Universidade Federal do Rio Grande – FURG

Instituto de Oceanografia - IO

Programa de Pós-Graduação em Oceanologia - PPGO

FONTES E FLUXOS CONTINENTAIS DE ELEMENTOS DISSOLVIDOS PARA O OCEANO COSTEIRO SUL DO BRASIL

GABRIEL KARAGIANNIS DE SOUZA

Tese apresentada à coordenação do PPGO como requisito parcial para a obtenção do título de doutor em Oceanologia.

Orientador: *Prof. Dr.* CARLOS FRANCISCO FERREIRA DE ANDRADE

Universidade Federal do Rio Grande (FURG), Brasil

Rio Grande, RS, Brasil

Junho, 2020.

FONTES E FLUXOS CONTINENTAIS DE ELEMENTOS DISSOLVIDOS PARA O OCEANO COSTEIRO SUL DO BRASIL

Tese apresentada ao Programa de Pós-Graduação em Oceanologia, como parte dos requisitos para a obtenção do Título de Doutor.

por

GABRIEL KARAGIANNIS DE SOUZA

Rio Grande, RS, Brasil

Junho, 2020.

SOUZA, GABRIEL KARAGIANNIS

Fonte e fluxos continentais de elementos dissolvidos para o oceano costeiro sul do Brasil / Gabriel Karagiannis de Souza. – Rio Grande: FURG, 2020.

Número de páginas 92 p.

Tese (Doutorado) – Universidade Federal do Rio Grande. Doutorado em Oceanologia. Área de Concentração: Oceanografia Química.

1. Elementos dissolvidos. 2. Fluxos. 3. Descarga de água subterrânea. 4. Planície costeira do Rio Grande do Sul. 5. Lagoa dos Patos. 6. Sangradouros. Fontes e fluxos continentais de elementos dissolvidos para o oceano costeiro sul do Brasil.

ATA DE DEFESA

UNIVERSIDADE FEDERAL DO RIO GRANDE - FURG
IO – INSTITUTO DE OCEANOGRAFIA
PROGRAMA DE PÓS-GRADUAÇÃ0 EM OCEANOLOGIA
E-mail: ccpofqg@furg.br – home-page: www.ppgo.furg.br

ATA ESPECIAL DE DEFESA DE TESE DE DOUTORADO – 07/2020

Às 09h30m do dia 12 de junho do ano de dois mil e vinte, por videoconferência, reuniu-se a Comissão Examinadora da Tese de DOUTORADO intitulada "**Fontes e fluxos continentais de elementos dissolvidos para o oceano costeiro sul do Brasil**", do **Acad. Gabriel Karagiannis de Souza**. A Comissão Examinadora foi composta pelos seguintes membros: Prof. Dr. Carlos Francisco Ferreira de Andrade - Orientador/Presidente – (IO/FURG), Prof. Dr. Luis Felipe Hax Niencheski - (IO/FURG), Profa. Dra. Eunice da Costa Machado – (IO/FURG), Prof. Dr. Miguel da Guia Albuquerque - (IFRS) e Dra. Cacinele Mariana da Rocha – (UFRGS). Dando início à reunião, o Orientador e Presidente da sessão, Prof. Dr. Carlos Francisco Ferreira de Andrade, agradeceu a presença de todos e fez a apresentação da Comissão Examinadora. Logo após esclareceu que o Candidato teria um tempo de 45 a 60 min para explanação do tema, e cada membro da Comissão Examinadora, um tempo máximo de 30 min para perguntas. A seguir, passou à palavra ao Candidato que apresentou o tema e respondeu às perguntas formuladas. Após ampla explanação, a Comissão Examinadora reuniu-se em reservado para discussão do conceito a ser atribuído ao Candidato. Foi estabelecido que as sugestões de todos os membros da Comissão Examinadora, que seguem em pareceres em anexo, foram aceitas pelo Orientador/Candidato para incorporação na versão final da Tese. Finalmente, a Comissão Examinadora considerou o candidato **APROVADO**, por unanimidade. Nada mais havendo a tratar, foi lavrada a presente ATA que após lida e aprovada, será assinada pela Comissão Examinadora, pelo Candidato e pelo Coordenador do Programa de Pós-Graduação em Oceanologia.

Prof. Dr. Carlos Francisco Ferreira de Andrade
Presidente

Prof. Dr. Luis Felipe Hax Niencheski

Profa. Dra. Eunice da Costa Machado

Prof. Dr. Miguel da Guia Albuquerque

Dra. Cacinele Mariana da Rocha

Prof. Dr. Rodrigo Kerr
Coordenador do PPGO

Acad. Gabriel Karagiannis de Souza

Agradecimentos

À minha família, principalmente aos meus pais por todo o tipo de apoio, proporcionando a realização de uma etapa muito importante da minha vida.

Aos meus amigos *das antigas* e aqueles que conheci nestes anos (melhor não citar pra não esquecer ninguém), obrigado por todos os momentos vividos e a força de sempre continuar e nunca desistir.

Ao meu orientador, Prof. Dr. Carlos Andrade, não só pelo conhecimento acadêmico, mas também pelo sentimento de amizade. Obrigado por toda atenção durante esses anos e espero que possamos sempre mantermos conectados 'oceanograficamente'.

A todos os meus amigos da Hidroquímica, obrigado pelas análises compartilhadas e as saídas à campo. Agradeço pelos debates, conversas, almoços, enfim, pelo companheirismo de sempre.

A todos os professores, incluindo os membros da banca, que me auxiliaram no conhecimento adquirido durante esses anos. Lembre-se que só pela profissão escolhida, para aqueles que fazem o que realmente gostam vocês tornam-se pessoas especiais.

Agradeço, também, ao Programa de Pós-Graduação em Oceanologia da Universidade Federal do Rio Grande (FURG) pela estrutura física e intelectual; e a Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) pela bolsa concedida.

Índice

Lista de Figuras da Tese

Lista de Figuras dos Manuscritos

Manuscript 1: Effects of coastal lagoon water level on groundwater fluxes of nutrients to the coastal zone of southern Brazil

Manuscript 2: Washouts as continental sources of dissolved elements to the coastal ocean in southern Brazil and its hydrogeological characteristics

Lista de Tabelas dos Manuscritos

Manuscript 1: Effects of coastal lagoon water level on groundwater fluxes of nutrients to the coastal zone of southern Brazil

Manuscript 2: Washouts as continental sources of dissolved elements to the coastal ocean in southern Brazil and its hydrogeological characteristics

Lista de Acrônimos e Abreviações

DAS: Descarga de Água Subterrânea

ELP: Estuário da Lagoa dos Patos

ENOS: El Niño Oscilação Sul

ENSO: El Niño-Southern Oscillation

GPR: Ground Penetrating Radar

LP: Lagoa dos Patos

PL: Patos Lagoon

PLE: Patos Lagoon Estuary

PLwl: Patos Lagoon water level

Q_{fw}: Componente de água doce da Descarga de Água Subterrânea

Q_{sw}: Componente de água marinha da Descarga de Água Subterrânea

RSCP: Rio Grande do Sul Coastal Plain

SGD: Submarine Groundwater Discharge

STE: Subterranean Estuary

Prefácio/Hipótese

Os fatores climáticos sazonais e interanuais, tais como os índices pluviométricos e o fenômeno do El Niño Oscilação Sul (ENOS) interferem nos processos de lixiviação, disponibilidade e retenção de compostos dissolvidos nos aquíferos costeiros. A zona de transição na região de praia é dominada por sedimentos arenosos permeáveis e caracterizada pela mistura da água subterrânea doce e marinha, onde forma-se o estuário subterrâneo. Esse processo altera a forma química dos elementos dissolvidos não somente pelo gradiente de mistura, mas pela formação dos sangradouros, outro vetor de fluxo de elementos dissolvidos da zona costeira. Como nem toda a água que se apresenta no solo arenoso pode escoar através dos sedimentos até a praia, formam-se ambientes alagados no pós-duna que dão origem aos sangradouros e que tendem a aumentar em número e vazão em períodos chuvosos. Sua distribuição é influenciada pelas características geomorfológicas sedimentares da barreira arenosa ao longo da costa. Nesse grande sistema, esses canais de escoamento atuam como a principal fonte de elementos dissolvidos para o oceano costeiro sul do Brasil.

Resumo

As zonas costeiras são ambientes de transição que desempenham importante função de ligação entre os ecossistemas terrestres e marinhos. Os intrínsecos processos de formação da Planície Costeira do Rio Grande do Sul (PCRS), como a presença de grandes corpos lagunares (Complexo lagunar Patos-Mirim) e inúmeras lagoas costeiras, contribuíram significativamente no desenvolvimento dos aquíferos costeiros do ambiente, os quais estão conectados com o oceano devido à formação de um gradiente hidráulico positivo entre esses corpos hídricos. Este processo favorece a advecção de água subterrânea em direção à costa, constituindo a descarga de água subterrânea, uma importante fonte de elementos dissolvidos para o oceano costeiro. Dessa forma, no primeiro manuscrito, a descarga de água doce continental associada aos nutrientes inorgânicos dissolvidos foi estimada considerando os cenários de alto e baixo nível de água da Lagoa dos Patos (LP). Os fluxos subterrâneos foram estimados a partir da Lei de Darcy, um método antes nunca utilizado na PCRS, e encontrado uma taxa de advecção de 0,043 m^3 km^{-1} dia^{-1}. Os diferentes cenários de nível da LP mostraram mudanças na disponibilidade dos nutrientes ao longo da interface aquífero-oceano. No cenário de menor nível de água da LP, as concentrações dos nutrientes nesse trajeto foram significativamente maiores, com um aumento de aproximadamente 25%. No cenário de maior nível de água da LP, as concentrações dos nutrientes tiveram uma diminuição de pelo menos 78%. Considerando a razão molar de Redfield, o fósforo (P) foi o elemento potencialmente limitante, podendo sustentar uma produtividade primária potencial de 2735 gC m^{-2} ano^{-1}. Além dos aquíferos costeiros, no litoral do Rio Grande do Sul encontram-se numerosos corpos d'água superficiais, denominados sangradouros, os quais fazem parte da drenagem da planície costeira. Considerando toda a extensão da costa, o número de sangradouros é bastante significativo. Portanto, o segundo manuscrito teve como objetivos avaliar de forma inédita a disponibilidade dos nutrientes, carbono e ferro dissolvidos nos sangradouros e sua contribuição em termos de concentração para o oceano. Além disso, devido a água subterrânea na região de praia ser uma das fontes majoritárias para a formação e manutenção desses corpos hídricos, utilizou-se o Radar de Penetração do Solo (GPR) como ferramenta para entender a interação entre os compartimentos superficial e subterrâneo, a influência de água doce dos sangradouros nos aquíferos e a extensão dessa interação. A influência do fluxo de água doce pelo sangradouro pode atingir 1,000 m de extensão e uma calha de até 3.2 m de profundidade. A vazão média de água doce dos sangradouros foi fortemente influenciada pelas taxas pluviométricas, variando entre 0.12 m^3 s^{-1} e 0.95 m^3 s^{-1}, nos períodos seco e chuvoso, respectivamente. Em toda a PCRS, os sangradouros podem representar 28% da vazão média do estuário da Lagoa dos Patos e ser 25% mais alto que a vazão de água doce da Lagoa de Tramandaí. A alta vazão no período chuvoso influenciou os fluxos dos elementos dissolvidos, com estimativas de 274 ton ano^{-1} para SiO_4^{4-}, 0,42 ton ano^{-1} para PO_4^{3-}, 7,07 ton ano^{-1} para N inorgânico total, 1,7 ton ano^{-1} para Fe e 262 ton ano^{-1} para C dissolvido total. A partir dos fluxos de nitrogênio inorgânico, os sangradouros podem sustentar uma produtividade primária potencial na zona de surfe de 18 gC m^{-2} ano^{-1}, considerando toda a PCRS. Portanto, o estudo mostrou que tanto os aquíferos costeiros, quando os sangradouros da PCRS devem ser considerados como fonte importante de água doce continental e elementos dissolvidos para o oceano costeiro na PCRS.

Palavras-chave: Planície costeira; aquíferos costeiros; descarga de água subterrânea; nutrientes; fluxos; sangradouros; elementos dissolvidos.

Abstract

Coastal zones are transition environments that play an important role in linking terrestrial and marine ecosystems. The formation processes of the Rio Grande do Sul coastal plain (RSCP), such as large lagoons (Patos-Mirim Lagoon Complex) and numerous coastal lagoons contributed significantly to the development of the coastal aquifers in the environment, which are connected with the ocean due to the positive hydraulic gradient between these water bodies. This process favors the advection of groundwater towards the coast, with the groundwater discharge being an important source of dissolved elements to the coastal ocean. Thus, in the first manuscript, fresh groundwater nutrient fluxes to the coastal ocean were estimated considering high and low PL water level scenarios. The groundwater fluxes were estimated applying Darcy's Law and the result was 0.043 m^3 km^{-1} day^{-1}. Different low and high PL water level scenarios showed a change in the nutrient availability along barrier. In the lowest PL water level scenario, the nutrient flux concentrations became more significant, which may have had an increase of approximately 25%. In the highest PL water level scenario, concentrations had a decrease of up to 78%. In the molar ratio, P resulted as a potentially limiting nutrient, providing a high primary productive potential to the environment (2735 gC m^{-2} y^{-1}). In addition to coastal aquifers, within the coastal zone of Rio Grande do Sul several surficial water bodies (washouts) are found, which take part on the drainage of the coastal plain. Considering the entire extension of the coast, the number of washouts is very significant, thus, this study aims to assess in an unprecedented way the availability of nutrients, carbon and iron, dissolved in washout waters and its contribution in terms of concentration to the coastal ocean. Furthermore, due to groundwater in the beach region being one of the major sources for the formation and maintenance of these water bodies and influencing their hydrochemistry, we used the Ground Penetrating Radar (GPR) as a tool to understand the interaction between the surficial and subterranean compartments, the influence of freshwater from the washouts on the aquifers and the extent of this interaction. The influence of the freshwater flux through the washout may reach 1,000 m in length and a trough of up to 3.2 m. The medium outflow of freshwater by the washouts was heavily influenced by the rainfall, ranging between 0.12 m^3 s^{-1} and 0.95 m^3 s^{-1}, in the dry and wet seasons, respectively. Throughout the RSCP, washouts may represent 28% of the medium freshwater outflow from the Patos Lagoon Estuary (PLE) and can top the outflow from Tramandaí Lagoon by 25%. The high outflow in the wet season impacted on the dissolved elements flux, with estimates of 274 ton y^{-1} for SiO_4^{4-}, 0.42 ton y^{-1} for PO_4^{3-}, 7.07 ton y^{-1} for total inorganic N, 1.7 ton y^{-1} for Fe and 262 ton y^{-1} for total dissolved C. Reckoning the values for the inorganic nitrogen flux, the washouts can support a potential primary production in the surf zone of 18 gC m^{-2} y^{-1}, considering the entire RSCP.

Keywords: Coastal plain; coastal aquifers; submarine groundwater discharge; nutrients; fluxes; washouts; dissolved elements.

Capítulo I:

Introdução

1. Introdução

As zonas costeiras são ambientes de transição que desempenham importante função de ligação entre os ecossistemas terrestres e marinhos. São ambientes complexos e diversificados, incluindo os estuários, manguezais, praias, costões rochosos, entre outros, e apresenta grande relevância para a sustentação da vida no mar (CARVALHO & RIZZO, 1994). A água é parte integral deste sistema, e componente fundamental na dinâmica do meio ambiente. Impulsiona os diversos ciclos biogeoquímicos e está diretamente ligada à sustentação da vida na Terra (SILVEIRA, 1997; PRESS et al., 2006). Cada espaço onde a água é armazenada constitui um reservatório, como os oceanos, as geleiras, os aquíferos, os rios, a atmosfera e a biosfera. O movimento dessa água através desses reservatórios interage com os mais variados componentes da atmosfera, do oceano e da paisagem, no qual a principal característica do volume de água é a sua instabilidade e mobilidade no ambiente (PRESS et al., 2006).

Parte importante desse sistema de interface continente-oceano são as planícies costeiras, regiões das mais dinâmicas do planeta devido aos intensos processos que ocorrem em escalas temporais distintas (diárias, sazonais, decadais) e seu arranjo no espaço (Barboza et al., 2009). Na região sul do Brasil, a planície costeira do Rio Grande do Sul (PCRS) desenvolveu-se, basicamente, a partir de dois tipos de sistemas deposicionais durante o Quaternário: (1) Sistema de Leques Aluviais, na porção mais interna, próximo às áreas-fonte; e (2) Sistema tipo Laguna-Barreira, na porção leste, cuja formação foi controlada por quatro grandes eventos transgressivos-regressivos do oceano (Sistemas Laguna-Barreira I, II, III e IV) (Villwock & Tomazelli, 2007; Barboza et al., 2009).

As barreiras geradas foram responsáveis pela formação dos grandes corpos lagunares no Estado do Rio Grande do Sul, caracterizando de forma única a paisagem desta região costeira, onde destacam-se a Lagoa dos Patos (LP), a Lagoa Mirim e a Lagoa Mangueira (BARBOZA et al., 2009). Os quatro sistemas deposicionais (Barreiras I, II, III e IV) correspondem a depósitos sedimentares predominantemente arenosos de origem praial e eólica e areno-lamosos de origem lagunar. As fácies sedimentares decorrentes destes sistemas deposicionais foram, então, moldadas pelos processos internos (de cada sistema), e externos, como o tectonismo, as variações climáticas e as flutuações do nível relativo do mar durante o período Cenozoico (VILLWOCK & TOMAZELLI, 2007).

Grande parte desta planície apresenta sedimentos permeáveis que expõe aquíferos superficiais como um sistema aberto. Neste grande sistema, a água possui um trânsito livre que permite o escoamento superficial e subterrâneo, tanto para os corpos lagunares, quanto para a região costeira (Windom *et al.* 2006; Niencheski *et al.* 2007; Santos, et al., 2009; Andrade et al., 2012). Os aquíferos costeiros rasos têm grande importância como fontes de elementos dissolvidos para as águas costeiras (Kroeger & Charette, 2008; Moore, 2010; Null et al., 2012). A zona sedimentar representada por sedimentos permeáveis faz parte de um ambiente onde a dinâmica dos elementos dissolvidos é governada pela reciclagem diagenética desses compostos (Billerbeck et al., 2006), pela recirculação da água subterrânea e/ou pela infiltração da água subterrânea continental, em um grande sistema de fluxos (Figura 1) (Charette & Sholkovitz, 2002; Ullman et al., 2003).

