions in the northeast and eastern portions of the lake.

The drainage basin is approximately 20 km<sup>2</sup>, and most of it is within a conservation area protected by law (Municipal Park) since 1981, with limited human influence and occupation. Two main rivers discharge in the lake, coming from the forested mountains (Fig. 1): Cachoeira Grande River (in the west portion of the lake) is 1.7 km long and rises at 280 m of altitude; Ribeirão Grande River rises at a 285-m altitude and is 4.6 km long. The lake is connected to the sea by a unidirectional outflow channel (seawater never enters the lake). Since 2000, the lake supplies potable water to the inhabitants of the south and east portions of the island (~100,000 people). The lake is polymictic and presents a relative spatial homogeneity concerning water quality features (Hennemann and Petrucio 2011). Nutrient concentration is low, but chlorophyll-a concentration and phytoplankton densities are high, with dominance of the potentially toxic cyanobacterium *Cylindrospermopsis raciborskii* most of the year (Komárková et al. 1999; Hennemann and Petrucio 2011; Tonetta et al. 2013). The climate is characteristically subtropical.



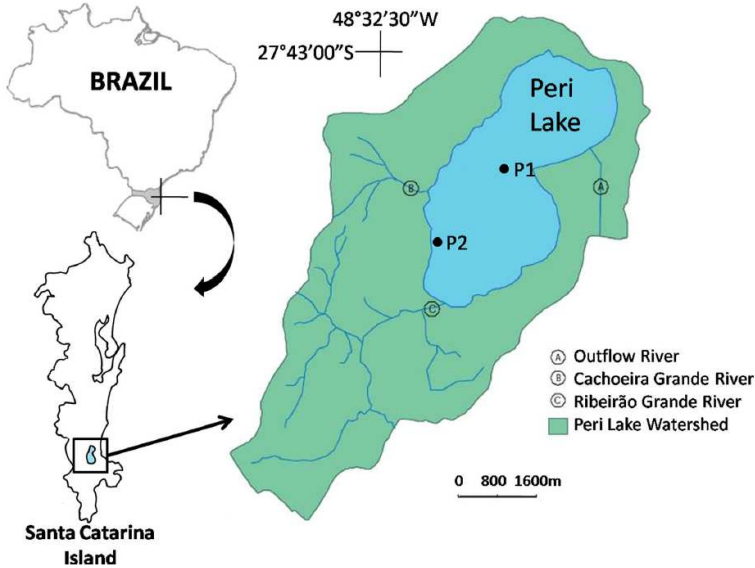


Fig. 1 Location map of Peri Lake with indication of the core sampling sites (P1 and P2) and the main characteristics of the drainage basin

Sampling and analysis

Because of the potential for wind-induced mixing of deposits in shallow lakes, the ability of sediments in such water bodies to preserve an accurate record of past environmental conditions has been questioned (Engstrom et al. 2006). In this sense, Peri Lake provides a very special condition to study depositional sediment history in shallow lakes, since it has two deeper sites ( $\approx 10$  m) in different locations: one in the centre of the lake and one very close to the margin (Fig. 1). All other areas in the lake are shallow ( $< 4$  m) and very susceptible to wind resuspension, and that is the reason why we took only two sediment cores in the two deepest regions. We are aware that sampling a limited number of cores restricted our capacity to describe different sedimentation patterns in other areas and may also have omitted or masked some important information, but we also believe that the location (centre and margin) and depth where the cores were taken are good representatives of the lake sedimentation history.

In this sense, two sediment cores were taken at the two deepest sites in Peri Lake in October 2012 with acid-washed 1-m PVC tubes (diameter 75 mm), adapted to a sediment corer. Core P1 (63 cm) was taken in the central portion of the lake, at a 9.0-m depth, and core P2 (60 cm) was taken at the south-western margin, at a 10.5-m depth, between the outfall of the two main rivers of the lake watershed (Fig. 1). After sampling, the cores were carefully transported to the lab, where they were sliced at 2-cm intervals, except for the interval between 20 and 35 cm in core P1 that was sliced at 3-cm intervals. Sediment lithology (colour, size and texture) was noted as the cores were sliced. After slicing, samples were dried at 60 °C for at least 72 h and ground in a mortar and pestle.

Organic matter content was estimated by weight loss on ignition at 550 °C, as described by Engstrom et al. (2009). Total phosphorus (TP) was determined as phosphate with ammonium molybdate and ascorbic acid reaction in a spectrophotometer (Koroleff 1976) after combustion and HCl extraction (Aspila et al. 1976). Sediments were analysed for total organic carbon



(TOC), total nitrogen (TN) and  $^{13}\text{C}$ : $^{12}\text{C}$  and  $^{15}\text{N}$ : $^{14}\text{N}$  isotopes at the UC Davis Stable Isotope Facility (California) using an Elementar Vario EL Cube elemental analyser interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer, after pre-treatment with HCl to remove carbonates. For a detailed description of the methods, please access: <http://stableisotopefacility.ucdavis.edu/13cand15n.html>.

## Results and discussion

### Organic matter and nutrients

Core P1 showed a pattern of decreasing OM with depth (Fig. 3a), varying between 3 and 31 % and closely related to alterations in fine (rich in OM) and coarse sediments. The first 33 cm of the sediment core had a dark brown colour and high OM content ( $\approx 25\%$ ) and was characterized by a predominance of silt, clay and very fine sand. A transition zone was observed between 33 and 47 cm, where fine sands appeared, and OM, silt and clay decreased, especially downward 43 cm. From 49 cm to the bottom of the core, OM, silt and clay decreased even more and fine and medium sands increased. The last two bottom samples (4 cm) showed increased OM content ( $\approx 20\%$ ).

The marginal core P2 showed a different pattern from core P1, with higher OM ( $>30\%$ ) in the top 20 cm, followed by a sharper decrease to less than 5 % between 24 and 32 cm, and a small increase and stabilization around 10 % from 34 cm toward the bottom of the core (Fig. 4a). Sediment grain size closely followed the OM pattern, with dark brown silt and clay and some very fine sand predominating in the top 22 cm, an increase in fine and medium sand between 24 and 30 cm, followed by an increase in the proportion of clay between 32 and 36 cm, and predominance of grey muddy sediments from this depth toward the bottom of the core.

As can be noted from the results presented above, in spite of the well-oxygenated water column (Hennemann and Petrucio 2011), OM content in Peri Lake sediments can be considered high. Clear variations along the depth of the cores were observed for the OM content, which was usually higher in core P2 when compared to core P1. In both cores, the relatively constant OM in the first 20–30 cm, when a gradual decrease was expected as a result of diagenetic processes, could be related to

increasing OM deposition in recent years. Significant decreases observed in the OM content in both cores from 20 to 30 cm downward followed changes in the composition of the sediments, with increase in coarse grains, which could be related to human alterations in the watershed. As can be observed in the 1938 picture in Fig. 2, a portion of the lake watershed was used for crop plantation in the past, what could have increased the input of coarser grained sediments (Wolin and Stoermer 2005), reducing the OM content in the sediment record. A significant recovery of the original Atlantic Rain Forest occurred in the last decades, as can be observed in the 2012 picture (Fig. 2).

The increase in OM from the bottom toward the top in both cores may be an indication of higher primary productivity in recent times, since higher primary production results in higher phytoplankton biomass, which increases the deposition of OM in the sediments. Higher allochthonous contribution from the marginal forest probably resulted in higher OM and TOC:TN in core P2, since it is located very close to the margin and receives leaf and other forest debris more directly and in higher amounts than central core P1. This will be further discussed in the next section. A sharper decrease is observed in the middle of core P2, followed by a slight increase and stabilization at 10 % OM from 40 cm toward the bottom, which may also indicate a period of higher productivity in relation to the period represented in the middle of the core.

TOC varied greatly between 9.43 and 258.40  $\text{mg g}^{-1}$  in core P1, but remained around 100  $\text{mg g}^{-1}$  in the first 35 cm, followed by a decrease until 57 cm, when the TOC content slightly increased to around 50  $\text{mg g}^{-1}$  (Fig. 3b). TOC was strongly and positively correlated ( $p < 0.05$ ) with OM, TN and TP, and negatively correlated with  $\delta^{15}\text{N}$  (Table 1). TOC also varied greatly between 2.55 and 152.85  $\text{mg g}^{-1}$  in core P2, showing higher values at the top 20 cm ( $\approx 130 \text{ mg g}^{-1}$ ), and then sharply decreasing to values lower than 30  $\text{mg g}^{-1}$  toward the bottom (Fig. 4b). TOC was positively correlated with OM, TN and the TN:TP ratio, and negatively with  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  in core P2 (Table 2).

In core P1, TN varied from 0.82 to 25.97  $\text{mg g}^{-1}$  and followed the same pattern as the TOC content (Fig. 3c), and was positively correlated ( $p < 0.05$ ) with OM, TOC and TP, and negatively with  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  (Table 1). TN in core P2 varied from 0.30 to 15.22  $\text{mg g}^{-1}$  and also showed the same pattern as the TOC content with a sharp decrease at 20 cm (Fig. 4c). TN was also



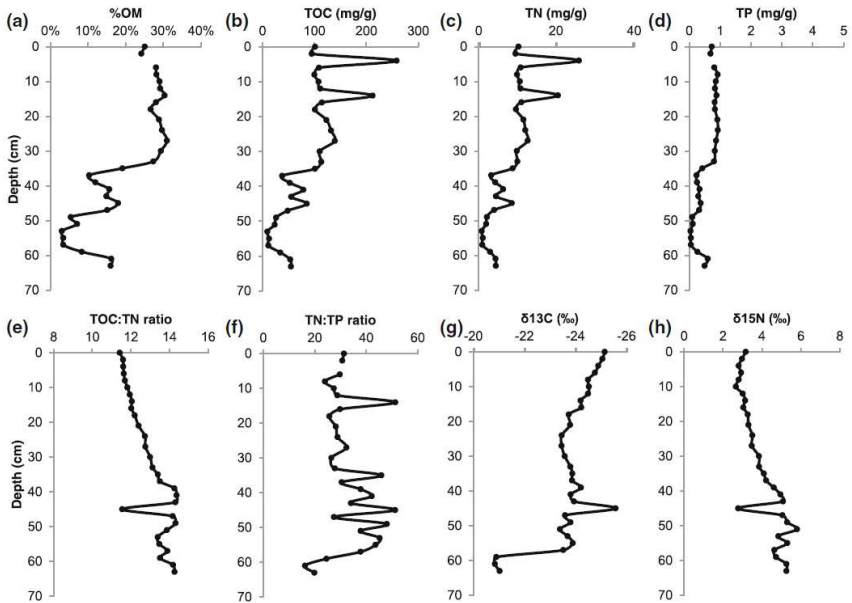
**Fig. 2** Peri Lake aerial pictures from 1938 and 2012. Differences in land use and forest cover in the lake watershed can be noticed. Pictures obtained from the Florianópolis prefecture geoprocessing system, available at <http://geo.pmf.sc.gov.br>

positively correlated with OM and negatively with  $\delta^{15}\text{N}$  in core P2 (Table 2).

TP varied from 0.04 to 0.93  $\text{mg g}^{-1}$  in core P1 and showed a pattern of variation similar to the OM, TOC and TN contents (Fig. 3d), with higher values around 0.75  $\text{mg g}^{-1}$  in the first 33 cm, followed by a sharp decrease and an increase at the bottom of the core. TP was also positively correlated ( $p < 0.05$ ) with OM, additionally to TOC and TN, and negatively with  $\delta^{15}\text{N}$  and the TOC:TN ratio (Table 1). Differently from core P1, TP varied greatly from 0.03 to 4.72  $\text{mg g}^{-1}$  in core P2, with lower values ( $<1.5 \text{ mg g}^{-1}$ ) at the top 32 cm, followed by a significant increase to more than 3.5  $\text{mg g}^{-1}$  from 34 to 38 cm, and then a slight decrease toward the bottom, varying around 2.5  $\text{mg g}^{-1}$  (Fig. 4d). TP was positively correlated with  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  and negatively with the TOC:TN ratio (Table 2).

Increased primary production stimulated by nutrient loadings to the basin results in increased sediment deposition of organic C. Sediment deposition of N and P has also been shown to increase with primary production (Wolin and Stoermer 2005). According to Augustinus et al. (2006), TOC values also reflect changes in situ lacustrine and terrestrial OM biomass, and peaks of TOC can possibly reflect increased influx of terrestrial OM.

In this sense, vertical variation in TOC, TN and TP in core P1 all followed a pattern similar to OM and showed a positive correlation with it ( $p < 0.05$ ), indicating higher nutrient content in recently deposited (upper) sediment layers, probably associated with the higher primary production (and probably stimulating it). Lower TOC, TN and TP from 30 cm toward the bottom of the core is an indication of lower productivity. TOC, TN and TP also increased slightly in the last bottom centimetres of the core, supporting the suggestion of higher productivity in the older layers. Core P2 TOC, TN and TP contents also followed the OM pattern, with the higher content in younger sediments indicating higher nutrient availability and productivity, followed by a sharp decrease at 20 cm and a slight increase in the bottom sediment layers, reinforcing the higher productivity hypothesis in the older portion of the cores. TP in core P2 showed a deviation from the pattern, with considerably high values from 34 cm toward the bottom of the core, which may be an indication of a more eutrophicated period with higher productivity. Differences in TOC, TN and TP contents in core P2 in comparison to core P1 are probably related to higher allochthonous contribution in the core closest to the forested margin and to the discharge points of the two main rivers in Peri Lake watershed.



**Fig. 3** Geochemistry data of central core P1. **a** Organic matter content—OM (%), **b** Total organic carbon—TOC ( $\text{mg g}^{-1}$ ), **c** Total nitrogen—TN ( $\text{mg g}^{-1}$ ), **d** Total phosphorus—TP ( $\text{mg g}^{-1}$ ), **e** TOC:TN ratio, **f** TN:TP ratio, **g**  $\delta^{13}\text{C}$  (‰), **h**  $\delta^{15}\text{N}$  (‰)

Lacustrine productivities are affected by environmental changes. Delivery of nutrients from the surrounding watershed is increased or decreased as local precipitation varies, sometimes making the accumulation of OM in sediments a useful paleoprecipitation proxy (Meyers 1997). Alterations in rainfall patterns and temperatures

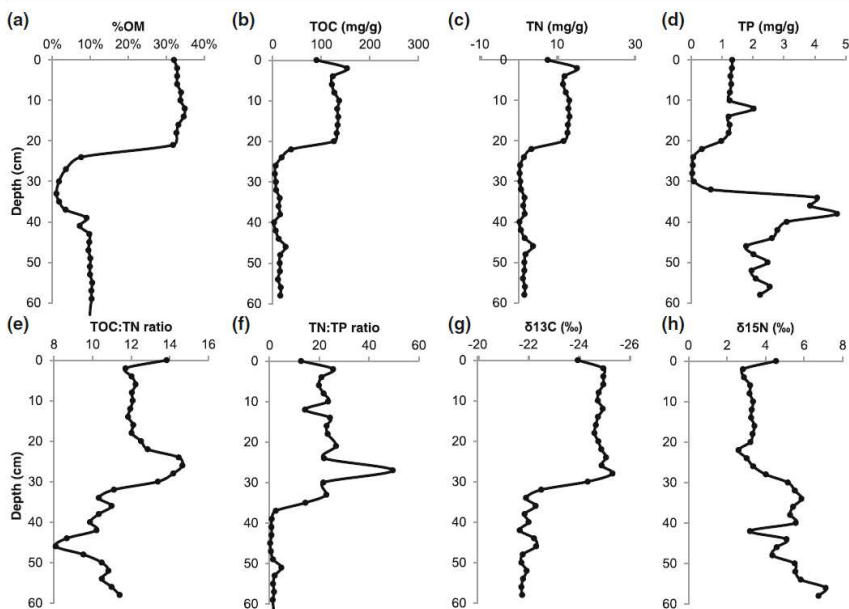
could have increased nutrient input to Peri Lake and stimulated primary production. Hennemann and Petrucio (2010) showed in microcosm experiments in the same lake that higher temperatures can indeed significantly increase chlorophyll-a concentration, especially in colder seasons and if followed by higher P inputs.

**Table 1** Spearman correlation matrix ( $r$  values) for all measured parameters in core P1

	%OM	TOC	TN	TP	TOC:TN	TN:TP	$\delta^{13}\text{C}$	$\delta^{15}\text{N}$
%OM	1.000							
TOC	<i>0.956</i>	1.000						
TN	<i>0.957</i>	<i>0.985</i>	1.000					
TP	<i>0.964</i>	<i>0.909</i>	<i>0.931</i>	1.000				
TOC:TN	-0.625	-0.604	-0.660	-0.616	1.000			
TN:TP	-0.313	-0.182	-0.195	-0.434	0.088	1.000		
$\delta^{13}\text{C}$	-0.222	-0.308	-0.375	-0.182	<i>0.654</i>	-0.317	1.000	
$\delta^{15}\text{N}$	-0.715	-0.687	-0.741	-0.700	<i>0.899</i>	0.130	<i>0.685</i>	1.000

Italicized values are significant at  $p < 0.05$





**Fig. 4** Geochemistry data of marginal core P2. a Organic matter content—OM (%), b Total organic carbon—TOC ( $\text{mg g}^{-1}$ ), c Total nitrogen—TN ( $\text{mg g}^{-1}$ ), d Total phosphorus—TP ( $\text{mg g}^{-1}$ ), e TOC:TN ratio, f TN:TP ratio, g  $\delta^{13}\text{C}$  (‰), h  $\delta^{15}\text{N}$  (‰)

The study conducted by Trolle et al. (2010) showed that vertical concentration profiles of C, N and P in lake sediments can be higher in the upper, most recently deposited sediment strata, driven largely by natural diagenetic processes and not necessarily

by eutrophication, since organic species of C, N and P will undergo a natural decay with time, thereby generating naturally lower concentrations in the deeper and older sediments. Variations in OM and nutrients may also be related to alterations in sediment grain

**Table 2** Spearman correlation matrix (*r* values) for all measured parameters in core P2

	%OM	TOC	TN	TP	TOC:TN	TN:TP	$\delta^{13}\text{C}$	$\delta^{15}\text{N}$
%OM	1.000							
TOC	<i>0.809</i>	1.000						
TN	<i>0.852</i>	<i>0.970</i>	1.000					
TP	0.069	-0.221	-0.106	1.000				
TOC:TN	0.011	0.274	0.128	-0.805	1.000			
TN:TP	0.325	<i>0.661</i>	<i>0.550</i>	-0.838	<i>0.737</i>	1.000		
$\delta^{13}\text{C}$	-0.169	-0.433	-0.352	0.726	-0.745	-0.799	1.000	
$\delta^{15}\text{N}$	-0.321	-0.539	-0.504	0.524	-0.493	-0.697	0.727	1.000

Italicized values are significant at  $p < 0.05$

size, due to alterations in the lake watershed (e.g. deforestation) and climatic factors (e.g. higher rainfall) (Meyers 2003). In the case of Peri Lake, a gradual decrease with depth in the cores was not observed for OM or nutrients in the upper, most recently deposited sediments, which may be an indication of increasing productivity and nutrients in the lake in more recent times. However, a general pattern of decrease in OM and macronutrients with time along the entire core length coincided with a decrease in fine-grained sediment and an increase in coarser sediments in deeper sediments and can be associated to deforestation observed in the watershed in the past.

According to Trolle et al. (2010), a significant correlation between surficial sediment TP concentrations and sediment OM is expected, as the organic C content of the sediment presumably will increase with increased water column productivity. The authors also found a significant correlation between sediment TC and TP concentrations in the vertical profiles, as observed in Peri Lake. Pulatsu et al. (2008) found that bacteria in oxic sediments can retain P, what could also have happened in the top layers of Peri cores, resulting in the higher TP content observed, especially in core P1. According to Fontes et al. (2013), bacterial community plays an important role in the metabolism of Peri Lake and, thus, influence nutrient dynamics and record in the sediments.

Lake sediment TP profiles may potentially be used as indicators of incipient eutrophication (Carey and Rydin 2011). Especially in core P1, in spite of the low water column nutrient concentration observed in Peri Lake (Hennemann and Petrucio 2011), increasing nutrients in the sediment records, in water column chlorophyll-*a* concentration and in cyanobacterial dominance in this lake are indicative that the water body is changing toward a more eutrophicated state. It is difficult to identify the source(s) causing this change (natural or anthropogenic), but climatic changes are possible factors contributing to it.

#### C:N and N:P ratios

The contribution from different sources of OM is variable in different lakes and even within a lake, and can be identified through variations in TOC:TN ratios of sediments, because the sedimentary OM derived from terrestrial vascular plants (>20) and from in-lake algae

(<10) has different TOC:TN molar ratios (Meyers and Eadie 1993; Meyers 1994, 2003).