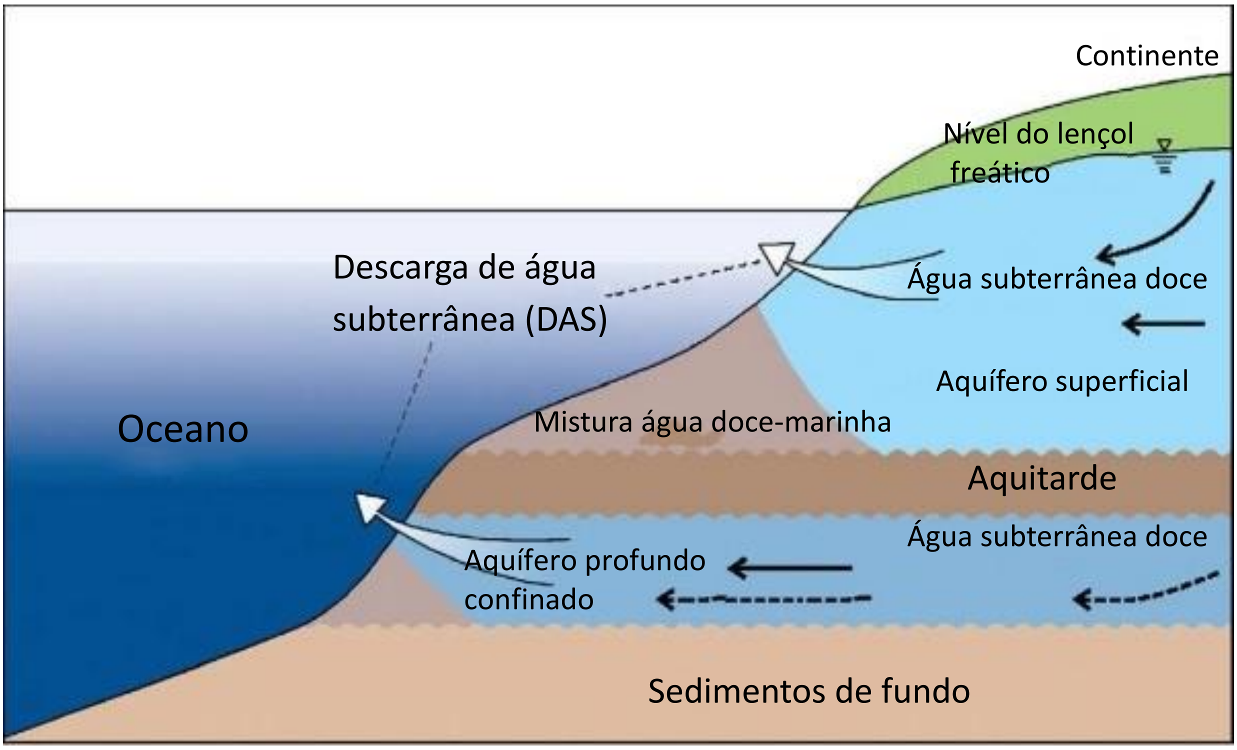

Figura 1: Sistema teórico de fluxos subterrâneos na interface continente-oceano (Adaptado de Burnett et al., 2006).

Esse processo ocorre onde os aquíferos apresentam um gradiente hidráulico positivo em relação ao nível do mar e, portanto, a descarga de água doce através dos sedimentos de praia é reconhecida como um processo generalizado. O aporte de água doce pode alterar os ciclos desses elementos (Bowen et al., 2007; Kroeger & Charette, 2008; Spiteri et al., 2008), de forma que as estimativas desses fluxos podem ser muito variáveis e sua quantificação ainda é um desafio. Fatores regionais como a geologia, as condições climáticas e os regimes de precipitação (recarga) dos aquíferos costeiros, contribuem nas interações geoquímicas ao longo da região de praia e, consequentemente, nas altas variabilidades desses processos.

As descargas de água doce continental para a costa do Rio Grande do Sul possuem ainda uma outra componente. A região de praia apresenta diversos cursos d'águas (sangradouros), os quais fazem parte da drenagem da planície costeira, dando escoamento às águas pluviais coletadas nas depressões e banhados localizados entre os cordões litorâneos, e em locais de relevo inexpressivo (Figura 2) (Figueiredo & Calliari 2005). Alguns sangradouros são permanentes e outros ocorrem somente nas estações chuvosas em resposta a elevação do nível do lençol freático (Figueiredo et al. 2007). Como nem toda a água que se apresenta no solo arenoso pode escoar através dos sedimentos até a praia, formam-se ambientes alagados no pós-duna que dão origem aos sangradouros e que tendem a aumentar em número e vazão em períodos chuvosos. Sua distribuição é influenciada pelas características geomorfológicas sedimentares da barreira arenosa ao longo da costa (Figueiredo & Calliari, 2005).

Figura 2: Distribuição dos sangradouros na planície costeira do Rio Grande do Sul. Fonte Figueiredo & Calliari, 2005.

Na PCRS, embora tenham sido descritos em relação a distribuição espacial, variação sazonal e geomorfologia (Pereira da Silva *et al.*, 2003; Figueiredo & Calliari, 2006; Figueiredo *et al.*, 2007), os sangradouros ainda não foram estudados quanto ao seu papel de fonte de água doce continental para o oceano costeiro adjacente, tampouco os fluxos de elementos dissolvidos, que influenciam diretamente na produtividade primária das praias arenosas, ambientes geralmente dependentes de fontes alóctones (Colombini & Chelazzi, 2003; Odebrecht *et al*., 2013). Mesmo atuando em escala local, quando investigados para os 620 km da região costeira, os sangradouros passam a ser grandes carreadores de material orgânico e elementos dissolvidos para as águas costeiras. Nesse sentido, a tese propõe estudos sobre os fluxos de água doce continental e de elementos dissolvidos nos compartimentos superficiais e subterrâneos da PCRS, geralmente negligenciados nos estudos dos ciclos biogeoquímicos regionais e globais.

No primeiro manuscrito, avaliamos a hidroquímica dos aquíferos costeiros frente às concentrações dos nutrientes inorgânicos dissolvidos e o aporte desses elementos para as águas costeiras adjacentes. Para isso, avaliou-se como o sistema de fluxos subterrâneos funciona na barreira arenosa que separa a Lagoa dos Patos do Oceano Atlântico, e como os parâmetros climático (taxas pluviométricas) e hidrológico (nível de água da LP) influenciam esse sistema. Utilizou-se uma técnica ainda não usada para essa região, que envolve o método de fluxos através da Lei de Darcy e, a parir de uma longa série de dados de nutrientes, investigou-se a descarga de água doce subterrânea em períodos de alto e baixo nível da LP e os fluxos subterrâneo dos nutrientes.

No segundo manuscrito, avaliou-se de forma inédita a concentração de nutrientes, ferro e carbono dissolvido nos sangradouros da planície costeira e os fluxos desses elementos para o oceano costeiro adjacente. Devido à interação hidrogeológica entre o ambiente superficial e subterrâneo, o estudo deu os primeiros passos no entendimento da conexão entre esses dois compartimentos, a influência da água doce dos sangradouros nos aquíferos costeiros de praias arenosas e a extensão dessa interação. Por razão do grande número de sangradouros na PCRS (Figueiredo & Calliari, 2005), avaliou-se de forma inédita a disponibilidade dos elementos dissolvidos e sua contribuição em termos de concentração para o oceano costeiro.

1.1. Área de estudo

A planície costeira do Rio Grande do Sul (PCRS), localizada entre os paralelos 29º15'S e 33º45'S, possui cerca de 620 km de extensão, sendo a mais ampla planície costeira do Brasil. Limitada a norte pelo município de Torres e a sul pela desembocadura do Arroio Chuí, a linha de costa é praticamente retilínea com orientação NE-SW (Tomazelli & Villwock, 2000; Barboza et al., 2009). Entre seus limites, a morfologia de praia arenosa é observada em toda a costa e somente interrompida, de forma não temporária, em duas regiões mais importantes, correspondentes ao estuário da Lagoa dos Patos e a Laguna de Tramandaí (Barboza et al., 2009).

A costa do Rio Grande do Sul é tipicamente dominada por ondas e ventos, com baixa influência da maré astronômica, cuja amplitude média é em torno de 0,5 m. Consequentemente, os processos de transporte e deposição de sedimentos são dominados pela ação das ondas e correntes. O litoral é exposto e diretamente influenciado por esses processos. A alta disponibilidade de sedimentos na plataforma, favorece a formação de extensas barreiras arenosas ao longo de toda a costa.

A região costeira é constituída de uma sucessão de terraços planos, intercalado com depressões alongadas, onde encontram-se lagunas, lagos e pântanos de diferentes estágios evolutivos. As praias são classificadas como intermediárias a dissipativas, com algumas variações nesse padrão em função da granulometria dos sedimentos (Calliari & Klein, 1993).

O clima está sob a influência do centro de alta pressão do anticiclone do Atlântico Sul, com predominância de ventos NE ao longo do ano. Durante a passagem de tempestades costeiras, ventos de NW-S são dominantes e comuns durante o inverno devido ao deslocamento do centro de alta pressão. Esses fatores provocam o empilhamento de água junto à costa por efeito de Ekman e, portanto, a elevação do nível do mar na costa e alterações na morfologia praial (Calliari *et al.,* 1998).

A precipitação pluviométrica anual não apresenta uma sazonalidade bem definida, embora maiores índices ocorram nos meses de inverno e primavera, e menores no verão. Por outro lado, fenômenos climáticos como o El Niño Oscilação Sul (ENOS) influenciam as variações interanuais nos padrões de precipitação pluviométrica na região sul do Brasil. Anomalias positivas ocorrem em períodos de *El Niño* e negativas em *La Niña* (Grimm *et al.,* 2000; Pasquini *et al.*, 2012), alterando diretamente a descarga de água doce continental.

1.1.1. Aquíferos costeiros

Os intrínsecos processos de formação da PCRS foram determinantes para a geração dos aquíferos costeiros da região. Diversos estudos foram desenvolvidos em relação ao transporte advectivo de substâncias através dos sedimentos permeáveis e a descarga de água doce desses aquíferos para as águas costeiras adjacentes. O sistema de aquíferos relatados aqui faz parte da chamada Barreira Múltipla Complexa (Villwock, 1984), formada durante a transgressão marinha pós-glacial do Holoceno e que separa a Lagoa dos Patos do Oceano Atlântico (Windom & Niencheski, 2003) (Figura 3). Essa barreira é caracterizada pela presença de sedimentos permeáveis e que ocupam os 240 km de costa da região central da PCRS, abrangendo toda a margem leste da Lagoa dos Patos (Dillenburg et al., 2002).

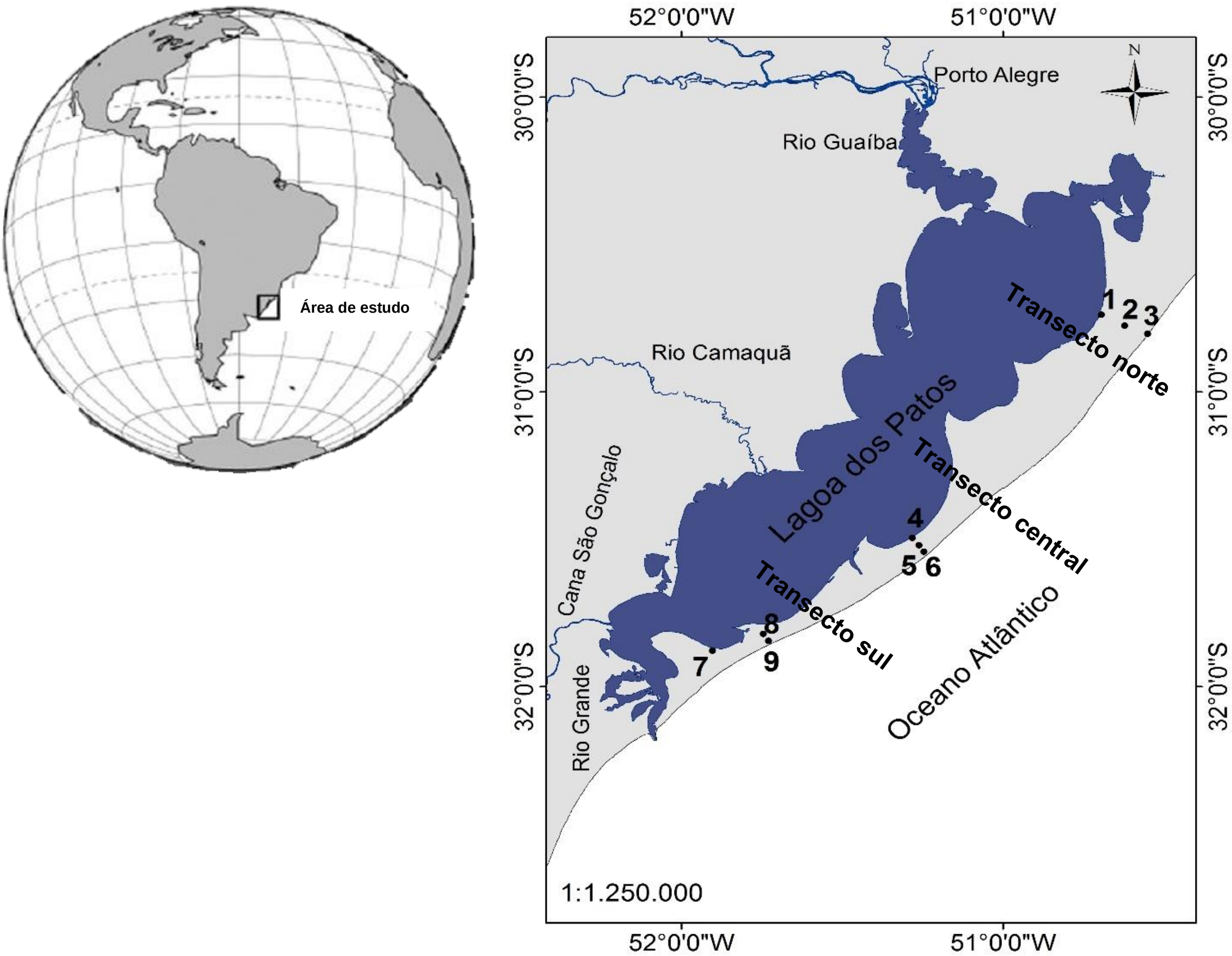

Figura 3: Representação da área de estudo e localização dos aquíferos da barreira arenosa que separa a Lagoa dos Patos do Oceano Atlântico, na forma de transecto (norte, central e sul).

A Lagoa dos Patos resultou, sobretudo, dos processos deposicionais ocorridos até a formação da planície costeira do Rio Grande do Sul. Situada entre 30° e 32° Sul, é a maior lagoa costeira do Brasil, possuindo aproximadamente 250 Km de extensão e largura média de 60 Km. Tem um perfil alongado no sentido NE-SW e é considerada um corpo hídrico relativamente raso, com profundidade média de 6 metros (Castelão & Moller Jr, 2003). Sua sedimentologia é caracterizada por sedimentos que variam de areia grossa a muito fina, silte e argila. Representado como um importante corpo hídrico na região, a Lagoa dos Patos é responsável pela drenagem hídrica de metade da área do Estado (200.000 Km2), na qual recebe aporte de vários rios, como o Camaquã, o Guaíba e a Lagoa Mirim a partir do Canal São Gonçalo (Castello & Moller Jr, 1977). Os regimes de fluxos superficiais da Lagoa dos Patos, como a saída de água continental e a entrada de água marinha através dos molhes da barra de Rio Grande, são controlados, principalmente, pela ação dos ventos e da chuva, relacionados aos desníveis que ocorrem dentro da lagoa e na zona costeira (CALLIARI, 1980).

A barreira arenosa que separa a LP do oceano é composta por sedimentos grosseiros clásticos, com a mistura de conchas e grãos mais finos de depósito lagunar. A maior elevação está associada às dunas que podem chegar a 20 m (Dillenburg et al., 2002). Dessa forma, existe um predomínio de fluxo de água doce através dos sedimentos permeáveis da barreira, que se mistura com a água do mar na região de praia, dependente dos fatores climáticos e hidrológicos do ambiente.

1.1.2. Sangradouros

Os sangradouros são canais de escoamento de água doce continental que fazem parte da drenagem da planície costeira, dando escoamento às águas pluviais das depressões e banhados localizados entre os cordões litorâneos, e em locais de relevo inexpressivo atrás do campo de dunas frontais (Figueiredo & Calliari, 2005). A distribuição e geração desses corpos de água são influenciadas pelas características geomorfológicas e sedimentares da planície costeira, como a presença de lagoas próximas à costa, depósitos de turfa e lama e a granulometria dos sedimentos (Figueiredo *et al*., 2007). De acordo com sua distribuição espacial, abastecimento de água e comportamento sazonal, os sangradouros podem ser efêmeros (de menor fluxo e presentes após eventos locais de alta taxa de precipitação pluviométrica), intermitentes (sazonais) ou permanentes (Pereira da Silva, 1998).

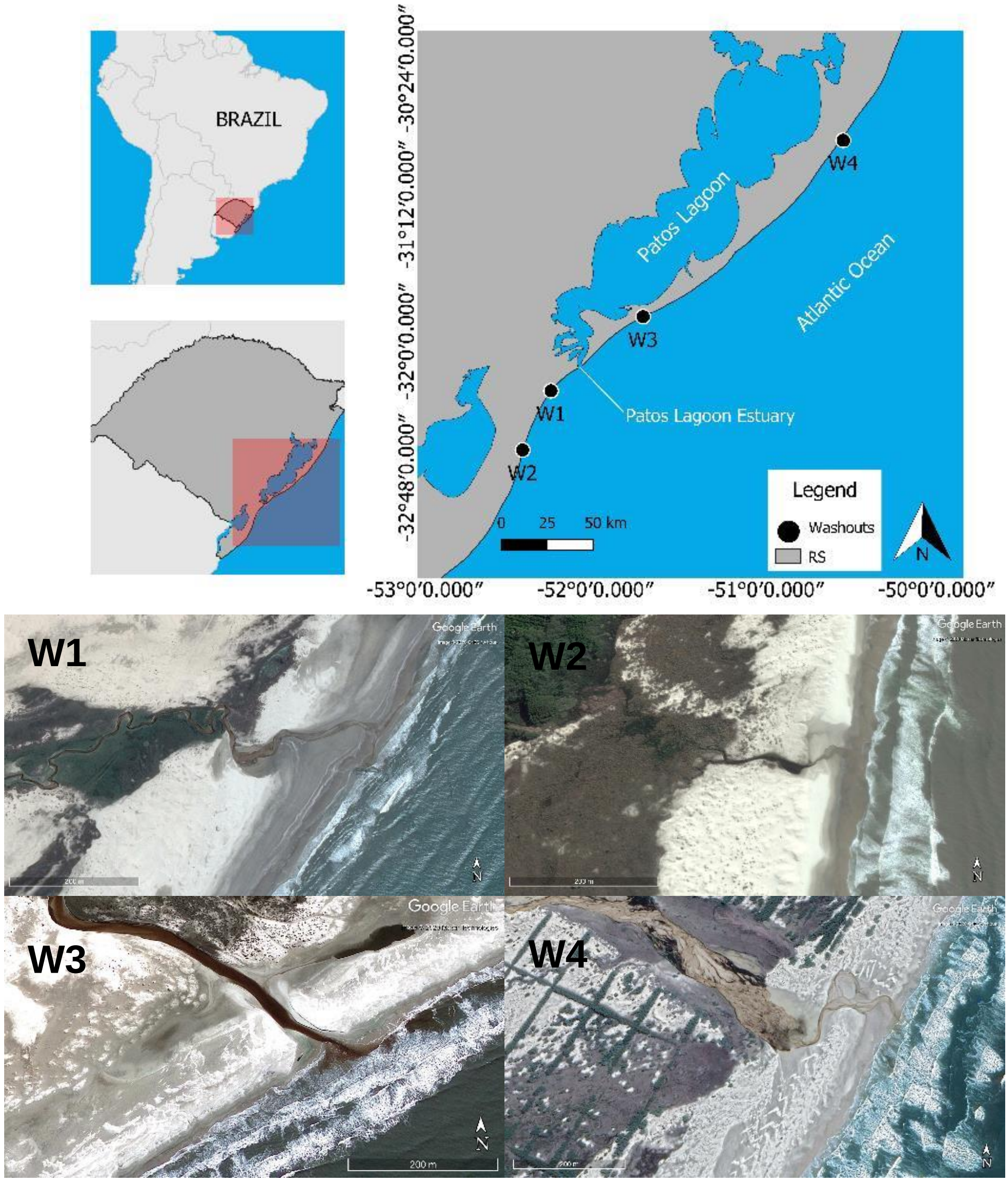

Figura 4: Localização dos sangradouros avaliados (W1, W2, W3 e W4) na planície costeira do Rio Grande do Sul e representação por satélite de cada um deles (Fonte: Google Earth, 2020).