In core P1, the TOC:TN ratio varied little, between 11 and 14, showing an increasing pattern from the top to the bottom of the core (Fig. 3e). The TOC:TN ratio was negatively correlated ( $p < 0.05$ ) with OM and macronutrients and positively with  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  (Table 1). The TOC:TN ratio showed a wider variation in core P2, between 8 and 15, and a different pattern, with higher ratios at the top 30 cm ( $\approx 12$ ), a decrease from 30 to 46 cm ( $\approx 8$ ) and a slight increase ( $\approx 11$ ) toward the bottom (Fig. 4e). A negative correlation was observed between TOC:TN and TP, and  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  (Table 2).

In Peri Lake, the TOC:TN ratios showed a general pattern of mixed autochthonous and allochthonous sources of OM, with higher algal contribution. In core P1, older portions of the core indicate a more mixed condition, and younger sediments show an increasing importance of autochthonous algal-derived OM toward the top of the core (Fig. 3e). This pattern can be related to the increasing nutrient content in the younger sediment layers that probably stimulated water column primary producers, increasing autochthonous OM. Alterations in rainfall patterns and temperatures associated to climatic changes could have increased nutrient inputs to lake and primary production rates, as previously discussed. Additionally, the deforestation and higher human interference that occurred in some portions of Peri Lake watershed in the past could have resulted in higher contribution from allochthonous materials in older sediment records. The negative correlation of TOC:TN with OM and macronutrients corroborates the above discussion, since higher OM and nutrients can be associated with higher primary production within the lake, which results in higher autochthonous contribution and lower TOC:TN ratios, as previously mentioned. Correlations with isotope ratios will be discussed in the next subsection.

Core P2 showed older sediments (downward 32 cm) with dominance of OM of algal origin, followed by an intermediate brief period of mixed allochthonous/autochthonous contribution (24–30 cm), and younger sediments also with a mixed contribution, but with predominance of autochthonous OM (Fig. 4e), similar to that observed in the top layers of core P1. The period of higher allochthonous contribution could also be associated to the deforestation and higher human interference that occurred in the past. Younger sediments in core P2 showed a slightly higher TOC:TN ratio (12)

than core P1 (11), which can be a consequence of the position of core P2 closer to the margin and to the river discharge points. Apparently, sediments in core P2 were deposited more slowly than in core P1, since alterations in OM, nutrients and TOC:TN ratios occur first (closer to the surface) in core P2. This is probably related to different internal water currents in the lake and to the deep central position of core P1, which receives and accumulates more materials from the shallower areas of Peri Lake.

Similarly to Peri Lake, TOC:TN values ranged between 10 and 14 at most sample intervals in coastal Lake Pupuke (New Zealand) core, indicating a mixed terrestrial-aquatic source for the OM (Augustinus et al. 2006). In Lake Natmålsvatn (Norway) sediments, C:N ratios ranged from 8 to 13, which was also considered an indication that OM comes predominantly from aquatic sources and that in-lake production was high (Janbu et al. 2011). The C:N ratios in Lake Ledvica (Slovenia) decreased in contemporary sediment, and this was associated to either a lower terrestrial contribution or an increased primary production in more recent sediments (Vreca and Muri 2006). Torres et al. (2012) associated the concurrent increase in TP and decline in TC:TN to eutrophication and greater primary production in the Lake Okeechobee (Florida), fuelled by greater P input, which could also be the case in Peri Lake, since the decrease in TOC:TN ratio was accompanied by a higher TP concentration in younger sediment layers.

The TN:TP molar ratio in core P1 (Fig. 3f) showed no clear depth variation pattern, varying from 16 to 51, with values higher than 20 along the majority of the core, except in the bottom layers. According to the Redfield ratio, the record in Peri Lake sediments indicates an environment potentially limited by P, which is in accordance with water column TN:TP ratios measured by Hennemann and Petrucio (2011) in the lake in 2008–2009. The TN:TP ratio in the margin core P2 (Fig. 4f) varied from less than 1 to values as high as 50, showing values around 20 in the top sediment layers, followed by a significant drop in the bottom samples, caused by both a decrease in TN and an increase in TP concentrations. These lower bottom ratios may be indicative of N limitation, and the shift from a condition of N limitation to a potential P limitation in younger sediments may have been influenced by the presence and increased importance of N<sub>2</sub>-fixing cyanobacteria in the lake in recent times (Tonetta et al. 2013).

Another possibility is that other factors lead to higher TN:TP ratios in recent times, and this new condition of potential P limitation allowed cyanobacteria, especially *C. raciborskii*, to succeed in Peri Lake. Elser et al. (2009) suggested that the enhanced N inputs from the atmosphere during the past several decades of human industrialization and population expansion appear to have produced regional phytoplankton P limitation and are favouring those relatively few species that are best able to compete for the limiting P, such as *C. raciborskii*. This species is known as an unusually capable competitor, especially in relation to P, showing high phosphate storage capacity and a high-affinity cellular P uptake system (Istvánovics et al. 2000). Moreover, it has been demonstrated that the species has the ability to grow under conditions of P limitation that are already limiting to other cyanobacteria (Jensen et al. 1994; Padišák 1997).

#### Carbon and nitrogen stable isotopes

Stable isotope analysis is an excellent tool to study C and N biogeochemical cycles in lacustrine systems (Gu et al. 2006). The isotopic composition of OM in lake sediments is important for assessing OM sources, reconstructing past productivity rates and identifying changes in the availability of nutrients in surface waters (Meyers 2003; Das et al. 2008).

For core P1, the lowest  $\delta^{13}\text{C}$  value was  $-25.58\text{‰}$  at 45 cm, and the highest value was  $-20.85\text{‰}$  at the bottom of the core (61 cm). A tendency of decreasing values could be observed from the older bottom sediment layers to the younger top ones (Fig. 3g). Additionally to the correlations previously cited,  $\delta^{13}\text{C}$  was also positively correlated with  $\delta^{15}\text{N}$  (Table 1).  $\delta^{13}\text{C}$  varied slightly less in core P2, from  $-25.33\text{‰}$  to  $-21.67\text{‰}$ , and followed a similar increasing pattern with sediment depth, but showed a sharper increase at 30 cm. An inverse pattern in relation to TOC and TN was observed in  $\delta^{13}\text{C}$  of core P2, with lower values in the top 30 cm (around  $-25\text{‰}$ ) and an increase to around  $-22\text{‰}$  from 32 cm toward the bottom (Fig. 4g). Additionally to the previously cited correlations,  $\delta^{13}\text{C}$  was also positively correlated with  $\delta^{15}\text{N}$  in core P2 (Table 2).

Phytoplankton discriminate against  $^{13}\text{C}$  in the water column when CO<sub>2</sub> concentration is high, resulting in lower  $\delta^{13}\text{C}$  in the sedimented OM, which should be the case in Peri Lake, due to its water pH values ranging



usually from 6 to 7, relatively low depth and relatively constant wind influence and high  $p\text{CO}_2$  values (Hennemann and Petrucio 2011; D. Tonetta pers. commun.). Carbon isotope values that are depleted in  $^{13}\text{C}$  can also be an evidence of contribution from bacterially assimilated C to the sedimentary C biomass, either coupled or uncoupled to surface water phytoplankton production (Terranes and Bernasconi 2005). Lower  $\delta^{13}\text{C}$  in younger sediment layers in Peri Lake could be related to higher contribution from bacterial C, which has been shown to have an important influence in the lake metabolism (Fontes et al. 2013). Torres et al. (2012) also attributed low  $\delta^{13}\text{C}$  in oligotrophic Lake Annie to contribution from the heterotrophic microbial community.

An additional possibility is that the  $\delta^{13}\text{C}$  shifts in the uppermost deposits may simply reflect very high rates of fossil fuel combustion in recent years that produced atmospheric  $\text{CO}_2$  with a more depleted C isotopic signature (the Suess effect) (Brenner et al. 1999). Furthermore, forested watersheds provide isotopically light C (Gu et al. 2004), which could be influencing in the decreasing  $\delta^{13}\text{C}$  toward the top of the cores, since the Atlantic Rain Forest in the lake watershed has been recovering from periods of deforestation in the past (Fig. 2).

$\delta^{15}\text{N}$  varied from positive values of 2.66 to 5.80 ‰ in core P1, with the same tendency of increasing values with sediment depth observed for  $\delta^{13}\text{C}$  and the same sharp decrease at 45 cm (Fig. 3h). In addition to previously cited correlations,  $\delta^{15}\text{N}$  was also negatively correlated ( $p < 0.05$ ) with OM (Table 1). In core P2,  $\delta^{15}\text{N}$  varied from 2.60 to 7.11 ‰, which was also slightly higher than in core P1, and showed a pattern similar to  $\delta^{13}\text{C}$ , with lower values at the top 26 cm, increasing toward the bottom of the core (Fig. 4h).

The  $\delta^{15}\text{N}$  isotope ratio has also been widely used as a proxy to determine OM sources and in lake processes (Brenner et al. 1999; Vreca and Muri 2006; Torres et al. 2012). Nitrate is the most common form of dissolved inorganic nitrogen (DIN) used by non- $\text{N}_2$ -fixing algae, whereas land plants receive  $\text{N}_2$  from atmospheric N fixers in soil (Meyers 2003). The typical higher  $\delta^{15}\text{N}$  values of dissolved  $\text{NO}_3^-$  (7–10 ‰), in comparison to the atmospheric  $\text{N}_2$  (0 ‰), help to investigate the sources of N and, hence, the sources of OM (Das et al. 2008). In Peri Lake, both cores showed a pattern of decreasing  $\delta^{15}\text{N}$  from the older bottom ( $\approx 5\text{--}6$  ‰) to the top most recent ( $\approx 3$  ‰) sediment layers. Although

multiple factors can control the  $\delta^{15}\text{N}$  of sedimented OM (Brenner et al. 1999), some possible explanations for  $\delta^{15}\text{N}$  variation in Peri Lake can be raised.

In well-oxygenated waters, nitrification converts isotopically light ammonium to nitrite and nitrate. Depending on which form of N is used, phytoplankton may either be enriched or depleted in  $^{15}\text{N}$  (Lehmann et al. 2004; Gu 2009). The changes in the N isotopic signature in Peri Lake sediment record may indicate a change in the sources of N along the time span represented by the core. Although the water column in the lake is well oxygenated, recent studies have shown that ammonium is the N source more available for primary producers than nitrite and nitrate (Hennemann and Petrucio 2011), what could be contributing to the lower  $\delta^{15}\text{N}$  in recent deposits. Vreca and Muri (2006) also attributed the progressive  $^{15}\text{N}$  depletion in Lake Ledvica to changes in sources of DIN during the last century.