Neste estudo foram escolhidos quatro sangradouros de fluxo permanente (W1, W2, W3 e W4), onde cada um deles representa uma característica específica da região costeira. O W1 (32.2899S 52.602W) e o W2 (32.6371S 52.4270W) estão localizados 20 km e 60 km ao sul da desembocadura do estuário da Lagoa dos Patos (ELP), respectivamente (Figura 4). A região de W1 tem baixo impacto antropogênico devido a uma condição incipiente de urbanização e sem proximidade com lagoas costeiras. Em W2 há uma certa influência da Lagoa Mirim (16 km de proximidade) e não há qualquer tipo de urbanização. O W3 (31.8558S 51.7207W) situa-se 45 km ao nordeste do ELP no distrito do município de São José do Norte-RS, denominado Estreito, e possui cerca de 2,400 habitantes (IBGE, 2000) (Figura 4). Na região de restinga, no limite do sistema de dunas costeiras, ocorre a plantação de *Pinus elliotis* como prática agrícola de pequenos produtores, destacando-se como um importante agente morfológico e ambiental (Gianuca & Tagliani, 2012). O W4 (30.8015S 50.5475W) localiza-se 120 km a nordeste do ELP e 55 km do município de Mostardas-RS (Figura 1). A região não sofre influência antropogênica significativa e nenhum tipo de prática agrícola, com vegetação de espécies adaptadas às condições arenosas (Cunha, 1997). A região de restinga em W3 e W4 possui pequenas lagoas costeiras (lagoas de bolso) (*e.g.* Lagoa do Estreito, Lagoa do Peixe, Lagoa da Figueira), que podem modificar as características hidrológicas locais.

Capítulo II:

Objetivos

2. Objetivos

2.1. Geral

Avaliar a disponibilidade e os fluxos dos nutrientes, carbono e ferro dissolvidos nos aquíferos costeiros e sangradouros da PCRS, e a contribuição de cada compartimento para o oceano costeiro contíguo.

2.2. Específicos

- Avaliar a dinâmica de nutrientes com base em uma série de nove anos de dados, frente aos fatores climáticos e hidrológicos sazonais e interanuais.
- Avaliar a distribuição espacial e temporal de nutrientes, ferro e carbono dissolvidos nos aquíferos, estuário subterrâneo e sangradouros.
- Estimar os fluxos dos nutrientes inorgânicos dissolvidos via descarga de água subterrânea (DAS) na interface aquífero-oceano da PCRS;
- Estimar a vazão de água doce continental, os fluxos de carbono, nutrientes e ferro dissolvidos via descarga de água superficial a partir dos sangradouros;
- Avaliar a conexão entre o ambiente subterrâneo e os sangradouros na região de praia da PCRS, a extensão e profundidade dessa interação.

Capítulo III:

Resultados e Discussões

Para a obtenção do título de doutor pelo Programa de Pós-Graduação em Oceanologia, é requerido que o discente realize a submissão de pelo menos dois artigos científicos como primeiro autor em periódico com corpo indexado. Desse modo, os resultados da pesquisa desenvolvida durante o período de doutorado e a discussão dos resultados serão apresentados em forma de artigo neste capítulo. O primeiro manuscrito, de autoria de Gabriel Karagiannis de Souza, Cátia Milene Ehlert Von-Ahn, Luís Felipe Hax Niencheski e Carlos Francisco Ferreira de Andrade, é intitulado “**Effects of coastal lagoon water level on groundwater fluxes of nutrients to the coastal zone of southern Brazil**” e foi aceito para publicação no periódico “J*ournal of Marine Systems”*. O segundo manuscrito, de autoria de Gabriel Karagiannis de Souza, Miguel da Guia Albuquerque, Carlos Augusto Barbosa da Silva, Luis Felipe Hax Niencheski e Carlos Francisco Ferreira de Andrade, é intitulado **Washouts as continental sources of dissolved elements to the coastal ocean in southern Brazil and its hydrogeological characteristics** e foi submetido no periódico “*Regional Studies in Marine Science”*.

Effects of coastal lagoon water level on groundwater fluxes of nutrients to the coastal zone of Southern Brazil

Gabriel Karagiannis de Souza[1*], Cátia Milene Ehlert Von-Ahn[2], Luís Felipe Hax Niencheski[1], Carlos Francisco Ferreira de Andrade[1]

[1]Laboratório de Hidroquímica, Instituto de Oceanografia, Universidade Federal do Rio Grande, Campus Carreiros, Km 8, s/n, 96201-900 Rio Grande – RS, Brasil

[2]Leibniz Institute of Baltic Sea for Baltic Sea Research (IOW), Geochemistry & Isotope BioGeochemistry Group, D-18119 Rostock, Germany.

[*] Corresponding author.
E-mail addresses: gksouza0@gmail.com (G.K. Souza),
catiavonahn@gmail.com (C.M.E. Von-Ahn),
niencheski@gmail.com (L.F.H. Niencheski),
carlos.fand@gmail.com (C.F.F. Andrade).

Abstract
Groundwater discharge represents a potentially important source of dissolved nutrients to the coastal ocean. The barrier complex along the coast of southern Brazil separates the Patos Lagoon (PL) from the South Atlantic Ocean and supports the formation of the adjacent surficial aquifers which are connected to both water bodies. Due to the high hydraulic head of the lagoon regarding the ocean, groundwater is transported towards the coast. In this study fresh groundwater nutrient fluxes to the coastal ocean were estimated considering high and low PL water level scenarios. The groundwater fluxes were estimated applying Darcy's Law and the result was 0.043 m^3 km^{-1} day^{-1}. Different low and high PL water level scenarios showed a change in the nutrient availability along the barrier. In the lowest PL water level scenario, the nutrient flux concentrations became more significant, which may have had an increase of approximately 25%. In the highest PL water level scenario, concentrations had a decrease of up to 78%. In the molar ratio (106C: 16N: 1P), P resulted as a potentially limiting nutrient, providing a high primary productive potential to the environment (2735 gC m^{-2} y^{-1}).

Keywords: groundwater; fluxes; nutrients, Darcy's law, Patos Lagoon, Brazil

1. Introduction

Coastal aquifers are key hydrogeochemical components that connect the ocean and groundwater resources (ROBINSON et al., 2018). These environments are complex zones due to the combined interaction of oceanic water and continental groundwater forces that lead to complex behavior of subsurface dissolved elements discharging into the ocean (SLOMP & VAN CAPPELLEN, 2004). Coastal aquifer-ocean interactions are important because they can influence coastal water quality and ecosystems due to the discharge of groundwater and its associated chemical elements to the coastal ocean (ROBINSON et al., 2018; MOORE, 2010).

In coastal aquifers associated with coastal sandy barriers, the high permeability of sediments favors advective transport and the recirculation of seawater from the coastal ocean, which maintains the subterranean estuary (STE) (MOORE, 1999; WINDOM & NIENCHESKI, 2003; ROBINSON et al., 2018). STEs are highly dynamic zones, where the magnitude and dispersion of groundwater flow and chemical elements from fresh groundwater and recirculated seawater can react and transform across the sediment-water interface (DORSETT et al., 2011).

The governing hydrological process in the STE is Submarine Groundwater Discharge (SGD) (BURNETT et al., 2003). SGD is recognized as a major source of dissolved constituents to the coastal ocean (MOORE, 2010) and consists of both meteoric groundwater and recirculated seawater (BURNETT et al., 2006). Fresh SGD occurs when an aquifer is hydraulically connected with the ocean and the water table is above sea level. The discharge is controlled by seasonal oscillations of the water table on the land and aquifer characteristics and is driven by hydraulic gradient (MULLIGAN & CHARETTE, 2006, PAIVA & NIENCHESKI, 2018).

In relation to sandy barriers along the coast of southern Brazil, the Patos Lagoon (PL) represents the major coastal lagoon of this barrier complex. The hydraulic gradient formed between the PL water level (PLwl) and sea level allows the fresh submarine groundwater to discharge through the sandy barrier. Rainfall over the PL drainage basin is actively connected to ENSO occurrences in the equatorial Pacific Ocean. A distinctly negative Southern Oscillation Index (SOI) usually results in excess rainfall, high riverine discharge and, accordingly, above normal PL water levels with decadal and inter-annual periodicities (PASQUINI et al., 2012).

Many studies have focused on methods to quantify SGD including physical and hydrologic approaches, direct measurements and chemical tracers (MOORE, 1999; MULLIGAN & CHARETTE, 2006, 2009). Some studies were conducted in the PL barrier using radium isotopes as tracer to estimate SGD flux of nutrients and trace metals (WINDOM et al., 2006; NIENCHESKI et al., 2007). However, none of them evaluated the seasonal fresh groundwater discharge of nutrient fluxes and the interaction with rainfall and PLwl. In this study, groundwater flow was calculated using the Darcy's Law method, an inexpensive and easy approach which says that the flow rate is linearly proportional to the hydraulic gradient (MULLIGAN & CHARETTE, 2009).

In this study, we aim to understand how the groundwater flow system acts on the permeable sand barrier of southern Brazil and how the climate (rainfall) and hydrological (PL water level) parameters influence this system. For this, we applied a method never used before in this region (Darcy's Law) and due to a comprehensive array of nine years of nutrient data, we investigated fresh groundwater discharge in high and low PL water level periods and nutrient fluxes associated of SGD.

2. Methods

2.1. Study site

The study area is defined as a barrier system formed during the Holocene Post-Glacial Marine Transgression (DILLENBURG et al. 2002; WINDOM & NIENCHESKI, 2003) (Figure 1). It is part of the Coastal plain of Rio Grande do Sul state in southern Brazil, and occupies 625 km. It was formed by two types of depositional systems during the Quaternary (Alluvial Fans System and Lagoon Barrier System I, II, III and IV) (TOMAZELLI & VILLWOCK, 2000), by which the Patos Lagoon was formed.

The PL is located between 30°S and 32°S. It is the largest coastal lagoon in Brazil, approximately 250 km long and has an average width of 60 km. It has an elongated profile in the NE-SW direction and is considered a relatively shallow water body with an average depth of 6 meters (MÖLLER et al., 1996; MÖLLER et al., 2001; CASTELÃO & MOLLER JR, 2003). Bottom sediments vary from coarse sands to silts, but coarse sediments predominate. The PL is an important water body in the region, responsible for water drainage from half of Rio Grande do Sul State (200.000 km^2). In addition, along with the Rio de la Plata, it is the only source of fresh water for the adjacent coastal region (CASTELLO & MÖLLER JR, 1977).

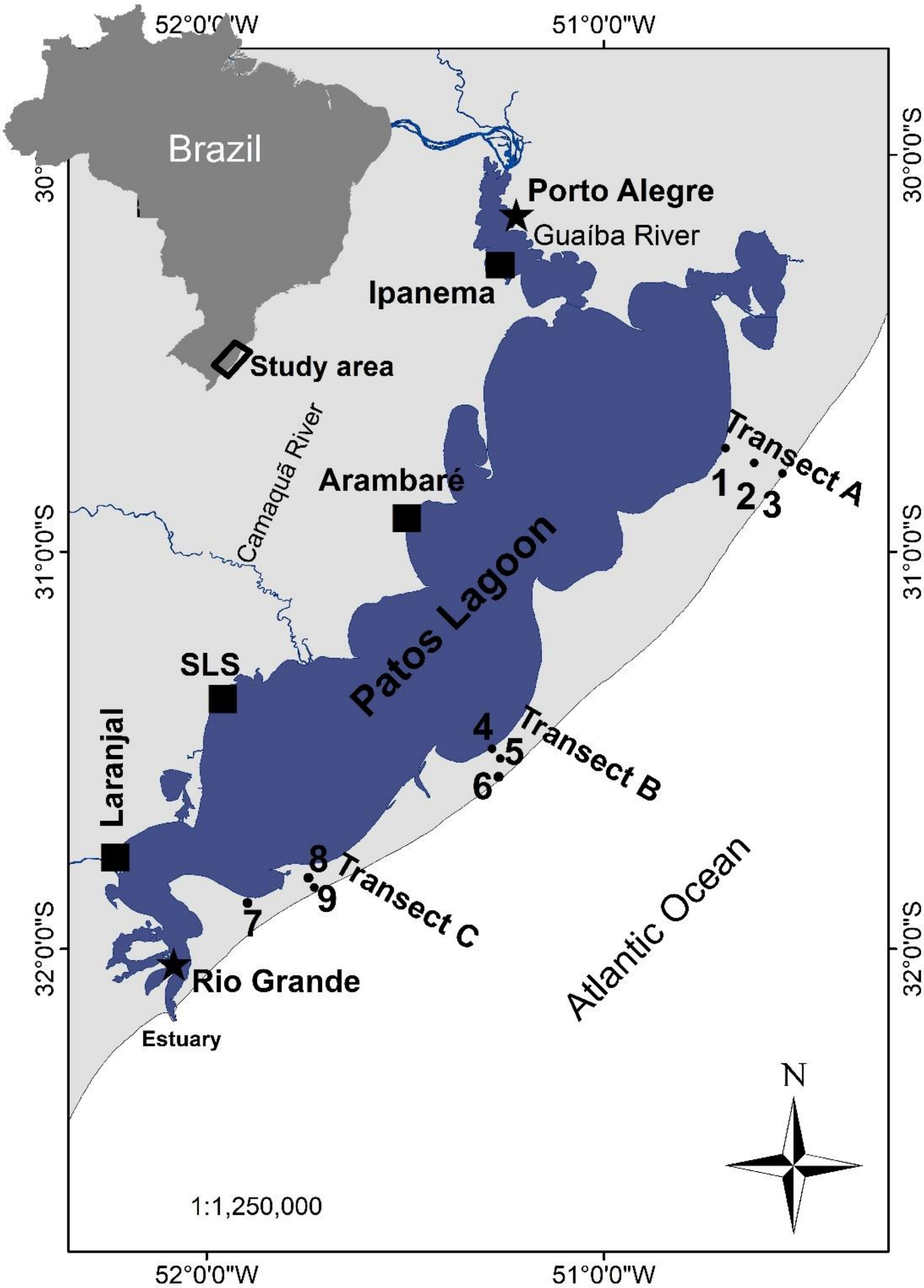

Figure 1: Patos Lagoon study site showing the location of the monitoring well transects (A-north, B-middle and C-south) and hydrometric stations (squares). The ocean-side wells are located behind the primary dune.

The barrier separates PL from the Atlantic Ocean and is composed of relic clastic coarse-grained material including shell hash with finer-grained lagoonal deposits, characterized by high permeability. Maximum elevations of the barrier occur along the axis and are up to ca. 20 m, but average elevations are only a few meters above sea level (DILLENBURG et al., 2002; NIENCHESKI et al., 2007). However, there is a significant flow of fresh water through permeable sediments of the barrier spit, which mixes with seawater depending on the PL flow. There is a predominance of groundwater flow toward the ocean (NIENCHESKI et al., 2007).

2.2. Field and laboratory methods

Sampling of the aquifer was conducted by using a 4-cm-diameter polyvinyl chloride (PVC) pipe. Each transect consisted of three sets of wells, one near the lagoon, one on the interior and one near the beach front (Figure 1). Each set generally included three wells which were screened nominally at 5 m, 10 m and 15 m, with a total of 25 wells. Collection of water samples from the wells began in 2003 and continued into 2012. These permanent wells were sampled approximately every quarter for nutrient and physical-chemical parameters.

Water sampling of the permanent wells was carried out with a peristaltic pumping system that consisted of a single length of acid (HCl)-cleaned silicone tubing. Prior to sampling, each well was pumped for several minutes to clear the well pipe. The samples were filtered with Aqua Prep 600® support and a 0.45 µM cartridge filter and placed directly into pre-cleaned polyethylene bottles. Then, they were kept on ice until returning to the lab at FURG in Rio Grande.

Patos Lagoon water level data was acquired from National Water Agency-ANA (http://hidroweb.ana.gov.br/) and standardized between 0-1. Pearson's linear correlation analysis was used to assess the association between the physical (rainfall and PL water level) and chemical (dissolved nutrients) variables.

The hydraulic conductivity (K) was determined by the Hvorslev slug-test method described in Fetter (2001) (Equation 1). Where K is the hydraulic conductivity (cm s^{-1}); r is the radius of well casing; R is the radius of well screen; L is the length of well screen; and t_{37} is the time required of the water level to rise 37% of the initial change, obtained from the graph of H_0 (distance the water level declines upon removal of a slug of water) and H (height of the water level below the static water level at the some time, "t", after the slug is removed).

$$K = \frac{r^2 \ln\left(\frac{L}{R}\right)}{2Lt_{37}} \quad (1)$$

Darcy's Law flow rate (Q) was estimated by equation 2, where Q is the flow rate, K is the hydraulic conductivity, h/L is the hydraulic gradient (h is the load dissipation in percolation and L is the load dissipation distance), and A is the section area (TODD, 1959). This hydrologic approach is typically applied to estimate fresh groundwater discharge toward any direction if there is a positive hydraulic gradient.

$$Q = K \times A \times (h/L) \quad (2)$$

In order to estimate the groundwater nutrient fluxes across the continent-ocean pathway, a drive-point piezometer system, similar to that used by Niencheski, et al., (2007) was applied to sample groundwater along the beach of the PL barrier down to a maximum depth of 1.5 m. For surf zone (SZ) and beach groundwater (BG) samples, the system was flushed with less water because of filter clogging. Samples were placed directly into 50 mL precleaned polyethylene bottles, stored in plastic bags and put on ice during the return trip to FURG for analysis. Samples were collected during November, 2003; February, 2004; July and December, 2005; January, 2006; July, 2007, February, 2009; and December, 2012.