Vreca and Muri (2006) also attributed a decrease of 3 ‰ in both  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  in Lake Ledvica to increased terrestrial contribution that could be reflected in a temporary increase of primary producers in this oligotrophic lake. In Peri Lake, the decrease in  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  in both cores associated to OM and nutrient enrichment in recent deposits is probably a consequence of increased primary production in the lake. Higher nutrient availability makes primary producers discriminate against the heavier isotope, decreasing C and N ratios, as will be further discussed. This hypothesis is corroborated by the negative correlation found between  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  and macronutrients and the positive correlation observed between  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  and TOC:TN in core P1, since lower TOC:TN indicates higher autochthonous production.

In core P2,  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  were negatively correlated with TOC:TN ratio. Higher allochthonous contribution to OM reflects in higher TOC:TN ratios and lower  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ , as discussed above, and this relationship observed only in core P2 can be a consequence of its location very close to the margin, resulting in a more intense influence from OM originated from the forest.

Gu et al. (2006) attributed the low  $\delta^{15}\text{N}$  in the particulate OM of Lake Wauberg, Florida, to an annual cyanobacterial bloom of *Cylindrospermopsis* sp. (Gu 2009). In this sense, the increasing abundance and dominance of *C. raciborskii* (Tonetta et al. 2013) could be also contributing to decreasing  $\delta^{15}\text{N}$  in Peri Lake, since N fixation from this heterocystous cyanobacterium

could be causing more  $N_2$  to be fixed and there is no fractionation in the N fixation process (Fogel and Cifuentes 1993; Eilers et al. 2004; Gu 2009).

Additionally, the TN:TP ratio in Peri Lake core sediments and in the water column (Hennemann and Petrucio 2011) indicates a condition of potential P limitation in recent times, which means that N is probably not limiting for primary producers, which can discriminate against the heavier isotope, decreasing the  $\delta^{15}N$  content in the sedimented OM (Meyers 1997). Lake Annie also showed a pattern of increasing  $\delta^{15}N$  with core depth, and this lower  $\delta^{15}N$  in recent times was attributed to high N availability, N fixation from allochthonous OM (since plants also discriminate against  $^{15}N$  during N fixation), and heterotrophic and methane-oxidizing bacteria (Torres et al. 2012). Isotopically depleted end products from the heterotrophic metabolism, such as  $CO_2$  and  $NH_4^+$ , will be utilized by primary producers that will display isotopically depleted autochthonous OM (Torres et al. 2012). Increasing in those end products is probably also contributing to lower  $\delta^{13}C$  and  $\delta^{15}N$  in recent times in Peri Lake.

## Conclusion

The data obtained in the sediment cores in Peri Lake indicate that variation of C, N and P cycles occurred in the lake in recent times, probably due to both natural and anthropogenic influences. Stratigraphic fluctuations in macronutrients and  $\delta^{13}C$  and  $\delta^{15}N$  values of sedimented OM probably reflect a combination of factors, including a shift in relative contribution of autochthonous/allochthonous OM, in relative microbial biomass and activity and in nutrient limitation, and increasing autochthonous primary productivity. These changes are probably associated to alteration and recovery of the forested watershed and to climatic changes. Increasing in OM and macronutrients in recent times of the sediment record, together with the observed increasing chlorophyll-a concentration and dominance of cyanobacteria in the water column in the last decade, indicates that the ecosystem is changing toward a more eutrophicated state. The results have important management consequences, especially because of the presence and dominance of the potentially toxic *C. raciborskii*.

The opportunity to sample in two deep sites located at the centre and the margin of a shallow lake showed interesting results, especially that general tendencies

remained similar in both cores and that differences associated to the higher marginal contribution (allochthonous materials) to core P2 influenced the depositional history registered in the core.

The paleolimnological record showed signs of incipient eutrophication in the studied lake that could not be observed even in long-term monitoring of macronutrient concentrations in the water column. Results also showed that the sampling site has important influences in the depositional history registered in the core and that sediment records are important tools to better understand lake history and evaluate the magnitude, direction and causes of changes, effectively contributing to the conservation of these important freshwater ecosystems.

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## 7. Capítulo 3

### Dynamics of sediment phosphorus related to water and sediment characteristics in a subtropical coastal lake in Southern Brazil

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# Dynamics of sediment phosphorus related to water and sediment characteristics in a subtropical coastal lake in Southern Brazil

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## Abstract

Phosphorus (P) has been recognized as the most critical nutrient limiting lake productivity. Phosphorus sources to lakes can be external (allochthonous) and internal (autochthonous). Especially in shallow oligo-mesotrophic lakes, sediments can be an important internal P source to the system. In this sense, the aim of the present study was to understand the temporal and spatial variation of P and its organic and inorganic forms in the sediments of an oligo-mesotrophic shallow lake (Peri Lake) in southern Brazil, and to assess if they are related to water column parameters and sediment characteristics (granulometry and benthic fauna). Sampling was conducted monthly from March 2007 to May 2009. The main results found were: 1) P forms and concentration varied seasonally, with organic P and total P increasing in the sediments in warmer periods; 2) P forms and concentration also varied among the sampling sites, associated mainly with sediment grain size composition and organic matter content; 3) quantities and qualities of P in the sediments were correlated with water characteristics, especially temperature, chlorophyll *a*, nitrate, dissolved oxygen, pH and total P; d) some benthic functional feeding groups showed significant relationships with temporal variation in sediment P, including gathering-collectors, shredders and filterers and filtering-collectors. The results suggest a strong importance of temperature mediated control of sediment-P release, both directly, through its direct effects in primary production and decomposition rates, and indirectly through its effects on other water and sediment characteristics, especially dissolved oxygen.

**Keywords:** Phosphorus release, subtropical lake, sediment phosphorus, macroinvertebrates, Southern Brazil.

## 1 Introduction

Phosphorus (P) has been recognized as the most critical nutrient limiting lake productivity. Phosphorus sources to lakes can be external (allochthonous), comprising point and non-point sources such as rainfall, runoff, soil leaching, industrial and municipal effluents, and internal (autochthonous) from the system itself, such as aquatic plants, phytoplankton, bacteria and sediments (Kaiserli et al. 2002, Torres et al. 2014).

Especially in shallow lakes, sediments can represent an important source of P, due to the high ratio of sediment surface to water column (Søndergaard et al. 2001, Dong et al. 2011). The factors governing P release from sediments comprise redox reactions, adsorption, mineral phase solubility and mineralization of organic matter (Gächter and Meyer 1993, Lijklema 1993). Dissolved oxygen (DO), nitrates, pH and temperature are among the most important controlling parameters, as demonstrated by a number of studies (e.g. Andersen and Jensen 1992, Kleeberg and Dudel 1997, Katsev et al. 2006, Spears et al. 2006, Anthony and Lewis 2012, Wu et al. 2014).

The classical model for P fluxes between sediments and water of Mortimer (1941) links sediment P efflux to redox conditions at the sediment–water interface that are effectively controlled by the DO concentration in bottom water. According to the model, when the sediment surface is oxic, dissolved phosphate is strongly adsorbed to iron oxyhydroxides, what limits the P efflux by preventing phosphate diffusion into the water column from deeper reduced sediments. When anoxic conditions occur in the sediment surfaces, iron oxyhydroxides are reduced and phosphate can be released into the water column.

Other factors potentially influencing sediment P retention in sediments include: quantity and quality of the organic carbon input, bioturbation by benthic organisms, types and quantity of primary producers, rooted plant activity, sediment resuspension by winds, sediment grain size, bacterial activity, among other sediment characteristics (Gächter and Meyer 1993, Wetzel 2001, Caliman et al. 2007, Chuai et al. 2013, Zhu et al. 2013, Kleeberg and Herzog 2014). Feedback interactions between the sediment and the water column can also critically affect the magnitude and dynamics of the P fluxes between the sediments and the water column (Katsev et al. 2006).

In this sense, the aim of the present study was to understand the temporal and spatial variation of P and its organic and inorganic forms in the sediments of a subtropical oligo-mesotrophic shallow lake and to assess if they are related to water column parameters and sediment characteristics (granulometry and benthic fauna). Based on the information presented above, we expected to find:

- a) Seasonal variation in P forms and concentration in sediments determined by temperature via its effects on primary producers and decomposition.
- b) Spatial variation in P forms and concentration among sampling sites related with different sediment grain size composition and OM content;
- c) Significant correlations between P in the sediments and some key water column variables, such as pH, temperature, DO and P concentration;
- d) Significant relationship in temporal sediment P variation and the benthic fauna, related to the behaviour of different functional feeding groups.

## **2 Material and Methods**

### **2.1 Study Area**

Lake Peri is located in Southern Brazil, in the south-eastern portion of Santa Catarina island (27°44'S and 48°31'W), in the city of Florianópolis. Its surface area of 5.07 km<sup>2</sup> is surrounded by mountains covered by Atlantic Rain Forest in the north, west and south portions, and by sandy Restinga in the east. Lake Peri is considered a coastal lagoon due to the geographic location and geological origin (Holocene marine transgression), but presents some features that are quite different from coastal lagoons in general, such as a maximum depth of 11.0 m, an average depth of 4.2 m, and no direct sea water influence (freshwater). The bottom of the lake is composed mainly by silt and clay (~70%), which predominate in the northwest, west and southern portions of the lake, and fine and medium sands (~25%), which can be observed in the northeast and eastern portions of the lake.

The drainage basin is approximately 20 km<sup>2</sup> and most of it is within an area protected by law (Municipal Park) since 1981, with

limited human influence and occupation. Two main streams discharge in the lake, coming from the forested mountains: Cachoeira Grande Stream and Ribeirão Grande Stream (Fig. 1). The lake is connected to the sea by a unidirectional outflow channel. Since 2000, the lake supplies potable water to approximately 100,000 people. The lake is polymictic and presents a relative spatial homogeneity concerning water quality features (Hennemann and Petrucio 2011). Nutrient concentration is low, but chlorophyll-a and phytoplankton densities are high, with dominance of the potentially toxic cyanobacterium *Cylindrospermopsis raciborskii* most of the year (Komárková et al. 1999, Hennemann and Petrucio 2011, Tonetta et al. 2013). The climate is characteristically subtropical, with rainfall and winds relatively well distributed along the year, but with higher frequencies and intensities in spring and summer (October – March).

## 2.2 Sampling and analysis

The present study consisted of monthly sampling of physical, chemical and biological parameters in the water column and sediments in five sites (Fig. 1), during 26 months (March 2007 to May 2009). Site 1 (S1) was located in the centre of the lake, and was the deepest one (8.0 m); site 2 (S2) was 2.8 m deep and close to the discharge point of Cachoeira Grande Stream; site 3 (S3) was located near the outflow of Ribeirão Grande Stream, with a mean depth of 2.3 m; site 4 (S4) was situated near the beach in the northeastern portion of the lake, with a 1.5 m mean depth; site 5 (S5) was 2.8 m deep, located in the extreme northern portion of Peri Lake. Site 5 was sampled from May 2008 to April 2009 (12 months).