In both permanent, piezometric wells and in the SZ, salinity, conductivity and pH were analyzed in situ with a conductivity meter (YSI 30, Yellow Springs) and pH meter (Mettler Toledo MO120), respectively. Nutrients were analyzed colorimetrically: nitrate, phosphate, and silicate using the method of Strickland and Parsons (1972). Ammonia was analyzed using the method of Aminot and Chaussepied (1983). Our precision estimates of the analyzes are: phosphate, ± 0.03 µM; silicate, ± 0.15 µM; ammonium, ± 0.1 µM; nitrite, ± 0.02 µM; nitrate, ± 0.05 µM. This procedure was standard for all data collection.

2.2.1. Estimating SGD

SGD was estimated for the northern region of the barrier spit, near the municipality of Mostardas-RS. PLwl one of the main parameters evaluated in this study has the most influence in this region of the barrier. Nutrient data from well 3 covers the entire sample series with at least two annual campaigns and nearly two consecutive years of monitoring the groundwater level in this well. Lastly, the soil has no agricultural impact and vegetation adapted to sandy conditions (CUNHA, 1997).

SGD = (Q_{fw} + Q_{sw}), where Q_{fw} is the freshwater component and Q_{sw} is the seawater flux into the permeable sands that is ultimately recycled in the SGD. Q_{fw} was determined using Darcy's Law (Equation 2). This method can be used to obtain this component for all permanent wells in the barrier spit and in any direction if there is a positive hydraulic gradient. Q_{sw} was calculated based on salt balance proposed by Fernandes & Niencheski (1998).

The salt balance allows to know the percentage of fresh or saltwater from a salinity value, as long as the system is considered a steady state (NIENCHESKI & WINDOM, 1994; NIENCHESKI et al., 2007). Variables such as rainfall, water draining past the root zone and water evaporating from discharge areas are not considered. The average salinity of the SZ over the entire study period is considered the maximum salinity (100%) and the average salinity of the BG is a portion of this percentage. Assuming a steady state, SGD must be equal to the mixture of the saltwater and freshwater fractions. SGD then is considered the mixing between fresh and seawater, which in this study represents the sum of Q_{fw} obtained through Darcy's Law and Q_{sw} obtained from the salt balance.

Nutrient fluxes of SGD were estimated using the mean of nutrient concentrations of the three depths from well 3 (nearest to the sea) in the north barrier transect as well as data from BG (piezometric wells, approximately 1 meter deep) and nutrient concentrations measured in the water column (surf zone) adjacent to well 3.

3. Results

3.1. Permanent wells

The hydraulic conductivity values show that the barrier spit permeability is quite variable. The K minimum was 23.18 m day^{-1} (well 4-south transect), near PL; and the K maximum was 118.85 m day^{-1} (well 3-north transect), near the ocean. The wells near the lagoon (1, 4 and 7) showed lower K values compared to the wells near the sea (3 and 9), with an average of 49.5 m day^{-1} and 84.6 m day^{-1}, respectively (Table1).

These results reflect the dynamics of the evolution of the Rio Grande do Sul coastal plain. The region nearest to the PL the sediments are characterized as medium to fine, semi-consolidated and with high clay content originated from the lagoonal system. Diversely, near the ocean the sediments are predominantly sandy with greater permeability as consequence of the last depositional system (Holocene-barrier IV) (VILLWOCK & TOMAZELLI, 2007). These variables influence directly the flow rate (Q). The lowest flow rates are observed in the wells near the PL (1 and 7- average of 0.02 m day^{-1}) and the highest in wells near the ocean (3 and 9-average of 0.51 m day^{-1}).

The PL provide local hydraulic gradients resulting in groundwater flow toward the coastline (WINDOM et al., 2006; NIENCHESKI et al., 2007). Thus, the flow rate (Table 1) were obtained from the distance between the permanent wells and coastline. Q data from the middle transect are not shown because it was not possible to acquire depth data from the wells. In addition, the northern region of the PL receives more than 50% of the entire lagoon drainage basin from the Guaíba River. During periods of high runoff, the discharge can reach extremes of *ca.* 25,000 m^3 s^{-1} (KJERFVE, 1986; HERZ, 1997) which results in a higher water level regards to the sea level. In contrast, the water level at the southern region of the lagoon reaches equilibrium with the sea level by the estuary entering seawater and wind action (NIENCHESKI & WINDOM, 1994; NIENCHESKI et al., 2007). Peaks of high and low lagoon levels are observed, which can indicate a drought-flood cycle or high and low rainfall rates. Figure 2 shows the PL water level and rainfall data from the northern barrier region.

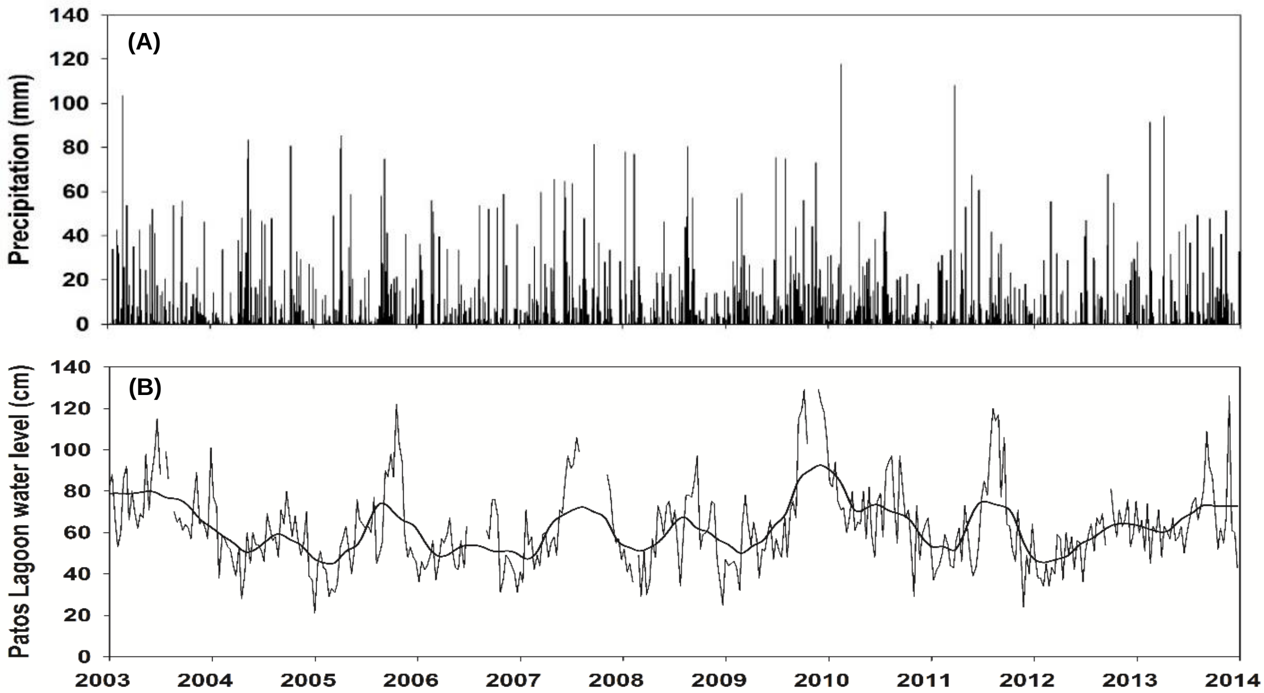

Figure 2: (A) Time series of the rainfall rate (mm) and (B) Patos Lagoon water level (cm) from the northern barrier region (Ipanema hydrometric station - National Water Agency, Brazil).

The Brazilian Geological Service (CPRM, 1985) and the Brazilian National Water Agency-ANA certify that the northern lagoon hydrometric station (Ipanema) is 3.1 m above sea level, while the southern hydrometric station (SLS), 1.4m. Based on the correlation analysis of the PLwl series in both hydrometric stations, most of the time (about 81%) the northern region exhibited a higher level than the southern region, with an average level of 0.2 m higher reaching up to 0.96 m. When comparing Q of the wells near the ocean, well 3-north and well 9-south, the average of Q was 0.9 and 0.13 m day^{-1}, respectively. In this case, the hydraulic gradient was the variable that most drive the water flow rate.

Table 1: Altimetry, depth, hydraulic conductivity (K), Darcy's Law flow rate (Q) and distance from shoreline for permanent wells distributed in the PL sandy barrier.

	Well	Altimetry (m)	Depth (m)	Distance from shoreline (m)	K (m day^{-1})	Q (m day^{-1})
North transect	1 - 10m	2.0	0.57	7400	48.03	0.009
	1 - 15 m		0.63	7400	30.9	0.006
	2 - 10 m	13.0	1.35	6500	99.33	0.18
	2 - 15 m		1.2	6500	26.08	0.05
	3 - 5 m	2.0	0.25	200	115.88	1.01
	3 - 10 m		0.3	200	118.85	1.04
	3 - 15m		0.3	200	74.86	0.64
Middle transect	4 - 5m	1.88	-	-	23.18	-
	4 - 10m		-	-	64.83	-
	5 - 10m	1.88	-	-	75.78	-
	5 - 15m		-	-	100.04	-
South transect	7 - 15m	3.6	0.15	6500	80.38	0.04
	9 - 11m	3.66	1.05	1300	69.53	0.14
	9 - 15m		1.1	1300	25.28	0.05
	9 - 27m		1.1	1300	103.2	0.2

Parameters such as pH, salinity and conductivity were analyzed *in situ*. The pH varied from 5.37 (well 8-10m) to 7.57 (well 9-11m) with a mean of 6.47. The majority of the samples were fresh (i.e. salinity < 0.1) except for a few samples collected from wells 6 and 9 near the ocean side of the barrier. The conductivity ranged from 91.03 µS (well 7-5m) to 74842.14 µS (well 9-15m). Nutrient concentrations ranged from 250.94-920.26 µM for silicate, 0.38-18.05 µM for phosphate, 3.16-180.34 µM for ammonium, 0.13-5.20 µM for nitrite and 1.42-28.40 µM for nitrate. Table 2 shows the average of the results acquired during the nine years of monitoring.

Table 2: Nutrients concentration, micro-moles L^{-1}; pH and conductivity ($\mu S\ cm^{-1}$) in the permanent wells: mean and standard deviation of nine years samples (n = 12-23 sampling campaigns).

Wells	Depth	pH		Conductivity		Silicate		Phosphate		Ammonium		Nitrite		Nitrate	
	(meters)	AVG	STD	AVG	STD	AVG	STD	AVG	STD	AVG	STD	AVG	STD	AVG	STD
1	5	6,98	0,39	494,15	156,69	867,90	504,62	4,33	1,75	25,89	15,19	0,73	2,00	3,99	5,85
	10	7,20	0,39	557,41	54,80	920,25	578,20	4,17	1,73	22,92	8,52	0,33	0,76	2,63	2,38
	15	7,21	0,33	904,00	134,50	859,29	550,64	4,72	2,96	18,56	12,46	0,89	2,91	5,68	11,39
2	5	5,93	0,52	273,23	252,55	320,88	286,10	1,84	2,02	15,15	21,00	1,07	2,40	1,97	2,11
	10	5,90	0,41	184,78	53,86	250,94	183,29	1,77	3,35	6,34	4,46	0,18	0,08	3,56	5,70
	15	6,00	0,44	180,96	50,71	336,53	278,23	5,98	10,42	30,94	38,09	0,89	0,54	6,31	10,22
3	5	6,55	0,44	181,53	23,12	539,73	279,40	2,22	1,05	11,23	5,98	0,29	0,18	1,72	1,82
	10	6,65	0,54	241,69	264,52	691,17	368,40	6,57	4,08	13,15	5,49	0,99	1,96	1,42	1,72
	15	6,44	0,22	196,28	30,12	632,44	342,27	3,53	2,66	15,43	5,99	0,61	0,34	2,50	4,14
4	5	5,76	0,44	156,20	79,59	369,09	286,77	0,46	0,38	3,70	2,60	0,16	0,09	28,40	14,56
	10	5,57	0,33	130,95	55,22	408,31	324,44	0,38	0,38	3,41	3,26	0,55	0,97	25,68	10,18
	15	5,75	0,42	120,73	7,59	545,83	516,99	0,73	1,25	3,76	2,94	0,21	0,16	21,68	12,33
5	5	5,72	0,38	302,48	70,03	258,51	258,64	1,00	1,97	7,16	8,35	0,62	0,69	9,58	4,94
	10	5,80	0,46	169,62	90,37	480,92	411,29	1,08	1,54	9,48	7,98	0,55	0,65	9,20	5,01
	15	5,84	0,32	141,26	20,28	525,41	430,08	0,94	1,35	11,24	12,51	0,53	0,69	8,11	7,92
6	5	7,14	0,47	912,10	362,02	684,09	299,73	7,84	5,54	38,47	27,46	0,18	0,12	4,40	5,53
	10	6,86	0,38	737,00	213,68	691,54	318,16	3,29	1,28	35,19	18,03	0,14	0,07	6,51	11,10
	15	7,18	0,45	868,70	176,62	795,83	351,52	5,71	2,01	25,83	12,74	0,13	0,07	4,69	9,17
7	5	5,73	0,42	91,03	69,73	374,31	304,90	1,14	0,64	4,10	2,87	0,61	1,21	17,23	9,81
	10	7,22	0,54	468,02	178,54	632,22	437,77	3,00	1,16	9,26	10,74	0,35	0,80	2,86	3,30
	15	7,18	0,46	397,80	19,60	911,04	633,27	2,39	1,07	11,71	6,98	0,16	0,17	9,07	8,89
8	10	5,37	0,31	167,35	65,07	306,31	277,44	0,44	0,45	3,16	4,33	0,15	0,05	28,28	19,68
9	11	7,57	0,37	15823,93	16547,12	431,95	256,72	18,05	20,89	38,41	28,85	1,58	3,42	3,69	4,23
	15	7,06	0,25	74842,14	5414,24	430,89	276,14	3,14	2,40	180,34	455,66	5,20	11,10	7,17	6,85
	27	7,16	0,26	32508,09	14045,73	471,58	344,49	2,01	1,88	58,09	37,30	0,32	0,17	10,96	20,44
Mean		6,47		5242,06		549,48		3,47		24,12		0,70		9,09	
Median		6,55		273,23		525,41		2,39		13,15		0,53		6,31	

3.2. Beach groundwater (BG) and surf zone (SZ)

Groundwater samples collected along the beach had a salinity range of 0 (near the dunes) to 30.4 (near the ocean), considering the beach extension of approximately 100 meters, with a total of 8 wells (Figure 3). The dissolved nutrient concentrations ranged from 97.8-396.54 µM for silicate, 0.05-4.37 µM for phosphate, 4.6-41.17 for ammonium, 0.16-0.41 for nitrite and 1.62-4.75 for nitrate. In the surf zone, salinity ranged from 29.6 to 36.3 with a mean of 33.4. Nutrient contents ranged from 9.77–78.73 µM for silicate, 0,16–0,8 µM for phosphate, 1.13–6.87 µM for ammonium, 0.00–0.29 µM for nitrite and 1.15–6.63 µM for nitrate.

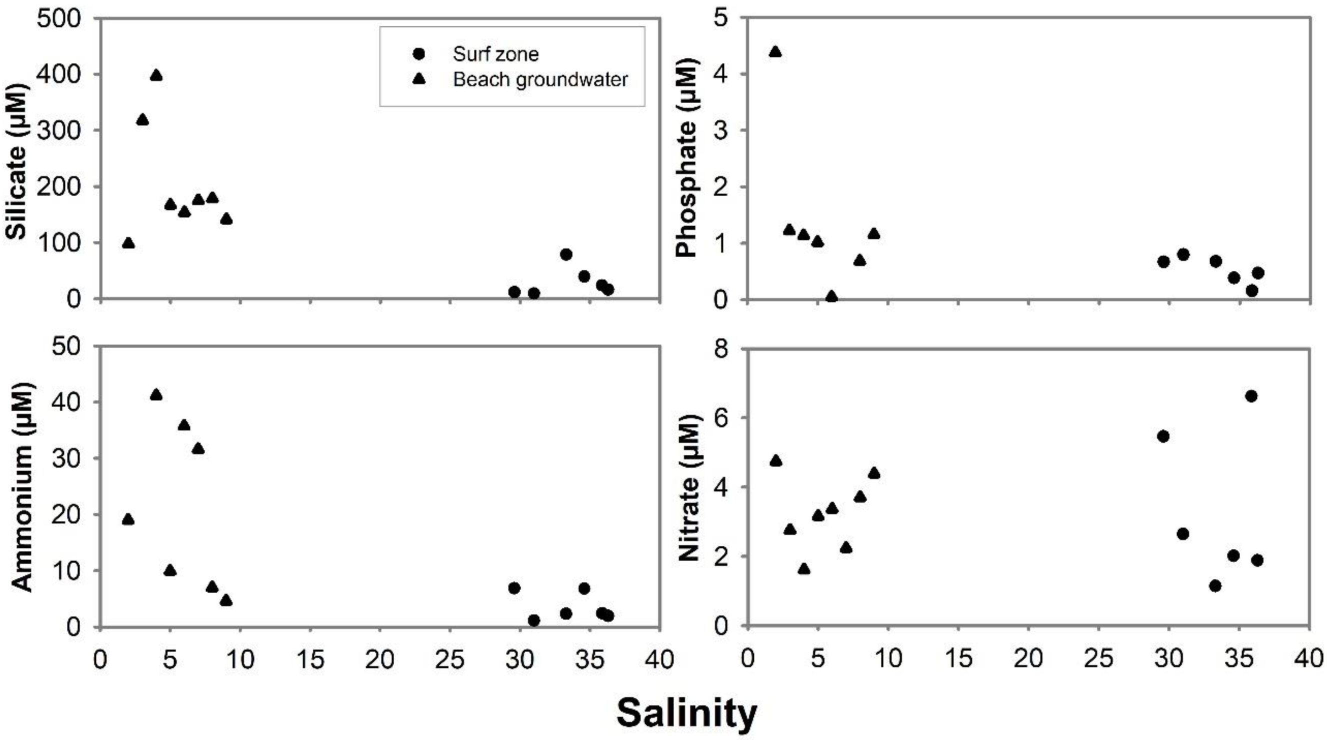

Figure 3: Concentrations of dissolved nutrients in beach groundwater (triangles) and in the surf zone (circles).