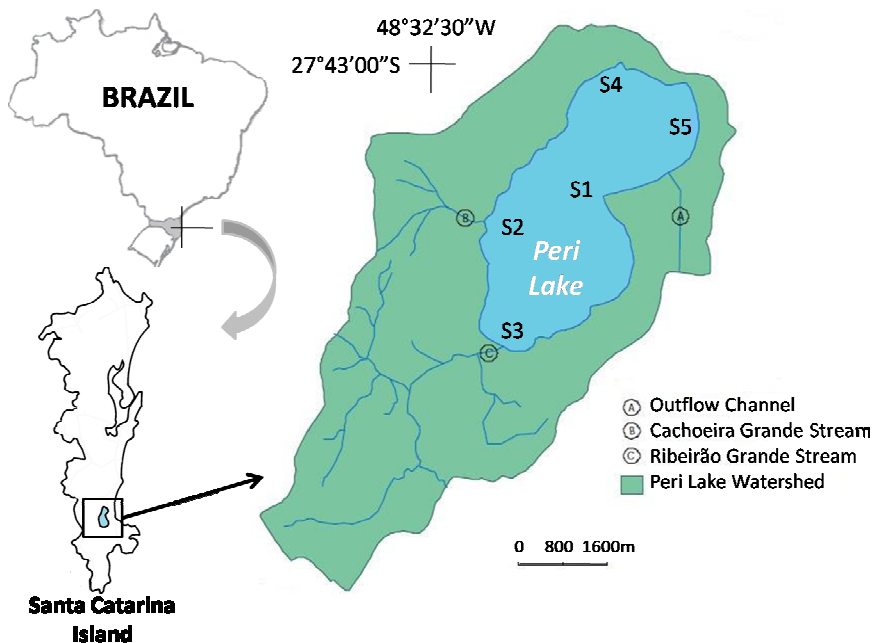


Figure 1. Location of Peri Lake and the five sampled sites. Adapted from Hennemann et al. 2015.

Transparency (Secchi depth) was measured using a black-white Secchi disk, and pH, dissolved oxygen (DO) and water temperature were measured *in situ* with specific probes (YSI and WTW). Climate data was provided by ICEA (“Instituto de Controle do Espaço Aéreo”) from the Defence Ministry, Brazilian Federal Government, from the Florianópolis airport station (5.5 km from Lake Peri).

Water was sampled using a 3 L van Dorn bottle. Dissolved inorganic nitrogen was determined as the sum of nitrite ( $N-NO_2^-$  - Golterman et al. 1978), nitrate ( $N-NO_3^-$  - Mackereth et al. 1978) and ammonium ( $N-NH_4^+$  - Koroleff 1976); inorganic phosphorus was measured as soluble reactive phosphorus (SRP - Strickland and Parsons 1960); total phosphorus and nitrogen (TP<sub>w</sub> and TN – Valderrama 1981) were also determined. Nutrients were measured in laboratory from filtered and unfiltered frozen water samples kept in polyethylene bottles



at  $-20^{\circ}\text{C}$ . Chlorophyll *a* (*Chl-a*) concentration was obtained by filtering 500 mL water samples through glass fibre filters Millipore AP40 followed by extraction with 90% acetone according to the method and equations described by Lorenzen (1967).

Sediment samples were collected right after water samples at the same five sampling sites between March 2007 and May 2009 using an Ekman-Birge grabber (15 x 15 cm). Samplings for granulometry and macroinvertebrates analysis were conducted only in the period of May 2008 to April 2009. At each sampling site, four samples were collected for analysis of aquatic macroinvertebrates and three samples were taken for sediment analyses (grain size, organic matter and phosphorus contents). In the laboratory, the samples were washed and sieved at 0.250 mm mesh size and all macroinvertebrates retained were sorted, counted and preserved in 70% alcohol. The aquatic fauna was sorted under microscope and identified to the lowest taxonomic level possible. The organisms belonging to Chironomidae family were mounted on semi-permanent slides and subsequently identified, under stereomicroscope, using appropriate literature (Epler 1995, Trivinho-Strixino and Strixino 1995).

Grain size distribution of the sediment particles was determined by sieving (Suguo 1973). Organic matter (OM) content was estimated by weight loss on ignition (LOI) at  $550^{\circ}\text{C}$ , as described by Engstrom et al. (2009). Total phosphorus (TP) was determined as phosphate with ammonium molybdate and ascorbic acid reaction in spectrophotometer (Koroleff 1973) after combustion and HCl extraction (Aspila et al. 1976). Inorganic phosphorus (IP) was determined similarly to TP, but no combustion was made previously to the HCl extraction (Aspila et al. 1976). Organic phosphorus (OP) was calculated from subtraction of IP from TP. Proportion of OP in relation to TP (%OP) was calculated as OP divided by TP.

### **2.3 Statistical Analysis**

Temporal and spatial variation concerning TP, IP, OP, %OP and OM content in the sediments were tested by one-way Analysis of Variance (ANOVA), followed by Tukey post-hoc. Pearson's correlation was also applied between sediment characteristics and water column parameters and climate data of the seven days previous to sampling

dates, in order to verify the linear relationship between each parameter. Data was  $\log x+1$  transformed in order to improve quality for the analyses. Statistical analyses and graphs were made in the R-Program version 3.2.2, Statistica 7® (StatSoft) and Microsoft Excel 2007®.

Non-metric multi-dimensional scaling (NMDS, vegan package), using Euclidian distance matrices, was performed to explore broad spatial between TP, OP and OM and four sediment grain size categories (silt, fine sand, medium sand and coarse sand) among all sampled sites. When the stress value was in the range of zero to 0.1, the two-dimensional representation was sufficient to distinguish the groups formed in relation to grain size and TP, OP and OM values (Clarke and Warwick 2001).

Multiple regression analysis was conducted to examine the relationship between TP, OP and OM and seven benthic functional feeding groups (predators, collectors, filtering-collectors, filterers, scrapers, shredders, gatherer-collectors). We evaluated the plausibility of each model by Akaike's model selection criterion, which selects the model closest to the "real" process underlying the biological phenomenon under study (Burnham and Anderson 2002). Grain size and benthic community information were taken from Lemes-Silva et al. (2016) and Lisboa et al. (2011).

### **3 Results**

#### **3.1 Temporal and Spatial Variation in Sediment P**

The TP concentration in the sediments of Peri Lake varied from 17.1 to 1,452.4  $\mu\text{g}\cdot\text{g}^{-1}$  (mean: 479.9  $\mu\text{g}\cdot\text{g}^{-1}$ ) and was significantly different among the five sampled sites (Fig. 2), with  $S1 > S3 > S2 > S5 > S4$ . The OP content prevailed in all sites in relation to IP, with mean %OP higher than 60%; site 4 showed the lowest OP proportion among all sampled stations. The %OP only differed significantly between site 4 and the other sampled sites (except site 5). On the other hand, OM content of the sediments in Peri Lake was significantly different in all sampled sites (Fig. 3), except between site 2 and 3, that showed similar OM content; site 4 also showed the lowest OM content.

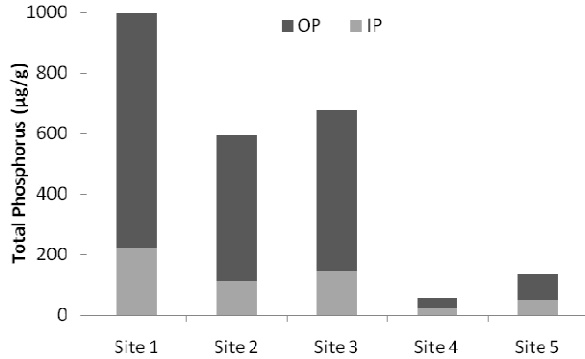


Figure 2. Mean total phosphorus content in the sediments of Peri Lake, in  $\mu\text{g}\cdot\text{g}^{-1}$ , in the five sampled sites, with differentiation between organic phosphorus – OP (dark grey) and inorganic phosphorus – IP (light grey), along the study period (March 2007 – May 2009).

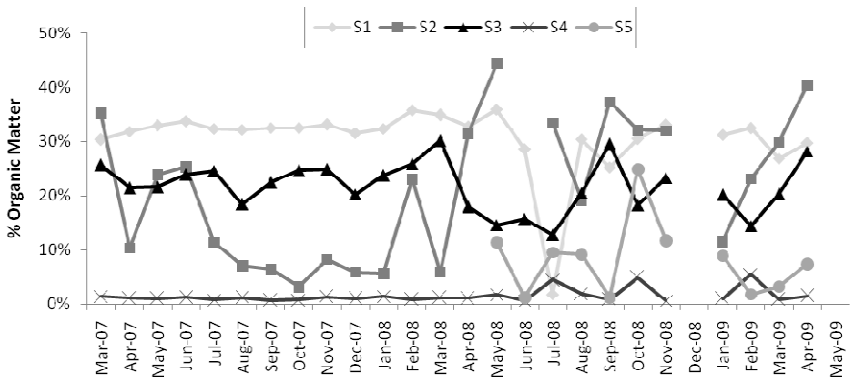


Figure 3. Monthly organic matter content in the sediments of Peri Lake, in %, in the five sampled sites along the study period (March 2007 – May 2009).

Concerning temporal variation in P content in the sediments of Peri Lake (Fig. 4), sites 1, 2 and 3 showed similar temporal variation patterns, generally with lower TP concentrations and lower OP content in colder months. In general, %OP was lower in 2007 seasons when compared to seasons in 2008 for all sites (except site 5).

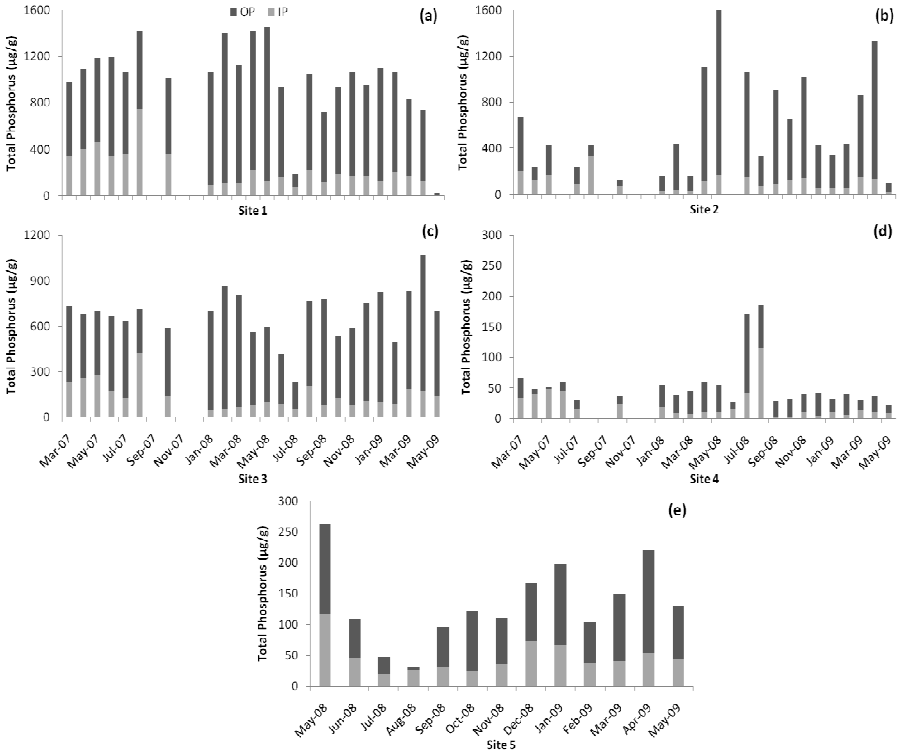


Figure 4. Monthly total phosphorus content in Peri Lake sediments, in  $\mu\text{g}\cdot\text{g}^{-1}$ , in site 1 (a), site 2 (b), site 3 (c), site 4 (d) and site 5 (e), with differentiation between organic phosphorus – OP (dark grey) and inorganic phosphorus – IP (light grey), along the study period (March 2007 – May 2009).

### 3.2 Correlations of Sediment P with Climate and Water Column Parameters

Correlations of P content in the sediment, including TP, IP, OP and %OP, along the study period with some water quality parameters were conducted for each sampling site (Table 1) in order to better understand which factors could be influencing the temporal variation in sediment P in Peri Lake. Climate data, dissolved nutrients (except for

nitrate), TN and Secchi depth were not correlated with any of the sediment P contents and are therefore not shown in Table 1. Sediment P in site 5 was also not correlated to any of the climate data nor to the water column parameters (probably because of the reduced sampling period) and is also not shown.

TP in the sediments was positively correlated with Chl-*a* in site 1, with DO and pH in site 3, and negatively with nitrate (NO<sub>3</sub>) in site 2. IP was positively correlated with DO and NO<sub>3</sub> in sites 1, 3 and 4, and negatively with pH in site 4, and with TPw in all sites. OP showed a positive correlation with Chl-*a* in site 1, with WTemp and pH in site 3, and with TPw in site 4. Negative correlations with OP were only observed in site 2 with NO<sub>3</sub>. %OP was positively correlated with Wtemp in sites 1 and 3, and with Chl-*a* and TPw in sites 1, 3 and 4. A negative correlation was observed between %OP and DO in sites 1, 3 and 4, and with NO<sub>3</sub> in sites 2, 3 and 4.

Table 1. Pearson's correlation between TP, IP, OP and %OP in the sediments and water column parameters for sampling sites 1, 2, 3 and 4, in Peri Lake, along the study period (March 2007 – May 2009). Significant correlations ( $p < 0.05$ ) are marked in bold.

		WTemp	pH	DO	Chl-a	TPw	NO <sub>3</sub>
S1	TP	0,19	0,17	0,14	<b>0,52</b>	-0,15	0,27
	IP	-0,12	0,13	<b>0,41</b>	0,17	<b>-0,51</b>	<b>0,53</b>
	OP	0,26	0,15	0,04	<b>0,60</b>	-0,07	0,10
	%OP	<b>0,48</b>	0,04	<b>-0,49</b>	<b>0,67</b>	<b>0,51</b>	-0,39
S2	TP	-0,03	-0,22	0,21	0,20	-0,23	<b>-0,53</b>
	IP	-0,35	-0,21	0,17	-0,07	<b>-0,44</b>	0,10
	OP	0,10	-0,18	0,19	0,24	-0,03	<b>-0,56</b>
	%OP	0,36	-0,03	0,07	0,23	0,25	<b>-0,56</b>
S3	TP	0,26	<b>0,47</b>	<b>0,41</b>	0,05	0,05	-0,10
	IP	-0,28	0,12	<b>0,59</b>	-0,36	<b>-0,41</b>	<b>0,42</b>
	OP	<b>0,47</b>	<b>0,46</b>	0,12	0,25	0,28	-0,26
	%OP	<b>0,45</b>	0,08	<b>-0,53</b>	<b>0,43</b>	<b>0,41</b>	<b>-0,42</b>
S4	TP	-0,09	-0,36	0,05	0,04	-0,03	0,18
	IP	-0,29	<b>-0,44</b>	<b>0,44</b>	-0,36	<b>-0,47</b>	<b>0,55</b>
	OP	0,26	-0,12	-0,41	0,33	<b>0,53</b>	-0,18
	%OP	0,40	0,25	<b>-0,58</b>	<b>0,45</b>	<b>0,66</b>	<b>-0,49</b>

### 3.3 Influence of Grain Size and Benthic Fauna on Sediment P

NMDS with grain size and P forms as related to sampling sites (Fig. 5) shows that sites 1, 2 and 3 are very similar, showing a higher silt content, and sites 4 and 5 have higher fine and medium sand contents. Site 4 had greater fine sand content while site 5 showed a higher medium sand proportion compared to other sites. The NMDS also shows that the sites with the higher silt content, are also the sites with the higher TP, OP and OM contents.

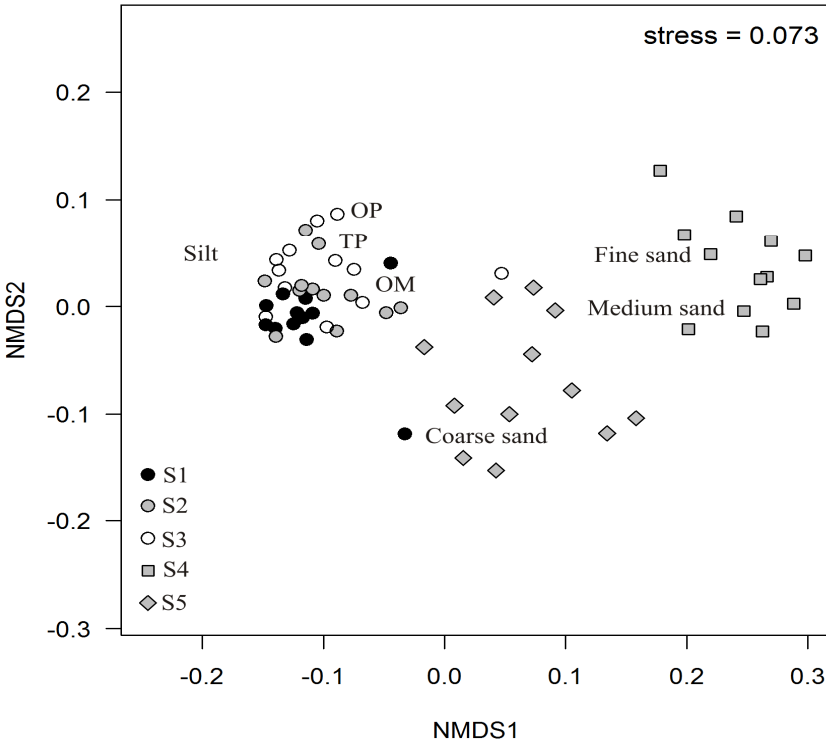


Figure 5. NMDS of the five sampling sites considering grain size categories (silt, fine sand, medium sand and coarse sand), phosphorus forms (TP, OP) and the organic matter (OM) content.

Multiple regression analysis between TP, OP and OM and the seven benthic functional feeding groups for each sampling site is shown in Table 2. For site 1, neither OM nor TP and OP were related to any of the seven functional groups. In site 2, TP, OP and OM were negatively affected by gathering-collectors, and positively affected by filtering-collectors. In site 3, TP, OP and OM were positively influenced by shredders. Differently, for site 4, filtering-collectors were negatively related to TP, while OP was positively related to filterers, and OM was not affected by any feeding group. Site 5 showed a positive relationship between OP and filterers, but no relationship between TP and OM and the seven benthic functional feeding groups.

Table 2. Results of the multiple regression analysis between TP, OP and OM and the seven benthic functional feeding groups for each sampling site. Only models selected by Akaike's criterion are shown.

	Total phosphorus			Organic phosphorus			Organic matter		
	Slope	F	P	Slope	F	P	Slope	F	P
SITE 2									
Gathering-collectors	-1141.4	18.801	0.002	-1025	17.215	0.003	-0.178	11.04	0.009
Filtering-collectors	-334.1	6.968	0.029	302.2	6.563	0.033	0.100	12.04	0.007
SITE 3									
Shredders	86.01	7.191	0.023	74.95	7.236	0.022	0.055	7.021	0.033
SITE 4									
Filtering-collectors	-17.176	8.161	0.028						
Filterers				0.607	27.551	0.0123			
SITE 5									
Filterers				0.707	18.391	0.001			



## 4 Discussion

### 4.1 Temporal and Spatial Variation in Sediment P

TP concentration in the sediments of the five sampled sites in Peri Lake was higher in  $S1 > S3 > S2 > S5 > S4$ , which was closely followed by the OM content in each site, showing that most of the P in the sediments is stored inside living cells and in organic detritus materials. The composition and TP content of sediment samples also showed substantial spatial heterogeneity in other shallow lakes (e.g. Liu et al. 2012, Kangur et al. 2013). This horizontal differences in sediment TP within the lake can be associated to macrofauna, sediment granulometry, debris from fauna and flora, water depth, wind influence, among others (e.g. Doremus and Clesceri 1982, Gachter and Meyer 1993, Lijklema 1993, Kleeberg and Dudel 1997, An and Li 2009).

Doremus and Clesceri (1982) showed that four times more P was sequestered in the humic fraction than in the inorganic (Fe/Ca) fraction in oligotrophic Lake George. The results of their experiments also suggest that microbial activity and OM, including non-living detritus, aid in the immobilization of P in sediments. In this sense, the higher content of OM and silt in sites 1, 2 and 3 in Peri Lake probably explain the high P content observed in these three sites, when compared to sites 4 and 5.

Besides grain size composition, different quantities and qualities of sediment bacteria may also have influenced in differences in TP, OP and IP content in Peri Lake. Gachter and Meyer (1993) have long demonstrated the importance of bacteria in sediment P content, showing that these organisms also depend on P as a nutrient and are able to take it up from the organic substrate or from the water. In this sense, a substantial part of the P might be incorporated in bacterial biomass and the net release can be controlled by bacterial demand for P.