In some of the samples, the nutrient concentration was higher in BG compared to SZ, mainly for NH_4^+ and SiO_4^{4-} (Figure 3). However, in some cases, these concentrations were equivalent. This shows that at one-meter depth there is a mixing zone where the groundwater corresponds to recirculating seawater mixing with fresh groundwater. This indicates that the samples were collected in the surface fraction of the water table. The process of seawater recirculation through the permeable sands is responsible for maintaining the SE, and significantly influences the geochemical processes that occur in the mixing zone (WINDOM et al., 2006; NIENCHESKI et al., 2007).

3.3. SGD for northern barrier of Patos Lagoon

Q_{fw} was calculated using Darcy Law, considering the average values of K of the three depths of the wells near the ocean and the altimetry of this region. The area used for estimating the flux is 90 km of coastline (northern region of the barrier) and 10 km offshore, due to a constant cross-shelf mixing (Windom et al. 2006). The Q_{fw} equaled 0.018 m^3 km^{-1} day^{-1}. Based on salt balance, 0.025 m^3 km^{-1} day^{-1} was the seawater flux into the permeable sands that is ultimately recycled in the SGD (Q_{sw}). For this, the average salinity of the SGD was assumed to be 21, the average of the BG, while that of the surf zone was 33.4. Thus, estimated SGD was 0.043 m^3 km^{-1} day^{-1}.

The results can be compared with Niencheski et al., (2007), which used Ra isotopes to calculate the SGD rate at the same study site. The authors found a rate of SGD = 0.035 m^3 km^{-1} day^{-1}, Q_{fw} = 0.013 m^3 km^{-1} day^{-1} and Q_{sw} = 0.023 m^3 km^{-1} day^{-1}. These results are very similar to the results of this study. The results obtained by using Darcy's Law proved that for an environment consisting basically of sandy barriers, the method was effective for calculating groundwater flows. Therefore, this method can be applied in regions that have similar geological characteristics.

4. Discussion

Due to the hydraulic gradient created by the barrier aquifer water levels and sea level, freshwater from the PL flows through permeable barrier sediments toward the adjacent coastal zone. PL is an important water body in the study region due to its size and volume. The influence of PLwl on the aquifer water level can be observed even in the region in the well 15 m deep. The correlation between the groundwater level and PLwl for survey of 2006 until 2008 from well 3-15m was 0.66 (Figure 4). When comparing short periods, the correlation varies between 0.35 and 0.84 in the low and high PLwl scenarios, respectively. The same pattern is observed in dry and wet periods.

Along with direct recharge by rainfall, PL it is the main source of groundwater recharge of barrier aquifers. Thus, we focused on the understanding of this process, which will determine the groundwater pathways of nutrient fluxes via SGD from the barrier. Combined with very low residence time of barrier groundwater, 8.3 days (WINDOM et al., 2006), these results suggest that the PLwl has a strong influence on dissolved nutrient concentration from the barrier.

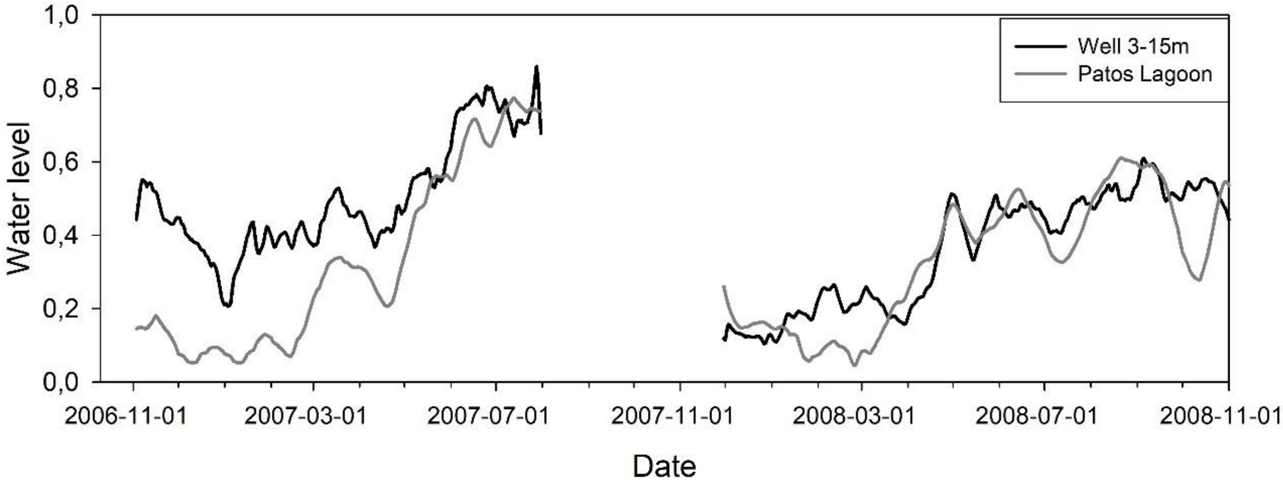

Figure 4: Patos Lagoon water level and groundwater level (well 3-15m) from November, 2006 until November, 2008. Water level data were standardized between 0-1.

The nutrient concentration is inversely proportional to the PLwl. When the PLwl increases, nutrient concentration in groundwater is diluted. In this case, the largest water column in the higher PLwl periods provides increased hydraulic load, and greater water flow. From the correlation analysis between the mean PL annual level and the mean nutrient concentration obtained by an analysis of variance between the sampling campaigns of each year, the PLwl has a negative correlation with all dissolved inorganic nutrients. This is highlighted by PO_4^{3-} (r = -0.74). In addition, there is a strong positive correlation between the PLwl and the accumulated annual rainfall (r = 0.85).

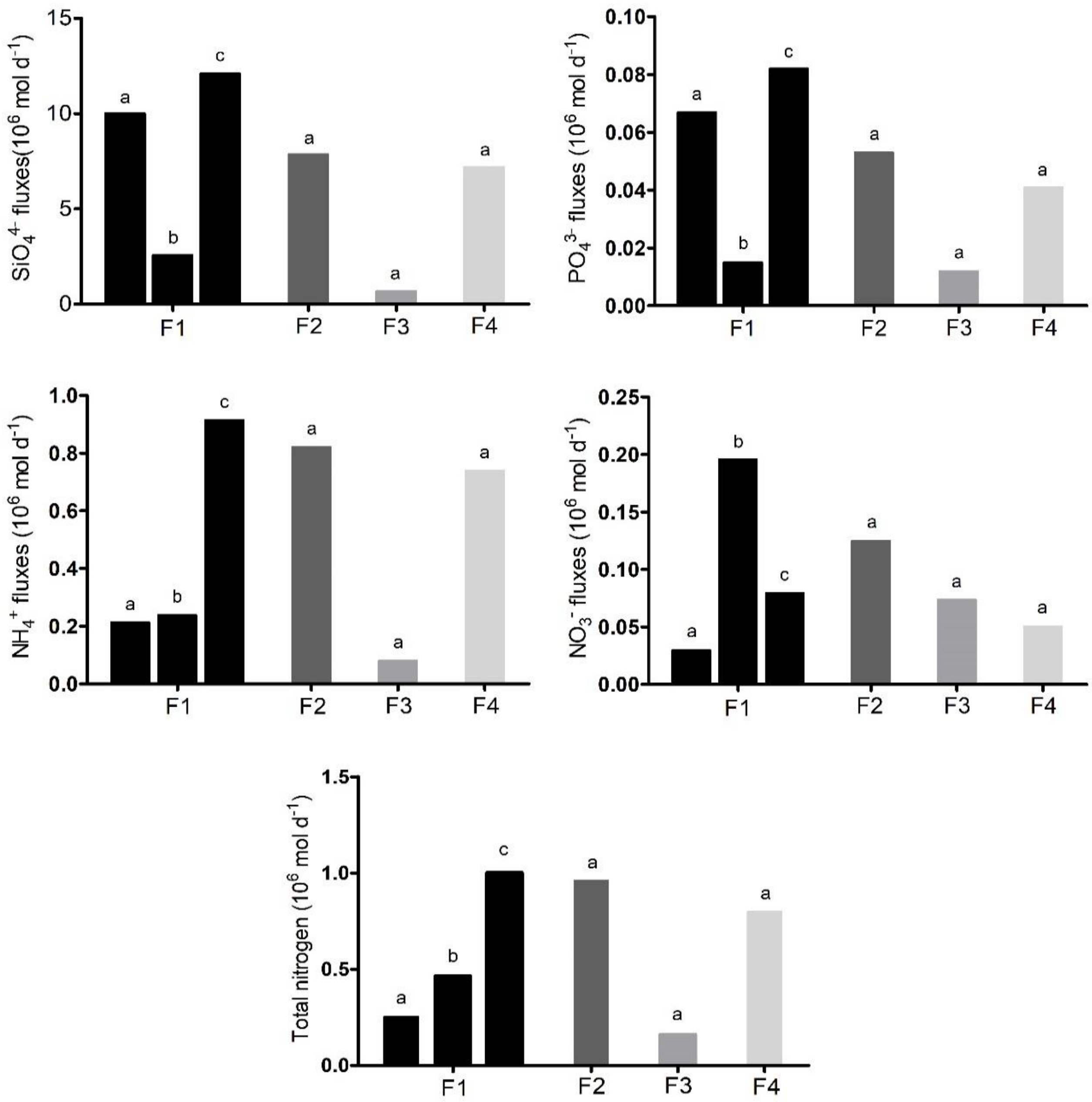

Figure 5:Estimated nutrient fluxes to the coast (x 106 mol day-1). Fresh groundwater discharge (F1) in different scenarios of high and low PL water levels. (a-average fluxes, b-high PLwl and c-low PLwl).

4.1. Nutrient fluxes

Niencheski et al. (2007) developed a conceptual model of nutrient flux in coastal surface water-groundwater systems. These fluxes include fresh groundwater moving toward the ocean (F1), SGD entering the ocean (F2), seawater recirculating through permeable sediments (F3) and the flux to the inner shelf (F4) (Figure 5).

This conceptual model will be used in the present study associating the mean nutrient contents of permanent wells and the mean nutrient contents of different periods of high and low PLwl (Figure 6) for F1. The years 2010 (*n* = 4) and 2004 (*n* = 4) were chosen as the years of highest ($F1_b$) and lowest ($F1_c$) PLwl, respectively due to greater field sampling campaigns.

Silicate fluxes

The highest concentration of the mean silicate fluxes was in $F1_a$ (continental water), with decreasing concentrations the greater the distance from the coastline. This nutrient is considered a natural tracer of groundwater (OEHLER et al., 2019) and, in its dissolved form, it has great importance in the metabolism of aquatic ecosystems as one of the main nutrients used by primary producers, mainly diatoms (ESTEVES, 1998). Consequently, when in contact with SZ surface waters still with high concentration ($F2_a$). There is a continual supply of silicate in fresh groundwater moving towards the shoreline (SOSPEDRA et al., 2018).

In $F3_a$ silicate content becomes significantly less by diluted and mainly by phytoplankton assimilation. Sandy beaches with well-developed surf zones are known to host dense populations of diatoms, which requires a large supply of nutrients for growth (CAMPBELL, 1996; PIEDRAS & ODEBRECHT, 2012). At the sandy and exposed beaches in southern Brazil, the diatom *Asterionellopsis glacialis* (Castracane) Round is the main microalga in the surf-zone and frequently dominates the phytoplankton (PIEDRAS & ODEBRECHT, 2012).

Niencheski et al. (2007) also found lower silicate concentrations for $F4_a$ compared to $F1_a$ due to silicate removal in the nearshore. Silicate may be biologically removed as biogenic silica at the sediment-water interface and associated with high rates of primary production. In addition, microbial degradation in the surf zone may provide an efficient mechanism for silica trapping (WINDOM et al., 2006; NIENCHESKI et al., 2007). Consequently, there is a reduction in the contribution to the adjacent shelf.

Considering the highest PLwl scenario ($F1_b$), silicate content that advects in the beach zone is significantly lower than the average flux ($F1_a$), by approximately 75%. The higher influence of surface water due to the increase of PL level causes a dilution in the silicate content. This corresponds with the high rainfall index, given the strong correlation of these variables (r = 0.85). In relation to the lowest PLwl scenario ($F1_c$), there is an increase of approximately 20% of the average silicate content flux ($F1_a$). Therefore, there is a higher concentration of this nutrient in the STE.

Phosphate fluxes

Phosphate showed the highest concentration of mean fluxes in $F1_{a.}$ The main sources of inorganic phosphorus for the oceans are the weathering of phosphate rock, such as apatite and detrital leaching from soil precipitation (RUTTEMBERG, 2005). Moreover, as shown by Slomp & Van Cappellen (2004), a reduction in PO_4^{3-} flux from the continent to the STE mixing zone is expected. Dissolved PO_4^{3-} is rapidly removed from groundwater through sorption to Fe-oxides or co-precipitation with dissolved Al, Ca or Fe in to mineral phases (BENITEZ-NELSON, 2000; SONG, 2010). Thus, sediment behaves as a large reservoir of P in the marine environment and can be an important source of this element in seawater (ZABEL et al., 1998; ZHUANG et al., 2014).

As can be seen in Figure 5, PO_4^{3-} fluxes have the same pattern as the SiO_4^{4-} fluxes with lower concentrations in $F3_a$. PO_4^{3-} flux reaches the beach zone ($F1_a$) in high concentrations. However, the iron oxide rich sand (WINDOM et al., 2006) acts as a geochemical barrier trapping PO_4^{3-} in the beach sediments. Thus, the concentration of PO_4^{3-} is lower in F2a. Once introduced to the surf zone ($F3_a$), PO_4^{3-} concentration decreases significantly (about 80%) due to mixing with surface water of lower concentrations and/or phytoplankton uptake. In the flux from surf zone to the inner shelf ($F4_a$), PO_4^{3-} concentration is similar to the fresh groundwater flux ($F1_a$) (about 63%). PO_4^{3-} is rapidly remobilized and remineralized in the nearshore region of the intense primary production (NIENCHESKI et al., 2007).

In the highest PLwl scenario ($F1_b$) there was a decrease of about 78% in the PO_4^{3-} flux, while in the lowest PLwl ($F1_c$), there was an increase of approximately 25% in the PO_4^{3-} content. These results corroborate the PO_4^{3-} adsorption/desorption process in groundwater and emphasize the strong negative correlation between PO_4^{3-} and the PLwl (-0.74), PO_4^{3-} and cumulative rainfall (-0.72) over the entire time series. In addition, the contrasting behavior of NO_3^- and PO_4^{3-} in oxic groundwater usually results in an increase of the dissolved inorganic N/P ratio along flow paths (SLOMP & VAN CAPPELLEN, 2004).

Nitrogen fluxes

Among the nitrogen compounds, nitrate had a lower concentration in $F1_a$. This is expected for this nutrient, since the dissolved oxygen concentration in groundwater is low or very low for all permanent wells (NIENCHESKI et al., 2007). This characterizes it as a reductant environment which promotes the ammonification and denitrification processes (SLOMP & VAN CAPPELLEN, 2004; NIENCHESKI et al., 2007). NH_4^+ represents almost the entire total nitrogen content.

When entering the beach zone ($F1_a \rightarrow F2_a$), NO_3^- concentrations increase about 24% as a result of the freshwater and more oxidized ion-rich seawater mixture in the SE. The same occurs with NH_4^+ with an increase of about 26%. Couturier et al. (2017) also found a strong NH_4^+ production along the salinity gradient of the SE with the highest concentration under suboxic conditions and associated to the presence of high dissolved organic nitrogen (DON). The authors attributed the increase of total dissolved nitrogen (TDN) in BG due to release of N from particulate organic matter of terrestrial origin, revealing the reaction of the system.

In the surf zone, NO_3^- and NH_4^+ contents decrease. This is due to phytoplankton uptake and the mixing with surface water of lower concentrations. However, when recirculating through permeable sediments in the beach zone ($F3_a$), NO_3^- returns with higher concentration than NH_4^+. This is because it is being directed from a more oxidized environment, where the high hydrodynamics of the surf zone, such as the waves and the low depth of the water column, contribute to the nitrification process.

In $F4_a$, NH_4^+ content is significantly higher than that of NO_3^- due to the rapid remineralization, which maintains the equivalence among the other fluxes. Couturier et al. (2017) reported that NH_4^+ and DON dominated the TDN load exported from the SE, while NO_3^- represented 1% of the total exported TDN.

When observing the flux averages of NO_3^- in the highest and lowest PLwl scenarios, the nutrient displays the opposite behavior when compared to the other compounds. While NH_4^+, PO_4^{3-} and SiO_4^{4-} concentrations decrease in the year of the highest PLwl, NO_3^- has an increase of about 6 times higher than the average content. In highest PLwl scenario (2010), surface waters of PL with high dissolved oxygen concentration provide greater contact with the surficial aquifer due to higher hydraulic gradient. Han et al. (2015) also found high NO_3^- concentration attributed to more recent recharge to shallow groundwater and in the wet season. This allows the oxidation of nitrogenous compounds and high nitrate concentrations. In contrast, NH_4^+ contents are reduced by about 41% of the average flux due to oxygenation of the groundwater, where part of NH_4^+ may be removed through nitrification and subsequent denitrification (SLOMP & VAN CAPPELLEN, 2004).

In the lowest PLwl scenario (2004), the low PL level provides a lower hydraulic gradient and the aquifer and PL levels are closer to hydraulic balance, resulting in a longer groundwater residence time in the barrier aquifer system. Consequently, NH_4^+ content in a low-level scenario ($F1_c$) is significantly higher than the average NH_4^+ flux ($F1_a$). This is characteristic of a reducing environment.

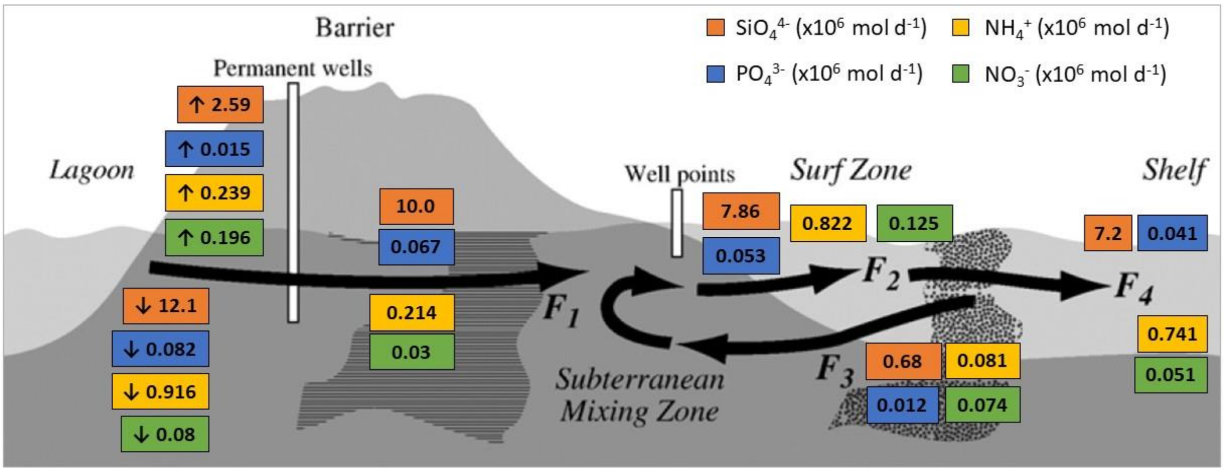

Figure 6: Conceptual model (not to scale) of mean nutrient fluxes in coastal surface water-groundwater system. Fresh groundwater component (F1) in different scenarios of high (↑) and low (↓) PL water levels. Adapted from Nienscheski et al. (2007).

4.2. Uncertainty of flux estimates

We acknowledge that there are considerable uncertainties in the flux calculations. As already mentioned in other studies (NIENCHESKI et al., 2007; MOORE, 2010; RODELLAS et al., 2014; CHO et al., 2018), there is likely more than one fresh groundwater system active in the region and flow is likely heterogeneous within the barrier.

The climate at the Patos Lagoon and surrounding area is complex, especially regarding rainfall rates and the supplying of the drainage basin (FERNANDES et al., 2002). The variability is associated with climatic mechanisms such as the El Niño-Southern Oscillation (ENSO), or the position of South Atlantic Convergence Zone (SACZ) (CARVALHO et al., 2004; PASQUINI et al., 2012). In addition, the sampling campaigns did not follow a set pattern. Sampling ranged from one to four annual campaigns in different months of the year.

We understand that mean nutrient concentrations of the reservoirs do not reflect their heterogeneity and inherited flux calculation uncertainties. Therefore, we used a comprehensive data series to make the flux calculations to assess the significance of the groundwater flux to coastal surface waters. The water flow rates shown here are the most representative of the entire sandy barrier and can be considered as the maximum nutrient flows.

4.3. SGD and coastal primary production

Due to the importance of SGD at the land-sea interface, it is essential to investigate how nutrients contribute to sustaining primary productivity in coastal waters. Since the concentrations of these nutrients can be much higher in groundwater compared to surface water, SGD nutrient fluxes impose significant potential for the enrichment of oceanic waters (SLOMP & VAN CAPPELLEN, 2004; ANDRADE, 2011). Piedras & Odebrecht (2012) indicated the inorganic N as the main nutrient that controls chlorophyll concentrations and phytoplankton growth in the surf zone of the southern Brazilian coast. This is similar to temperate marine environments. The authors point out that phytoplankton composition and diversity are based on Si, P and N availability. These elements are transported to the surf zone mainly through the Patos Lagoon Estuary fluxes and from the SGD.

Figure 7 shows the molar ratio of nitrogen (N) and phosphorus (P) proposed by Redfield et al. (1963) for the fluxes on the continent-ocean pathway. In relation to groundwater flux from the continent to the beach zone, nitrogen was potentially the limiting nutrient, as well as the PL low-level scenario ($F1_a$ and $F1_c$). In the highest PLwl scenario ($F1_b$), due to low PO_4^{3-} concentration, P was the limiting nutrient. The same occurs in F2 (SE to SZ flux) because PO_4^{3-} is trapped in the SE through the adsorption process in the soil particles and Fe-oxide may precipitate and bind all P (CHARETTE & SHOLKOVITZ, 2002; SLOMP & VAN CAPPELLEN, 2004).

In F3, where seawater is recirculated through permeable sediments, nitrogen is again the limiting nutrient. This is because when nitrogen is in the surf zone, this element is consumed by phytoplankton growth and, therefore, returns to lower concentrations in the STE. Finally, as in F2, in the flux to the inner shelf (F4), P is again the limiting nutrient. This may be related to the rapid remineralization of nitrogen, especially in the NH_4^+ form, the first form released by respiration. In addition, NH_4^+ depletes faster than other nutrients (CARMOUZE, 1994; BURFORD & ROTHILISBERG, 1999). However, due to the wide variation in the nutrient concentration of the time-series data, SGD estimates and associated nutrient fluxes have an implicit standard deviation that can change the N/P molar ratio.

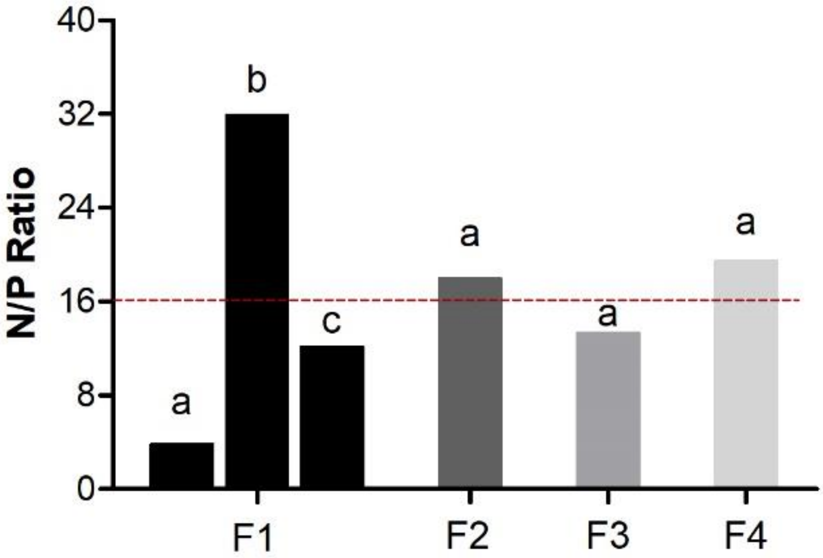

Figure 7: N/P ratio for SGD nutrient fluxes (a-average fluxes, b-high PLwl and c-low PLwl).

To estimate the potential primary productivity sustained by SGD through the Redfield ratio (REDFIELD et al., 1963), the groundwater flux to the surf zone (F2) is used. In this case, the PO_4^{3-} was the potentially limiting nutrient and then from PO_4^{3-} flux was estimated to have a primary production of 7.49 gC m^{-2} day^{-1} and 2,735 gC m^{-2} y^{-1} considering 100 m of SZ and 90 km study coastline. However, not all the production found can be considered new, since about 25% of the inorganic phosphorus in SGD is from recycled seawater represented as F3. Niencheski et al. (2007) found 3,000 gC m^{-2} y^{-1} for the same region adjacent to the PL barrier assuming nitrogen limits production in the nearshore. However, the authors estimated only the average SGD fluxes of nutrients and did not evaluate the interaction of fresh groundwater discharge with the PL hydraulic gradient, which was confirmed in this study.

5. Conclusions

The results reported here show that coastal aquifers characterized by permeable sediments such as coastal lagoon barriers have nutrient rates that are controlled by seasonal processes. The aquifers may be connected to longer climate cycles, such as El Niño and La Niña. This is mainly due to the influence of rainfall rates in tropical and mid-latitude regions, which until now have been disregarded in most SGD studies.

The application of Darcy's Law to a sandy barrier environment was effective in estimating the SGD, confirming previous studies along the southern Brazilian coast. The processes of transformation, removal and addition of the dissolved elements occur with greater intensity in the subterranean mixing zone, where the circulation of freshwater and seawater through the permeable beach/nearshore sands originate from the STE.

Nutrient inputs to the coastal ocean through SGD are continuous processes which contribute significantly to the primary production of the adjacent coastal water. Fresh groundwater discharge proved to be the most relevant flux and is dependent on climatic periodicities before mixing with recirculated seawater in the STE. If this occurs for the nutrients, we have to apply for other elements such as metals and radioisotopes. In addition, it is necessary to evaluate the influence of microbial activity on nutrient recycling and the potential evapotranspiration to estimate potential recharge from the difference between effective rainfall.

These fluxes can vary in relation to the N/P ratio and, therefore, causes changes to the phytoplankton species throughout the year. Under the assumption that phosphorus limits production in the nearshore and surf zone region, the SGD flux can support a primary production rate of about 2,735 gC m^{-2} y^{-1}.

Acknowledgements

The authors wish to acknowledge all the people who helped in field sampling and analyzes and the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) which provided financial support for this research.

Washouts as continental sources of dissolved elements to the coastal ocean in Southern Brazil and its hydrogeological characteristics

Gabriel Karagiannis de Souza[1*], Miguel da Guia Albuquerque[2], Carlos Augusto Barbosa da Silva[1], Luis Felipe Hax Niencheski[1], Carlos Francisco Ferreira de Andrade[1]

[1]Laboratório de Hidroquímica, Instituto de Oceanografia, Universidade Federal do Rio Grande, Campus Carreiros, Km 8, s/n, 96201-900 Rio Grande - RS, Brasil

[2]Departamento de Geoprocessamento, Instituto Federal do Rio Grande do Sul, Rio Grande - RS, Brasil

[*] Corresponding author.
E-mail addresses: gksouza0@gmail.com (Souza, G.K.),
migueldaguia@gmail.com (Albuquerque, M.G.),
carlosabdasilva.eaqta@gmail.com (Silva, C.A.B.)
niencheski@gmail.com (Niencheski, L.F.H.),
carlos.fand@gmail.com (Andrade, C.F.F.).

Abstract

Within the coastal zone of Rio Grande do Sul several surficial water bodies (washouts) are found, which take part on the drainage of the coastal plain. Considering the entire extension of the coast, the number of washouts is very significant, thus, this study aims to assess in an unprecedented way the availability of nutrients, carbon and iron, dissolved in washout waters and its contribution in terms of concentration to the coastal ocean. Furthermore, due to groundwater in the beach region being one of the major sources for the formation and maintenance of these water bodies and influencing their hydrochemistry, we used the Ground Penetrating Radar (GPR) as a tool to understand the interaction between the surficial and underground compartments, the influence of freshwater from the washouts on the aquifers and the extent of this interaction. The influence of the freshwater flux through the washout may reach 1,000 m in length and a trough of up to 3.2 m. The medium outflow of freshwater by the washouts was heavily influenced by the rainfall, ranging between 0.12 $m^3 s^{-1}$ and 0.95 $m^3 s^{-1}$, in the dry and wet seasons, respectively. Throughout the RSCP, washouts may represent 28% of the medium freshwater outflow from the Patos Lagoon Estuary (PLE) and can top the outflow from Tramandaí Lagoon by 25%. The high outflow in the wet season impacted on the dissolved elements flux, with estimates of 274 ton y^{-1} for SiO_4^{4-}, 0.42 ton y^{-1} for PO_4^{3-}, 7.07 ton y^{-1} for total inorganic N, 1.7 ton y^{-1} for Fe and 262 ton y^{-1} for total dissolved C. Reckoning the values for the inorganic nitrogen flux, the washouts can support a potential primary production in the surf zone of 18 gC m^{-2} y^{-1}, considering the entire Rio Grande do Sul coastal plain.

Keywords: washouts; flow rate; dissolved elements fluxes; ground penetrating radar; Rio Grande do Sul coastal plain.

1. Introduction

The Rio Grande do Sul coastal plain (RSCP) exhibits a shoreline that extends for approximately 620 km, being the widest coastal plain in Brazil. It evolved from several transgressive-regressive ocean cycles during the Quaternary, with beach and wind deposits which integrate with lagoonal, lacustrine, paludal, fluvial and deltaic environments (Tomazelli & Villwock, 2000; Villwock & Tomazelli, 2007). The generated barriers were responsible for shaping great lagoonal bodies (Patos-Mirim-Mangueira Lagoonal System) and several smaller coastal ponds, characterizing the landscape of the region in a unique way.

Throughout the coastal plain, only four outfalls connected to the ocean stand out, being responsible for the continental drainage of pluvial and fluvial freshwater from the whole state. Mampituba river, Tramandaí lagoon mouth, Patos Lagoon estuary and Chuí creek mouth (Figueiredo & Calliari, 2005). However, there is another surficial component for the continental freshwater discharge that takes part on the coastal plain drainage. The beach region exhibits several water streams, called washouts (Figueiredo & Calliari, 2006, Figueiredo *et al*., 2007). According to their spatial distribution, water supply and seasonal behaviour, washouts can be ephemeral (with lower water flow, occurring after local events of high rainfall), intermittent (seasonal) or permanent (Pereira da Silva, 1998).

Washouts were previously described for other sandy coastal regions of the globe (*e.g.,* in Australia, Mexico, Spain, United States, Uruguay and Parana state in Brazil), focusing on the biological implications of sandy beach environments (Santos, 1991; Gandara-Martins *et al.,* 2014). The distribution and generation of these water bodies are influenced by geomorphological and sedimentary features of the coastal plain, such as the presence of nearshore ponds, turf and mud deposits, and granulometry of the sediments (Figueiredo *et al*., 2007).

On the RSCP, although washouts had been described regarding spatial distribution, seasonal variation and geomorphology (Pereira da Silva *et al.*, 2003; Figueiredo & Calliari, 2006; Figueiredo *et al.*, 2007), they were never studied concerning their role as a continental freshwater source for the surrounding coastal ocean, neither the dissolved elements fluxes, which directly influence on the primary productivity of sandy beaches, environments that generally depend on allochthonous sources (Colombini & Chelazzi, 2003; Odebrecht *et al*., 2013). Despite acting on a local scale, when evaluated for the 620 km of coastal region, washouts become great nutrient and organic matter carriers.

Surficial flow takes place allied to the submarine groundwater discharge (SGD). The occurrence of permeable sediments favours the advection of SGD to the coastal waters (Windom *et al.* 2006; Niencheski *et al.* 2007; Santos, *et al*., 2009; Andrade *et al*., 2012). A slow but persistent flow will take place at any area where there is a positive hydraulic gradient between the aquifer and the sea level. Almost every sandy coastal area can undergo this process, where flow might be irregular, diffusive, temporally variable and cover several aquifers (Moore, 1996; Burnett *et al*., 2006).

The shallow coastal aquifers, just as surficial reservoirs, play a major role as a source of dissolved elements for the coastal waters (Kroeger & Charette, 2008; Moore, 2010; Null *et al.,* 2012). Regional factors, such as geology and climate conditions, contribute to the geochemical interactions along the beach region and, hence, on the variability of this process. Just as the rainfall, groundwater represents a major source of freshwater to the formation and maintenance of the washouts, imposing distinctive spatial and temporal dynamics. The height of the water table contributes to the erosion and occurrence of the washouts, which are flow channels from the wet areas of the backshore towards the shore (Figueiredo *et al*., 2007).

Previous studies showed the importance of the groundwater discharge associated with chemical elements to the southern Brazil coastal waters (Windom *et al.* 2006; Niencheski *et al.* 2007; Andrade *et al*., 2012; Rocha, 2018), and it is known that this region inputs a great volume of continental freshwater and high concentrations of elements in a global scale via SGD (Paiva & Niencheski, 2018; Rocha, 2018). However, the fraction of the total input corresponding to the washout's contribution is still not known.

Due to this strong hydrogeological interaction between the underground and surficial environments, this study is taking the first steps to understand the connection between both of these two compartments, the influence of freshwater from the washouts on the shallow aquifers of sandy beaches and the extent of this interaction. Moreover, due to the large number of washouts on the RSCP (186 and 558 on the dry and wet seasons, respectively), we assessed in an unprecedented way the availability of dissolved nutrients, carbon and iron, and their contribution to the coastal ocean.

2. Material and Methods

2.1. Study Area

The RSCP is located between the latitudes of 29ºS and 34ºS and oriented NE-SW (Figure 1). The tidal regime is of microtides with periodic occurrences of meteorological tides, according to the wind regime (Soares *et al.,* 2001). The coastal region is constituted of a succession of plain terraces, interleaved with elongated depressions where lagoons, lakes and marshes of various evolutionary stages are found. The beaches are classified from intermediate to dissipative, with some variations in this pattern due to the sediment granulometry (Calliari & Klein, 1993). The littoral is exposed to moderate/strong wave action and influenced by astronomical microtide regimes (annual mean ~0.5 m) (Calliari *et al*., 1996; Pereira *et al*., 2010).

The climate is under the South Atlantic anticyclone high pressure centre, with dominance of NE winds throughout the year. NW-S winds are dominant during the passage of coastal storms, and common during winter time due to the displacement of the high-pressure center. These factors cause water to stack by the coast as a result of the Ekman transport and, thus, elevate the sea level on the coast and alter the beach morphology (Calliari *et al.,* 1998).

The annual rainfall does not show a well-defined seasonality, although higher rates occur on months of winter and spring, and lower rates occur on summertime. On the other hand, climate phenomena such as *El Niño* Southern Oscillation (ENSO) act on the inter-annual variability of the rainfall patterns on the southern Brazil region. Positive anomalies occur during *El Niño* periods and negative anomalies occur during *La Niña* (Grimm et al., 2000; Pasquini et al., 2012), directly altering the continental freshwater discharge. We will consider the summer sampling campaigns as dry seasons and the winter sampling campaigns as wet (rainy) seasons.

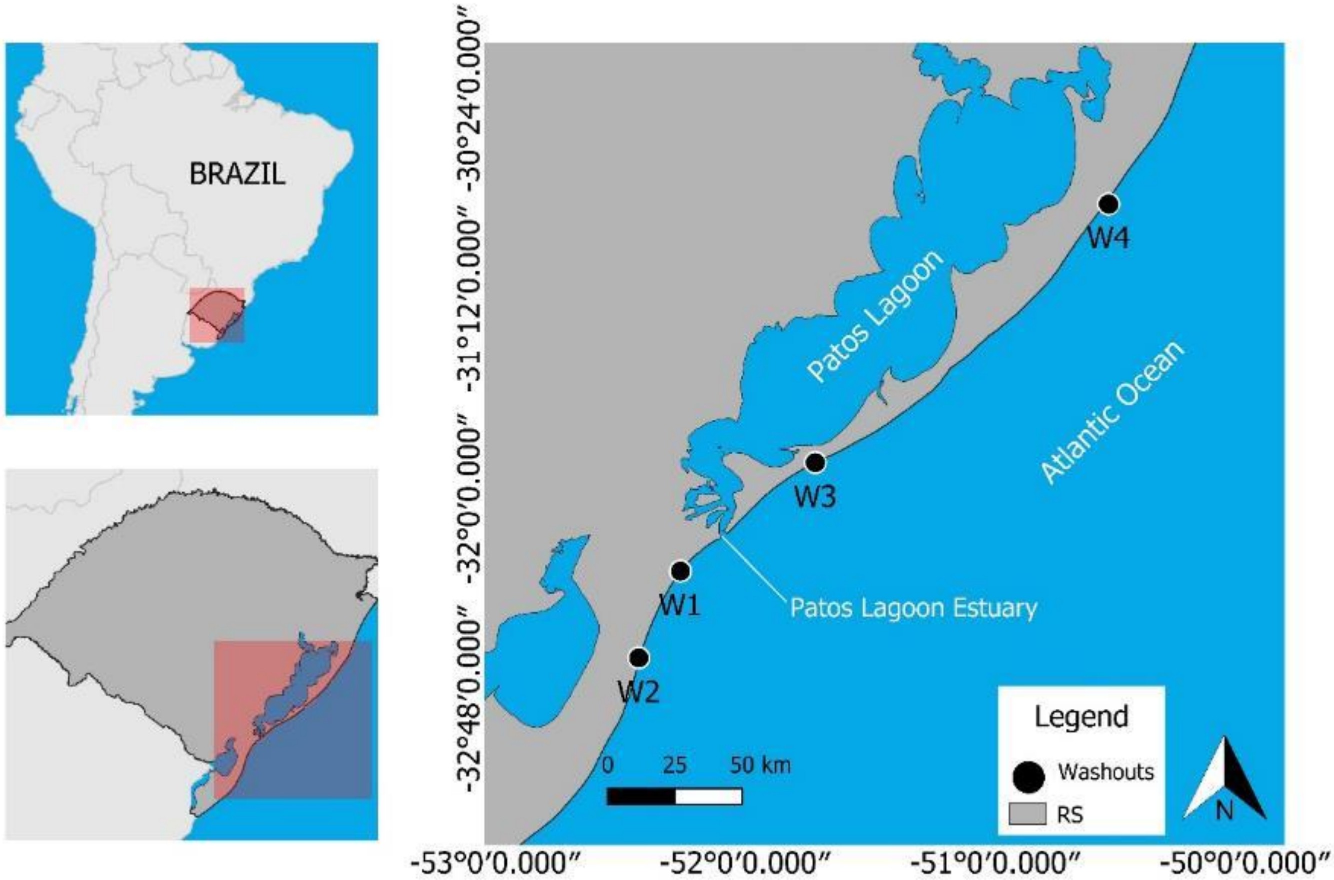

Figure 1: Study site and washouts location (W1, W2, W3 e W4) in the Rio Grande do Sul coastal plain.