The mineralization of organic material also influences in the P content of sediments, and since OM comes from various sources, with variable phosphate contents and biodegradability (Lijklema 1993), it can also influence in spatial P heterogeneity. In Peri Lake, detritus distribution among various shore compartments can show variability, related to differences in macrophytes presence, proximity to the discharge points of rivers, litter from the lake margins (Pieczyńska

1993, Hennemann et al. 2015), and along with differences in sampling site depth (different light availability), can be important factors influencing in the quality of OM sources and rates of mineralization, what can also contribute to the observed differences in P content among sites.

It is important to highlight that differences in P content observed in the sediments were not reflected in water column TP and SRP concentration, since Hennemann and Petrucio (2011) have already demonstrated that there is no significant differences among the same sampling sites concerning water quality parameters, in a similar period. This is probably associated to the shallow depths observed in the lake and relatively frequent and significant wind influence in this coastal waterbody, since wind velocities higher than  $4 \text{ m.s}^{-1}$  are capable of completely mixing a water body to a depth of 6 m, by creating waves and circulation currents (Kleeberg and Dudel 1997).

Concerning the temporal variability in sediment P in Peri Lake, according to Lijklema (1993), within a year the sediment matrix will be fairly constant except for the pool of non-refractory organic material. Consequently, the adsorptive capacity of the sediment for phosphate varies mainly due to changes in redox conditions related to the temperature cycle and the course of organic deposition. Phosphate in microbial biomass and iron associated phosphate can be important as transient pools since they are influenced by temperature and redox conditions (Caraco 1993, Montigny and Prairie 1993).

Burger et al. (2007) attributed the large seasonal differences in release rates observed in shallow polymictic Lake Rotorua (New Zealand) in part to variable sedimentation rates and to changes in temperature, which controls rates of biological activity, oxygen consumption and redox potential. Although seasonal differences were not as large in Peri Lake, the temporal variation observed can also be associated to variable sedimentation rates (influenced by shallowness and wind), temperatures and DO concentration in the sediment-water interface.

A complex of climatic, hydrological as well as hydrochemical factors was regarded as the cause of differences observed in P release from sediments in 1992 and 1993 in Lake Müggelsee (Germany – Kleeberg and Dudel 1997). Differences in water temperature, which influences biological processes and especially DO concentration in the

water, was the probable explanation for the differences in P release between the two years. Differences between years were also observed in our study, especially in %OP.

According to Kangur et al. (2013), feedback in the P cycling can also have an important effect in increasing short term temporal differences: an increase in P release from the sediments leads to increased primary production in the water column, which can increase OM sedimentation flux, which increases the amount of OP and the rates of oxygen and ferric oxyhydroxide consumption in the sediment, which, in turn, further increases the release of P from the sediments.

Correlations between sediment P characteristics and climate and water column parameters along the studied period add in the understanding of factors influencing in temporal P dynamic in Peri Lake and will be discussed in the next section.

## **4.2 Correlations of Sediment P with Climate and Water Column Parameters**

Water temperature had a positive influence in the OP content in Peri Lake sediments. The effect of temperature on P concentration in the sediments has been demonstrated in several studies. Jensen and Andersen (1992) found that water temperature alone could explain nearly 70% of the seasonal variation in sediment P release in three shallow eutrophic lakes. Kleeberg and Dudel (1997) associated increasing temperatures with higher aerobic mineralization processes and consequently lower DO in the water column, which can increase P release from the sediments. Spears et al. (2006) also associated high temperatures to elevated O<sub>2</sub> consumption by bacteria, which temporally removes the oxygenated surface layer and also releases P to the water column.

In the P-limited Peri Lake, enhanced IP release from the sediments (increasing %OP) associated to higher O<sub>2</sub> consumption and lower DO solubility in higher temperatures is capable of increasing primary production in the water column, which results in higher OM deposition, further increasing the OP content. Higher temperatures also stimulate conversion of IP in OP by benthic primary producers, increasing OP content in the sediments even more. Wu et al. (2014) presented a similar explanation for the temperature effects on P release

from shallow Lake Xuanwu (China) sediments in their laboratory experiments. According to the authors conclusion, the higher the temperature, the more P is released and the longer the time to achieve equilibrium of release.

As observed in Peri Lake, no substantial difference between the DO concentration in surface and near-bottom water was detected in summer in shallow polymictic Lake Peipsi (Kangur et al. 2013). In this sense, we can assume the entire water column was well oxygenated in the sampling days. See appendix for additional DO information in Peri Lake. The negative correlations found in summer DO concentrations in the water with sediment OP and TP concentrations in Lake Peipsi (Kangur et al. 2013) are similar to the negative correlations found between DO and %OP in Peri Lake. This result can be a consequence of higher temperatures in summer, which decreases DO solubility and increases assimilation of P by primary producers and bacteria, what increases %OP in the sediments, as previously discussed.

On the other hand, IP in the sediments of Peri Lake was positively correlated to DO. A higher DO concentration in the overlying water generally decreases P effluxes from sediments (Kangur et al. 2013), which can maintain a higher IP content trapped in the sediments. Results found in both Lake Peipsi and Peri Lake show that variation in O<sub>2</sub> concentration in the water column can significantly affect P release rates from the sediments.

Concerning pH correlations with P forms ( site 4) pH showed a negative correlation with IP, what indicates that in this site with low OM content, increase in pH may be leading to IP release from the sediments. Indeed, according to Boers (1991), a higher pH causes the desorption of phosphate from Fe<sup>3+</sup> hydroxides, resulting in a release of phosphate from the sediments. Boers (1991) also affirmed that enhanced photosynthetic activity can lead to higher pH by withdrawing CO<sub>2</sub> from the water and shifting the CO<sub>2</sub>/HCO<sup>-</sup>/CO<sup>-</sup> equilibrium. In this sense, the positive correlation observed between TP/OP with pH in site 3 could be associated with higher primary production in warmer months, which increased pH and TP/OP accumulation in the sediments.

The positive correlation of NO<sub>3</sub> with IP in sites 1, 3 and 4 can be associated to the effect that NO<sub>3</sub> has in the P cycling through its influence on the iron cycling. According to Caraco (1993), the presence of NO<sub>3</sub> can indirectly inhibit P release from sediments, since NO<sub>3</sub> can

inhibit the reduction of oxidized iron ( $\text{Fe}^{3+}$ ) to the reduced form ( $\text{Fe}^{2+}$ ), maintaining higher  $\text{Fe}^{3+}$  levels and preventing P release. Conversely, the OP content in the sediments showed a negative correlation with  $\text{NO}_3$  in sites 2, 3 and 4, which could be associated to temperature, since it is capable of increasing bacterial denitrification processes (consuming  $\text{NO}_3$ ) and increase OP content in the sediments as previously discussed. Jensen and Andersen (1992) argued that  $\text{NO}_3$  concentration could reduce P release in winter and early summer, but increase it in late summer. In other words:  $\text{NO}_3$  can have different effects on P release depending on seasonal aspects (especially temperature), as apparently happens also in Peri Lake.

TP concentration in the water column showed a negative correlation with IP in the sediments in the four sampled sites showed in Table 1. This can also be an effect of temperature, since higher temperatures can increase IP release from the sediments to the water column (by increasing mineralization rates and decreasing DO), stimulating primary production and increasing TP concentration in the water. Increased IP release from the sediments and OM production and deposition from the water column associated to higher temperatures both contribute to the positive correlation observed between TP in the water and %OP in the sediments.

As can be concluded from the discussion above, temperature and DO in the water column seem to be critical in sediment P fluxes in Peri Lake. According to Gachter and Meyer (1993), if the sediment surface of a lake is permanently oxic, it will accumulate P until its P content reaches its P binding capacity, and then, the sediment would start to release P even under oxic conditions. Relatively high P content in Peri Lake sediments and the well oxygenated water column may be an indication that the systems is accumulating P in the sediments. When it reaches the P-binding capacity, higher P release rates are probable, which can have dramatic consequences to this P-limited lake dominated by potentially toxic Cyanobacteria.

### **4.3 Influence of Grain Size and Benthic Fauna on Sediment P**

The higher TP, OP and OM content in sites with higher silt content found in Peri Lake was expected, since studies have shown that the P adsorption rate increases with the increase in fine particles of the

sediments, due to high surface area, and that sorption rates are mainly affected by the percentage of fine particles less than 63  $\mu\text{m}$  (An and Li 2009, Zhu et al. 2013). Heterogeneity in particles spatial distribution in the lake can be influenced not only by depth and proximity to margins and rivers discharge points, but can also reflect the impact of water currents in the lake (Kangur et al. 2013).

Concerning relationships found between TP, OP and OM and the seven macroinvertebrates feeding groups in each sampling site, they could represent only an indirect effect related to seasonal temperature variation, but they may also represent an important influence of the benthic organisms in the P cycling in the sediment-water interface, since studies have shown that macroinvertebrates can have strong relationships with P in the sediments (Wazbinzki and Quinlan 2013, Zhang et al. 2014).

In site 1, no significant relationship was identified by the multiple regression analysis followed by selection of the best model by Akaike's criterion. This could be related to the deepness of this sampling site (~8m), absence of light and low richness in the macroinvertebrate community (Lemes-Silva et al. 2016). The deep regions of aquatic ecosystems have restrictions limiting the development of some species due to the decrease of light penetration in the water column and many aquatic organisms not adapting to the prevailing conditions (Pech et al. 2007), what may explain the very poor species number in this site with dominance of tolerant taxa such as oligochaetes.

In site 2, both P forms and OM were negatively affected by gathering-collectors, and positively affected by filtering-collectors. Gathering-collectors feeding on fine particles OM in the sediments (Merrit and Cummins 1984, Cummins et al. 2005) move through the sediments actively, and could be moving and resuspending sediments and breaking the oxic surface layer, releasing P from the sediments to the water column. On the other hand, filtering-collectors remain buried in the sediment, collecting and filtering materials from the sediment surface and bottom waters, and excreting inside the sediment matrix, which could be increasing P and OM content in the sediments (Malmqvist et al. 2002).

Shredders influenced TP, OP and OM positively in site 3. This feeding group feeds on leaves and other organic material, such as wood, needles and fruits by biting into them or by cutting or boring through

them. So, shredders excrete materials usually composed of particles that are smaller and of a different quality than what they ate (Tomanova and Usseglio-Polatera 2007), facilitating incorporation in the sediments and by smaller organisms, increasing P and OM in this site.