For every 10 km on the coast, there are between 3 and 9 washouts (Figueiredo & Calliari, 2005). The study of every washout would require a complex logistics. Therefore, four washouts of permanent flow were chosen for the completion of this study, where each one of them depicts a specific feature of the coastal area. W1 (32.2899S 52.602W) and W2 (32.6371S 52.4270W) are located 20 km and 60 km south of the Patos Lagoon estuary (PLE) mouth, respectively (Figure 1). W1 region has low anthropogenic impact due to an early urbanization condition and no proximity to coastal ponds. At W2 there is some influence by Mirim Lagoon (16 km of proximity) and there is no urbanization of any kind. W3 (31.8558S 51.7207W) is located 45 km north-east of PLE, in the district of the São José do Norte-RS municipality, called Estreito, and it has approximately 2,400 inhabitants (IBGE, 2000) (Figure 1). In the sandbanks region, at the limit of the coastal sand dunes system, there are crops of *Pinus* *elliotis* as agricultural practices by small farmers, standing out as a main morphological and environmental agent (Gianuca & Tagliani, 2012). W4 (30.8015S 50.5475W) is located 120 km north-east of the PLE and 55 km from the Mostardas-RS municipality (Figure 1). The region does not suffer from significant anthropogenic influence or any kind of agricultural practices, with vegetation of species adapted to the sandy conditions (Cunha, 1997). The sandbanks region in W3 and W4 has small coastal ponds (pocket ponds) (*e.g.* Lagoa do Estreito, Lagoa do Peixe, Lagoa da Figueira), that can modify the local hydrological features. All the assessed washouts are of permanent flow and occur on the beaches throughout the year.

2.2. Sampling Procedure

The sampling campaigns for the gathering of washout water took place on February and July, 2015 and on March, 2017 at W1 and W2. And on March and June, 2018 at W3 and W4. Totalling three samplings during the southern summer, and two samplings during the southern winter (*n* **=** 10) was performed. The gathering of washout water was realized using a Masterflex® peristaltic pump and tubing, previously washed with HCl. All of the samples were gathered near the washouts mouth, approximately 20 m from the swash zone limit, exhibiting only freshwater samples (S < 0.1). The samples were filtered *in situ* using Aqua Prep 600® capsules and cellulose acetate filters 0.45 µm, and stored in precleaned polyethylene bottles, which were kept refrigerated until the time of the analyses. This was the standard procedure for all of the sampling campaigns.

Washout superficial outflow (m^3 s^{-1}) was calculated based on the cross-section (width *x* depth, m^2), multiplied by the laminar flow (m s^{-1}) (Carvalho, 2008). The laminar flow was calculated as being the time required for a plastic floater to cover a linear distance of two meters inside each washout and in the absence of winds. The measurements for width, depth and flow were obtained on the day of each sampling and for each washout individually. Flows were, then, calculated according to equation 1.

$$Q = W \times h \times v \qquad (1)$$

Where Q is the outflow (m^3 s^{-1}); W is the width of the washout (m); h is the medium depth in the cross-section of the washout; and v is the water flow velocity (m s^{-1}). Outflow (Q) was multiplied by the concentration of the elements to calculate the dissolved elements flux (µmol L^{-1} d^{-1}).

To assess the connection/interaction between the washouts and the underground environment from salinity data, groundwater was sampled on the beach and surf zone surrounding the washouts. A drive-point piezometer system, similar to that used by Niencheski, *et al*., (2007) was applied to sample groundwater down to a maximum depth of 1.5 m. For surf zone (SZ) and beach groundwater (BG) samples, the system was flushed with less water because of filter clogging. Samples were placed directly into 50 mL precleaned polyethylene bottles, stored in plastic bags and put on ice during the return trip to FURG for analysis. Precipitation data were obtained through the National Water Agency (ANA-Brazil, http://hidroweb.ana.gov.br/) for the region of each washout.

2.3. Chemical analyses

Dissolved oxygen, salinity and pH were measured *in situ* using a Hoestch® oximeter, a thermosalinometer (YSI 30, Yellow Springs) and a Metler Toledo MO120 pH meter, respectively. Equipments were calibrated on each sampling day following the manufacturer's instructions. Dissolved inorganic nutrients were determined colorimetrically. NO_x^- (NO_2^- + NO_3^-), PO_4^{3-} e SiO_4^{4-} were determined using Strickland & Parsons (1972) method, and NH_4^+ using Aminot & Chaussepied (1983) method. Analyses precision estimates are: phosphate, ± 0.03 µM; silicate, ± 0.15 µM; ammonium, ± 0.1 µM; nitrite, ± 0.02 µM and nitrate, ± 0.05 µM.

For the determination of Fe, samples were digested in microwaves (Mars Xpress-CEM) with HNO_3 p.a. acid, following the analytic method described in APHA (2012). After this procedure, samples were neutralized and flushed through a Chelex 100 resin column (3,0-4,0 g of resin in sodium form, pH 8,0; 200-400 Mesh; Bio-Rad) with a maximum velocity of 2,0 mL min^{-1}. Using a 2 mol L^{-1} HNO_3 Suprapur® solution, the metal was eluted, removed the salt matrix and pre-concentrated (Pai, 1988). The analyses were made by graphite furnace atomic absorption spectrometry (GF-AAS, Shimadzu AA-700). The detection and quantification limits were calculated based on Christian (1994) and varied between LOD 0.01-0.06 mg L^{-1}, LOQ 0.05-0.2 mg L^{-1}. Certified reference materials (SLRS-5, National Research Council Canada) were used as analytic quality control. The recovery percentage varied from 85 to 100%. Dissolved carbon analyses (total, inorganic and organic) were made using a Shimadzu, TOC-VCPH, SSM-5000ª model, with combustion detector. The detection limit of the method is 4 μg kg^{-1}.

2.4. Ground Penetrating Radar (GPR)

The GPR is a noninvasive geophysical technique that uses electromagnetic (EM) waves propagation to image the subsurface (Annan, 2002). The equipment emits electromagnetic waves and, as the waves cross the ground, the materials will present reflection, deflection or absorption. The GPR contains basically two accessories: the control unit and the antennae. The antennas can be shielded or unshielded and are used to transmit and receive the electromagnetic waves emitted into the ground. Whereas the GPR acts as a broadband receiver, the antenna shield acts as a filter for external signal interference. The control unit is used to generate, regulate, and display the signal received.

In this study, the GPR data were collected using the System IDS (*Ingegneria dei Sistemi*). Antenna frequencies may range from 25 to 2500 MHz. In field, a monostatic shielded antenna with a frequency of 400 MHz was utilized. This antenna is designed for relatively low penetration (6m approximately) while maintaining good vertical resolution. For coastal environments, studies conducted by Annan (2005) have shown that, a higher frequency antenna could miss the water table, and the lower frequency antenna is more effective at locating the groundwater water table.

The physical data collection principle is based on the dielectric constant of the targets. The signal velocity propagation (υ) within any medium is controlled by the dielectric constant (ϵr (equation 2), and this velocity is converted of the time scale for the depth scale using the equation 3.

$$\upsilon = \frac{c}{\sqrt{\epsilon r}} \tag{2}$$

Where c is the EM velocity in a vacuum.

$$z = \frac{\upsilon . t}{2} \quad (3)$$

Where z and t are the depth and two-way travel time to a subsurface reflector, respectively.

2.4.1. GPR Data processing

GPR data was processed using the software GRED. Five types of filters were utilized to remove noises and maximize the resolution of images. 1) Move start time or zero-time correction: this step is made to the first break time correction in a reflection of radargram; 2) Background removal: function used to remove background noise, which can be seen on the radargram as horizontal lines. The use of this function allows subtle signals to present a better resolution in the image; 3) Bandpass filter: this filter is based on FFT applications directly for the transition of information from the time domain to the frequency domain, acting independently in each trace of the radargram. This filter has the function of supplying the interference from components of high or low frequency. 4) Linear gain: this option allows a gain in the data curve of the radargram, acting to emphasize the time intervals where the structures present manifestations; and 5) Smoother gain: is the enhancement of the small recorded signals even after much of the noises has been removed.

3. Results and discussion

3.1. Freshwater outflow and dissolved elements flux

Rainfall and evaporation rates are the variables that directly influence the spatial and seasonal distribution of washouts. Accumulated rainfall varied between 158 mm (W1 and W2) and 335 mm (W1 and W2) (Table 1). Values cover the month of the sampling campaign as well as the previous month, at the region of each washout. Rainfall in RSCP is not seasonally well-defined due to the influence of climate mechanisms such as El Niño-Southern Oscillation (ENSO) and the placement of the South Atlantic Convergence Zone (SACZ) (Carvalho *et al*., 2004; Pasquini *et al*., 2012). However, it is observed that in the summer months rainfall can be 52% lower than in the winter months. Frontal systems and extratropical cyclones are more frequent in the autumn and winter (Diaz *et al*., 1998; Krusche *et al*., 2003; Galluci & Netto, 2004; Rodrigues *et al*., 2004) and responsible for the high rainfall in the coastal region of southern Brazil.

It was not possible to obtain evaporation rates for the sampled periods. However, Serpa (2013) assessed rainfall and evaporation rates with the occurrence of washouts in the RSCP. The study showed that, in 2011, evaporation rates reached 424 mm in the months of summer (January, February and March), and 218 mm in the months of winter (June, July and August). Therefore, evaporation rates are influenced by the atmospheric temperature (Krusche *et al*., 2003). Seasonal rainfall and evaporation regimes directly influence on the outflow and maintenance of the washouts. Consequently, these variables cause changes on the mouth of these water bodies (shallow and narrow in summer; wide and deep in winter) (Pereira da Silva *et al*., 2003), as well as modify the beach morphology and depth of the water table (Gandara-Martins *et al*., 2014). Flow varied between 0.1 $m^3 s^{-1}$ (W1, W2 and W4, summer) and 1.0 $m^3 s^{-1}$ (W3 and W4, winter) (Table 1). Values were very similar among the different washouts and within the same sampling period, showing once again the strong influence of the climate parameters on them.

Table 1: Accumulated rainfall (mm), flow rate ($m^3 s^{-1}$), pH, dissolved oxygen (mg L^{-1}) and dissolved nutrients, Fe (µmol L^{-1}) and carbon (mmol L^{-1}) concentrations in the washouts of Rio Grande do Sul coastal plain. S – summer campaigns and W – winter campaigns.

	Date	Accumulated rainfall (mm)	Flow rate ($m^3 s^{-1}$)	pH	D.O. (mg L^{-1})	SiO_4^{4-}	PO_4^{3-}	NH_4^+ (µmol L^{-1})	NO_x^-	Fe	TC	IC (mmol L^{-1})	OC
W1	2015-S	252	0.2	7.57	8.86	210.44	1.62	7.31	0.71	0.34±0.043	0.98±0.00	0.64±0.004	0.34±0.004
W1	2015-W	335	0.9	7.72	9.15	173.66	1.88	2.86	2.36	0.83±0.006	1.90±0.00	0.64±0.002	1.25±0.002
W1	2017-S	158	0.1	7.83	8.86	64.72	2.29	7.83	0.49	0.53±0.004	1.35±0.024	0.84±0.001	0.51±0.022
W2	2015-S	252	0.2	7.53	12.2	315.38	0.41	3.97	7.60	0.19±0.002	2.17±0.015	1.05±0.011	1.12±0.004
W2	2015-W	335	0.9	7.8	12.71	227.36	0.61	2.51	4.90	0.28±0.001	1.86±0.015	1.29±0.009	0.56±0.006
W2	2017-S	158	0.1	7.80	8.76	107.79	2.44	12.13	0.72	0.46±0.004	2.67±0.001	1.67±0.021	0.99±0.019
W3	2018-S	214	0.2	7.80	8.75	14.39	0.08	2.15	0.30	1.35±0.010	1.51±0.003	0.47±0.005	1.03±0.002
W3	2018-W	260	1.0	8.00	10.01	34.31	0.57	1.99	1.59	0.28±0.004	2.90±0.059	1.67±0.004	1.23±0.055
W4	2018-S	202	0.1	7.70	8.20	50.96	0.03	8.58	2.53	2.69±0.004	0.47±0.007	0.18±0.006	0.29±0.001
W4	2018-W	251	1.0	7.82	10.06	170.54	0.27	6.66	4.46	0.86±0.000	0.56±0.004	0.25±0.002	0.31±0.003
Mean	S	108	0.12	7.7	9.27	127.32	1.15	7.00	2.1	0.93	1.53	0.81	0.72
Mean	W	246	0.95	7.8	10.5	151.4	0.84	3.51	3.33	1.88	1.81	0.97	0.84
Median		136	0.15	7.80	9.01	139.171	0.592	5.320	1.979	0.499	1.689	0.746	0.780

Table 1 shows the concentrations of dissolved elements in each washout on the evaluated periods. Being the first study to determine the chemical compounds content in the washouts of RSCP, it was not possible to obtain data from other studies for comparison purposes. Spatial differences between the washouts did not follow a pattern or relation to the region embodying each of them. From Spearman's non-parametric correlation analysis ($p < 0.05$), there was a positive correlation between D.O. and NO_x (0.7), since NO_x represents the two oxidized species of nitrogen compounds (NO_2^- + NO_3^-). Waters with higher D.O. content favour the nitrification process, imposing higher concentrations of these compounds (Carmouze, 1994; Slomp & Van Cappellen, 2004). This process explains the higher concentrations of NO_x during the high rainfall season, a period of constant recharge and oxygenation of the washout waters, W2 2015-S being the only exception. D.O. also showed a negative but significant correlation with Fe (-0.71). Iron oxidize rapidly in oxygenated waters, changing the proportion between Fe^{2+} (reduced form) and Fe^{3+} (oxidized form), and is retained in the environment by flocculation and precipitation processes (Charette & Sholkovitz, 2006; Paiva *et al*., 2012).

Figueiredo & Calliari (2005) described the washouts' seasonal and spatial variability at the central and northern regions of RSCP, according to geological and geomorphological features of the coast. This work is the most recent regarding the number of washouts, which varied from 3, in the dry season (summer) and 9, in the rainy season (winter), for each 10 km of coastline. Taking the 620 km extension of RSCP into account, it is estimated that the number of washouts may reach 186 in the dry season, and 558 in the rainy season. These numbers will be further utilized in order to assess the continental freshwater discharge into the surrounding coastal ocean, as well as the dissolved elements flux associated with the washouts outflow.

When the washouts outflow (Q) was extrapolated to an annual temporal scale, Q varied between the maximum of 3.15×10^7 m^3 y^{-1} in winter (rainy season) in W3 and W4, at the central region of the littoral, and a minimum of 3.15×10^6 m^3 y^{-1} (one order of magnitude smaller) in W1, W2 and W4 in summer (dry season) (Table 2). Considering that all of the assessed washouts are of permanent flow, significant differences in outflow happen between the climatic seasons and not between the washouts.

Using data from Figueiredo & Calliari (2005), the water outflow through the washouts for the entire RSCP varies between 0.9 and 16.7 ($x10^9$) m^3 y^{-1}, in the dry and wet seasons, respectively. Individually evaluated, washouts act in a local scale if compared to larger runoff channels (*e.g.,* pocket lagoons, intermittent closed/open lakes and lagoons, barrier island systems) (Gandara-Martins *et al*, 2014). However, due to the large number of washouts in RSCP and high outflow during the wet seasons, the amount of freshwater exported to the ocean can be expressive. Comparing to other runoff channels in RSCP, washouts outflow can reach 28% of the mean outflow from PLE (Marques *et al*., 2014). It can reach an order of magnitude higher than the flow of the Mampituba River (D'Aquino *et al*., 2011), in the northern region of the coastal plain, and can be 25% higher than the flow from Tramandai Lagoon's mouth (Silva *et al*., 2016). Also, the outflow from washouts might represent 54% of the groundwater discharge through the sandy barrier separating Patos Lagoon from the ocean, in the central region of RSCP (Niencheski *et al*., 2007). And at least three orders of magnitude higher than underground flows in other coastal regions of Brazil (Babu *et al*., 2008; Godoy *et al*., 2013).

Salinity data from the surf zone indicate that the washouts outflow changes the salinity of the waters surrounding its mouths even in the period of lower outflow. In W1 (2017-S), W2 (2017-S), W3 (2018-S) and W4 (2018-S and 2018-W), water gathered in the surf zone showed salinity values of 14.6, 13.5, 6.2, 18.2 and 5.9, respectively. In all cases, samples were collected about 100 m from the mouths. In W3 and W4, salinity values of 7.4 and 17.1 were also observed at 500 m north of the washout mouths, respectively. Waters gathered in the four regions, within the surf zone and without the influence of washouts, had salinity values greater than 25.

Table 2: Outflow (Q - $m^3 y^{-1}$) and fluxes of dissolved elements from washouts of the Rio Grande do Sul coastal plain. S – summer campaigns and W – winter campaigns.