Differently, for site 4, which showed a very low OM content, and higher fine sand proportion, the benthic community was poor, dominated mainly by Tanaidaceans (gathering-collectors) and Diptera larvae of *Lopescladius* sp. (filterer). Gathering-collectors are organisms adapted to feed on fine particles deposited on the substrate surface (Wallace and Webster 1996) and filterers are organisms adapted to feed on particles in suspension. Some filter feeders (Simuliidae, Chironomidae and Philopotamidae) and gathering-collectors (Tanaidacea and Oligochaeta) may increase the quantity of OM in the environment by ingesting minute particles and egesting compacted fecal particles larger than those originally consumed. Thus, these animals may perform two very important functions: (a) the removal of fine particles of OM from suspension (which would otherwise pass unused through that area) and (b) the supply of larger particles via their feces to a broad spectrum of deposit-feeding detritivores (Wallace and Webster 1996).

The positive relationship between OP and filterers in site 5 could be associated to P-rich excretion in the sediments by filterers taking particles from the bottom waters, which is increased and stimulated by higher benthic activities in warmer temperatures. This site is rich in suspended OM from leaves and has a higher fine and coarse sand proportion.

## **5 Conclusions**

From the results and discussion above, we can conclude that: 1) P forms and concentration varied among the sampling sites, probably associated with different silt contents, depth of the water column, bacterial and macroinvertebrates quantity and composition; most of the P was in organic form (OP), so sites with higher OM content showed higher P contents as well. 2) P forms and concentration also varied seasonally, with OP and TP increasing in the sediments in warmer periods (especially spring and summer), as a result of higher primary production and decomposition rates; effects of temperature in other parameters, such as DO and pH, could also increase its influence on

seasonal P dynamics. 3) Quantities and qualities of P in the sediments were correlated with water characteristics, especially temperature, Chl-*a*, NO<sub>3</sub>, DO, pH and TP; temperature has probably both a direct effect through stimulation of primary production and decomposition, and an indirect effect through its effect on other variables (DO, pH, NO<sub>3</sub>); DO concentration in the water column also plays a fundamental role in sediment P dynamics in shallow Peri Lake. 4) Some benthic functional feeding groups showed significant relationships with temporal variation in sediment P, including gathering-collectors, shredders and filterers and filtering-collectors; their behavior and feeding habitats could be associated with the kind of the relationship identified (positive or negative).

These results offer strong evidence to suggest the importance of temperature mediated control of sediment-P release, through its direct effects in primary production and decomposition rates, and also indirect influence through its effects on other water and sediment characteristics, especially DO concentration in the water.

The information obtained in the present study should improve our understanding on how shallow lake systems and sediment P content may respond to changes in water quality parameters in the future. Further studies including *in situ* and laboratory experiments are needed to better understand the relationships found and to develop management strategies under different land use and climate change scenarios.

## **6 Acknowledgements**

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## Appendix

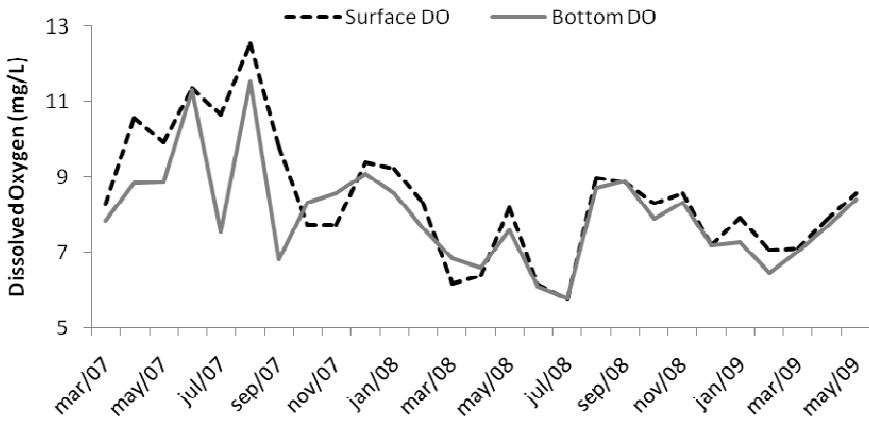


Figure A: Monthly dissolved oxygen (DO) concentration (in  $\text{mg}\cdot\text{L}^{-1}$ ) in the surface and near bottom ( $\sim 6\text{m}$ ) depths in Site 1 in Peri Lake, from March 2007 to May 2009.

## 8. CONCLUSÕES GERAIS

Em relação aos parâmetros de qualidade da água, observou-se variação sazonal apenas para as concentrações de fósforo e clorofila-a, sendo que esta variação pôde ser associada à variação sazonal típica de ambientes subtropicais na temperatura do ar e na intensidade e frequência dos ventos. Variações interanuais significativas também foram observadas, especialmente entre o período inicial de amostragem (2007-2009) e o período final (2010-2013), as quais podem estar relacionadas a diferenças climáticas entre os anos amostrados, especialmente nas precipitações acumuladas e temperaturas médias anuais.

A Lagoa do Peri mostrou-se um corpo d'água potencialmente limitado por fósforo durante a maior parte do período de estudo. Esta constatação foi reforçada pela correlação positiva observada entre as concentrações de clorofila-a e de fósforo total e dissolvido. Por meio de análise de regressão múltipla, constatou-se que a biomassa fitoplanctônica parece ser controlada principalmente pela temperatura da água e pela disponibilidade de fósforo (por meio da razão TN:TP e do fósforo solúvel dissolvido).

Dessa forma, com base nos resultados acima encontrados, foi possível concluir que as altas concentrações de clorofila-a encontradas na Lagoa do Peri podem estar associadas, principalmente, à limitação da comunidade por fósforo, à pouca profundidade (que facilita a resuspensão do fósforo no sedimento) e à baixa transparência da água, condições estas que favorecem a dominância de cianobactérias, em especial de *Cylindrospermopsis raciborskii*.

Os dados obtidos nos dois testemunhos de sedimento coletados na Lagoa do Peri mostraram que alterações nos ciclos de carbono, nitrogênio e fósforo ocorreram em tempos mais recentes. As variações estratigráficas nos macronutrientes, nas razões entre nutrientes e nas razões isotópicas da matéria orgânica sedimentar refletem prováveis mudanças nas contribuições relativas de fontes autóctones e alóctones de matéria orgânica, na biomassa e atividade bacterianas, na limitação por nutrientes, e na produtividade primária do sistema. Essas mudanças podem estar associadas a alterações e recuperação da vegetação no entorno da lagoa e sua bacia hidrográfica, bem como a mudanças climáticas (temperatura, ventos e pluviosidade). As evidências de

aumento nas concentrações de nutrientes e matéria orgânica nos testemunhos de sedimento em tempos mais recentes indicam que o ambiente está passando a um estado trófico mais elevado, e, embora as concentrações de nutrientes atuais na coluna d'água não demonstrem isso, as concentrações elevadas de clorofila-a e dominância de cianobactérias podem estar refletindo estas mudanças.

Em relação à variação espacial e temporal na matéria orgânica e concentrações de fósforo no sedimento, o presente estudo observou variações sazonais significativas, com concentrações de fósforo e matéria orgânica maiores em períodos mais quentes, associadas a taxas mais elevadas de produção primária e decomposição. Também foram observadas diferentes concentrações de fósforo e matéria orgânica entre os pontos amostrados, o que pode ser associado ao conteúdo de silte, bactérias e macroinvertebrados bentônicos, bem como à profundidade em cada ponto. A maior parte do fósforo encontrada consistiu em fósforo orgânico, de forma que os pontos com maior conteúdo orgânico apresentaram as maiores concentrações de fósforo.

As quantidades e formas de fósforo nos sedimentos da Lagoa do Peri puderam ser relacionadas com características da água, especialmente temperatura, pH e concentrações de clorofila-a, nitrato e oxigênio dissolvido. A temperatura da água parece ser o fator mais importante, podendo tanto ter efeitos diretos quanto indiretos nas concentrações de fósforo no sedimento.

Relações significativas também foram observadas entre as concentrações de fósforo no sedimento de cada ponto de coleta e diferentes grupos funcionais de macroinvertebrados, através de análises de regressão múltipla. Os padrões de comportamento de locomoção e alimentação de catadores-coletores, fragmentadores, filtradores e filtradores-coletores puderam ser associados às relações positivas ou negativas encontradas.

Os resultados encontrados no presente conjunto de estudos fornecem forte evidência da importância da temperatura no controle de processos chave no funcionamento do ecossistemas lagunares subtropicais. A temperatura tem capacidade de influenciar nas taxas de produção primária e decomposição na água e no sedimento, bem como na ciclagem de fósforo – considerado um recurso limitante ao sistema, entre os compartimentos pelágico e sedimentar.



Os resultados obtidos também permitem concluir que esta lagoa costeira vem passando por um processo de aumento em sua produtividade, ou seja, de elevação em seu estado trófico, que parece estar associado mais a condições naturais do que a influências antrópicas diretas.

As conclusões acima têm grande importância do ponto de vista do gerenciamento de ecossistemas costeiros como a Lagoa do Peri, especialmente em um contexto de futuras mudanças climáticas globais envolvendo aumento da temperatura e alterações nos padrões de precipitação e ventos, bem como de possíveis processos de eutrofização cultural. Os resultados encontrados ressaltam a importância de se proteger os corpos d'água costeiros e suas bacias hidrográficas, preservando-se a vegetação nativa e mantendo-se um controle do uso e ocupação humanos em seu entorno. As informações obtidas também contribuem para uma melhor compreensão de como sistemas de lagos e lagoas costeiros podem responder a mudanças na qualidade da água no futuro.

O registro de informações nos sedimentos mostrou-se uma ferramenta importante para entender a história do corpo d'água e avaliar a magnitude, direção e causas de alterações, contribuindo efetivamente para a conservação de ecossistemas de água doce de grande relevância, como a Lagoa do Peri.

A manutenção da qualidade da água da lagoa é fundamental para que o Parque Municipal da Lagoa do Peri continue a fornecer os diversos serviços ecossistêmicos que vem oferecendo nos últimos anos, especialmente em relação à provisão de água para abastecimento e recursos pesqueiros, ao seu valor turístico/recreativo, e ao suporte à manutenção da biodiversidade, à produção primária e aos ciclos biogeoquímicos.

Experimentos adicionais específicos envolvendo a relação entre nutrientes, temperatura e as comunidade bacterianas e de produtores primários, bem como estudos mais detalhados acerca da influência do sedimento na dinâmica da qualidade da água desta lagoa costeira, serão importantes para melhor compreender a dinâmica de parâmetros tróficos relevantes, bem como a dominância e comportamento de cianobactérias em corpos d'água subtropicais com baixas concentrações de fósforo.

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