		Q	**SiO_4^{4-}**	**PO_4^{3-}**	**NH_4^+**	**NO_x^-**	**Fe**	**DOC**	**DIC**
		($m^3 y^{-1}$)				**(mol y^{-1})**			
W1	2015-S	6.31x10^6	1330	10.2	46,1	4.48	2.14	2190	4050
W1	2015-W	2.84x10^7	4930	53.4	81.3	67.2	23.6	35600	18400
W1	2017-S	3.15x10^6	204	7.24	24.7	1.55	1.67	1610	2660
W2	2015-S	6.31x10^6	1990	2.64	25.0	48.0	1.20	7100	6620
W2	2015-W	2.84x10^7	6450	17.3	71.2	139	8.00	16000	36800
W2	2017-S	3.15x10^6	340	7.72	38.3	2.29	1.47	3140	5280
W3	2018-S	6.31x10^6	90.8	0.511	13.6	1.94	8.55	6550	3000
W3	2018-W	3.15x10^7	1080	18.1	63.0	50.1	9.02	38800	52800
W4	2018-S	3.15x10^6	161	0.101	27.1	8.00	8.49	933	574
W4	2018-W	3.15x10^7	5380	8.77	210	141	27.2	9970	7980
Mean	S	4.73x10^6	686	4.74	29.1	11.0	3.92	3600	3700
Mean	W	3.00x10^7	4460	24.4	106	99.3	54.2	25100	29000
Median		6.31x10^6	1205	8.24	42.21	27.98	8.25	6824	5952
PCRS*		(0.9-16.7) x10^9	(0.13-2.5) x10^6	(0.09-1.36) x10^4	(0.5-5.9) x10^4	(0.2-5.54) x10^4	(0.07-3.0) x10^4	(0.07-1.4) x10^7	(0.07-1.6) x10^7

* Considering 186 and 558 washouts throughout the RSCP in the dry and rainy periods, respectively.

The high outflows observed in the wet seasons (87% higher than in the dry seasons) reflected in the dissolved elements fluxes. Even those that had higher concentrations in the dry seasons, were masked by the high outflows and showed more significant fluxes (Table 3). Emphasis on SiO_4^{4-}, NO_x^-, Fe, DOC e DIC, which fluxes were ≥ 90% higher in the rainy season, compared to the dry season. Washouts in RSCP are relevant both in numbers and in outflow. They act as lotic systems and as channels for the dissolved elements flux that add up to the other carriers of organic material and nutrients to the coastal ocean. With particular spatial and temporal dynamics and a direct relation with the underground environment, washouts can play an important role in the biogeochemical structure of sandy beaches.

Table 3: Freshwater outflow ($m^3\ y^{-1}$) and elements fluxes ($ton\ y^{-1}$) from washouts and regional investigations.

Site	Country	Freshwater outflow ($m^3\ y^{-1}$)	SiO_4^{4-}	PO_4^{3-}	NH_4^+	NO_x (ton y^{-1})	Fe	OC	IC	References
Surface flows										
Patos Lagoon estuary*	RS-Brazil	5.99×10^{10}	1.34×10^5	563	1274	5050				Niencheski & Windom (1994); Marques et al., 2014
Mampituba River*	RS-Brazil	5.87×10^8								D'Aquino et al., 2011
Tramandaí Lagoon*	RS-Brazil	4.1×10^9								Silva et al., 2016
Rio de la Plata*	Argentina/ Uruguay	7.3×10^{11}					2.4×10^4			Piola et al., 2005; Martin & Meybeck (1079)
Groundwater flows										
Patos Lagoon barrier***	RS-Brazil	3.1×10^{10}	6.1×10^4	5.9×10^3	1.1×10^4	2.8×10^4	6.5×10^3			Niencheski et al., 2007; Windom et al., 2006
Arraial do Cabo*	RJ-Brazil	9.5×10^5								Godoy et al., 2013
Pontal do Paraná*	PR-Brazil	5.84×10^6								Babu et al., 2008
PCRS**	**RS-Brazil**	**$(0.9\text{-}16.7) \times 10^9$**	**11.7-229**	**0.1-0.42**	**0.1-1.07**	**0.22-6.0**	**0.04-1.7**	**8.01-168**	**8.26-194**	**This study**

*Average flows.
**Considering 186 and 558 washouts throughout the RSCP in the dry and rainy periods, respectively.
***Considering 240 km of coastline.

The flux of SiO_4^{4-} through the washouts can reach up to 0.2% of the surface flux from the PLE, and up to 0.5% of the flux via groundwater discharge (Niencheski & Windom, 1994; Niencheski *et al*., 2007). NH_4^+, NO_x^- e PO_4^{3-} can reach 0.1% of PLE flux (Niencheski & Windom, 1994). Although these values might seem low, the fluxes through washouts are responsible for the allochthonous supply of nutrients, in other words: new production. When in the surf zone, nutrients can be regenerated constantly, supporting high rates of primary productivity. In addition, the fluxes can be even more significant if the interaction of the washout with the aquifer is considered. As shown above, washouts might mean a lot more than what is seen in the surficial runoff.

Sandy beaches with well-developed surf zones are known to host dense populations of diatoms, which require a high supply of nutrients to grow (Campbell, 1996; Piedras & Odebrecht, 2012). On exposed sandy beaches in southern Brazil, the diatom *Asterionellopsis glacialis* (Castracane) Round is the main microalgae in the surf zone and frequently dominates the phytoplankton populations (Piedras & Odebrecht, 2012). Inorganic nitrogen is the main nutrient that controls the chlorophyll concentrations and the growth of these microorganisms and, based on the Redfield molar ratio (Redfield *et al*., 1963), it was the limiting nutrient in the washout's fluxes. Based on this molar ratio, it is estimated that inorganic nitrogen fluxes may support a potential primary productivity of 18.0 gC m^{-2} y^{-1}, considering 620 km of coastal plain, and 50 m of surf zone.

Regarding the dissolved carbon fluxes, the washout flux to the coastal ocean in RSCP can reach 362 ton y^{-1}, during periods of higher outflow (table 3). Although it has not been possible to compare them with the other runoff channels in the region due to lack of previous studies, it is necessary to include washouts as an exporting channel of chemical compounds to coastal waters. For a better understanding of how coastal waters contribute to the carbon cycle at regional and global scales, all sources should be assessed, including washouts. Therefore, considering that these water bodies represent a fraction of the underground supply and that beach aquifers are important sources of water and dissolved elements for the washouts, the connection between these two compartments is verified.

3.2. Connection washout-aquifer

As it was the first time that GPR was used to study the washout-aquifer connection, we chose W3, an easily approachable washout and with important and permanent contribution to the coastal region, to test our hypothesis about the occurrence of an underground channel formed by the washout' flow and their extension. The survey took place on 11-23-2019. On that day, the mouth of W3 was oriented to SW and showed low flow. Even so, the GPR probing, carried out in the berm region and parallel to the coastline, showed that the washout has a strong influence on the underground environment. In the first 100 m of NW orientation (samples S2 and S3), radargram showed slightly brackish water lenses in the unsaturated zone, with salinity ranging between 10 and 12 (Figures 2B and 2C). These water lenses showed lengths ranging from 6.0 m 14.0 m, approximately, and depths ranging from 1.1 m to 3.2 m. Over the remaining 900 m, the formation of another 12 small water lenses was observed, with amplitudes of 2.0 m.

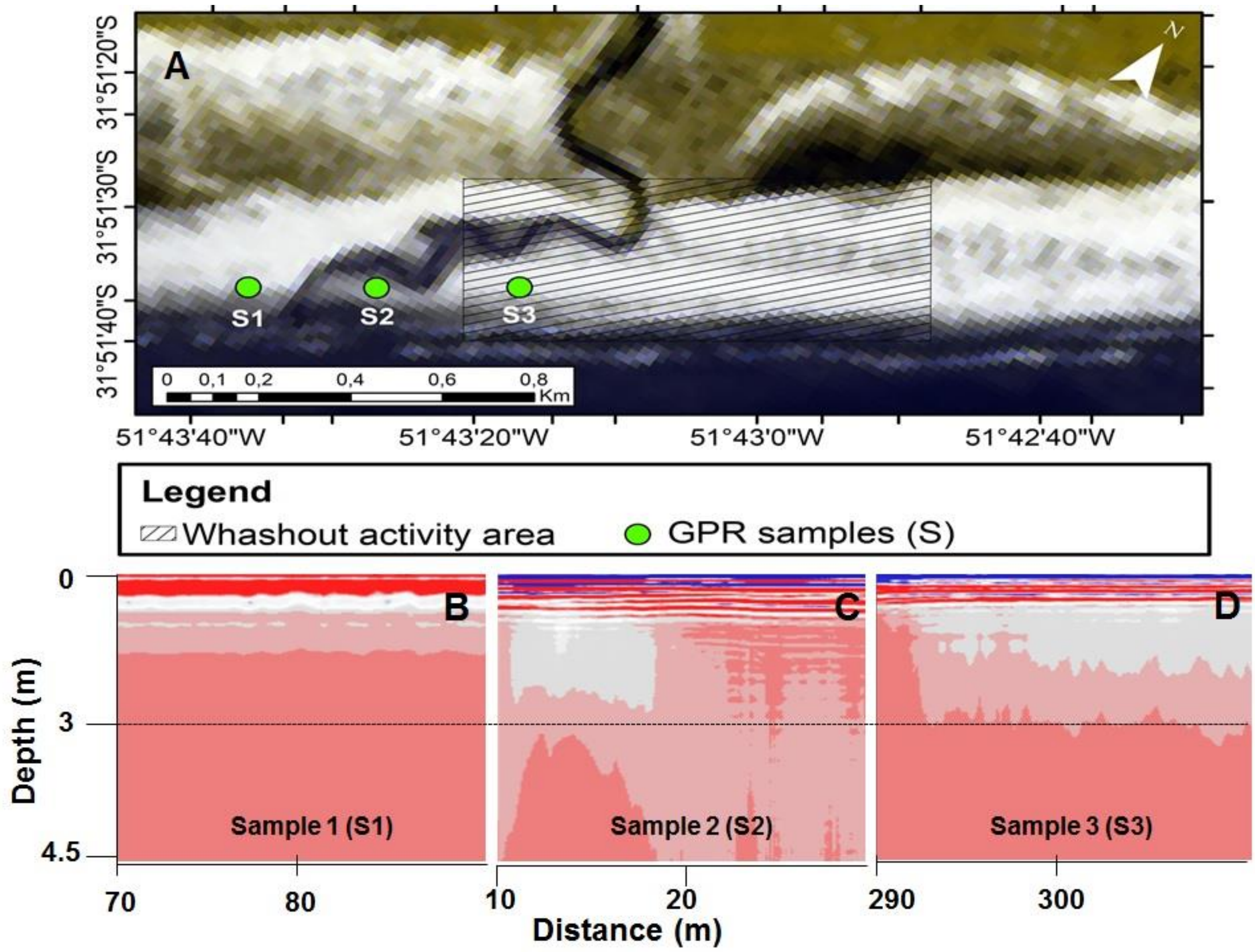

Figure 2: Non-invasive GPR soil profile on the day of the field research (11/23/2020). A – Washout activity area and GPR samples (S1, S2 and S3). B – GPR profile of sample S1; C – GPR profile of sample S2; and D – GPR profile of sample S3. White tone represents freshwater in the soil; darker red represents the soil without water; and intermediate red tone represents the soil with the presence of brackish water.

Since the mouth was positioned to SW, the presence of brackish water lenses at the sampling points S2 and S3 are associated with the active migration zone of the washout (Figure 2A). The appearance of other lenses of lesser extension can be explained by the fact that they are in regions of lower topography (Serpa, 2013). For the SW direction, the GPR data did not show evidence of water lenses. This statement can be visualized at the sample point S1 (Figure 2B), which presented a homogeneous stratigraphy along the traced profile. The GPR profile made for SW is outside the active washout meandering zone and, therefore, no brackish water lenses are observed in the aquifer.

The low water content in the unsaturated zone of the aquifer results in a great contrast in the GPR image (Paz *et al*., 2017). As it is a non-invasive sounding method, this contrast favours deductions of the water table depth and water volume. In general terms, fluids flow in aquifers is affected and ruled by the reservoir's internal structure (Harrari, 1996). Regarding the washouts, factors such as rainfall, coastal drift, local topography, drainage subsystems on the back side of the dunes and the direction and intensity of the winds have an influence on the underground water flows (Alvez, 2020). From a single value decomposition analysis (SVD) applied to a series of high frequency measurements of the level of the coastal water table, it was possible to identify that the rainfall regime, followed by the direction and intensity of the winds, as being the main factors responsible for the groundwater level variation (Alvez, 2020). Added to this discussion are the notes made by Gonzaga et al., 2020, which highlight the role of the coastal component (waves, coastal drift) along with groundwater flows.

Regarding the behaviour of the trough, W3 has four configurations. The first is related to the position of the trough almost perpendicular to the coastline (Figure 3B). A second configuration is the trough's displacement of approximately 1 km (Figures 3A and 3C), both to the north and to the south. This situation is very common when there is an above-average rainfall surplus that, associated with wind and coastal drift conditions, favour the migration of the trough over large extensions. However, it is important to note that, throughout the year, this configuration is considered sporadic.

The third configuration happens with a displacement of around 200 m to 500 m, and is called active meandering zone. In this region, the washout's trough can assume a NW and / or SW orientation, depending on the wind and coastal drift conditions (Figures 3D and 3F). Finally, there is one last configuration, which is characterized by the closing of the trough and interruption of its connection to the sea (Figure 3E). In this situation, the water accumulation is observed in a 500 m strip, both to the north and to the south. In periods of low rainfall, the migration of the washout's trough is interrupted, favouring its natural closing process.

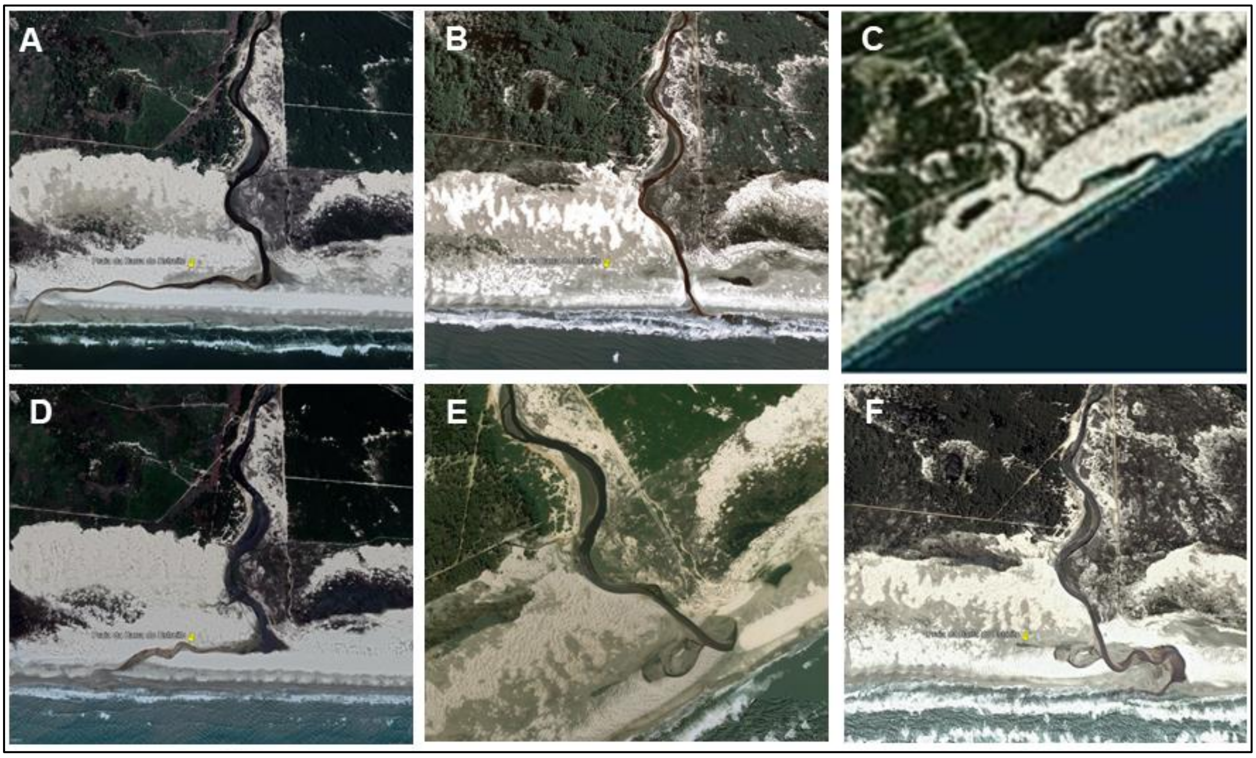

Figure 3: Migration of the mouth of the washout (W3). A and C are the position of maximum migration (~1 km) for SW and NE, respectively. B, D, E and F are the position of the mouth of W3 within the active migration zone.

SW wind situations favour water stacking on the coast, being reflected along the coastal water table. Considering that winds from the NE quadrant are predominant in the Rio Grande do Sul coast, these favour a greater frequency of the washout’s trough SW positioning. Rainfall and the direction and intensity of winds is what differentiates the length of this trough along the coast. Essam et al. (2020) highlights that the level of groundwater, like any part of a dynamic flow system, varies within aquifer systems. In this context, the meander works as a parallel drainage system, considering that there are drainage subsystems on the back side of the dunes.

The interaction between the washouts and the underground environment is also confirmed for the other assessed washouts by salinity data. Groundwater collected at 1.5 m depth and about 15 m perpendicular to the mouth of the washouts, both to the north and south, varied between 2.6 (W2, 2017S) and 16.0 (W1, 2017-S). On the other hand, waters gathered in the same position at the beach, but without the influence of the washouts, showed salinity values between 25.0 and 31.0.

Water outflow through the washouts, in the beach environment, represents only a fraction of its entire structure. It is important to know how the system works on the underground. The GPR analysis showed that the surficial underground system is not homogeneous and has a large dimension. The aquifer is variable in the same way as the surface. Each old trough left a mark (*in printing*) on the sedimentary package and continues to act as a channel connecting groundwater to the adjacent coastal ocean. The contact between the aquifer and the surf zone is permanent and becomes more significant with the occurrence of washouts. The coastal plain covers several types of integrated environments and ecosystems, such as coastal lagoons, wetlands and different types of vegetation. There are more than one system of freshwater flow feeding the washouts and coastal aquifers, imposing a certain heterogeneity to the environment.

The use of GPR on a permanent washout of the coastal region characterized by the presence of small coastal lagoons (pocket lagoons) was effective and, therefore, we must replicate the studies on other washouts. We must consider the application of GPR on studies of washouts in coastal regions without lagoons or with distinct sedimentary characteristics, and those of intermittent flows, for better understanding of the washout-aquifer system regarding water flow and element fluxes. These strategies can reduce the uncertainties regarding the heterogeneity of the flows, and classify washouts according to the hydrogeological characteristics of the coast.

4. Conclusions

The freshwater discharge by the washouts was seasonally influenced by rainfall. The average outflow in the period of highest rainfall can be almost 90% greater than the outflow in periods of low rainfall. Compared to other vectors of the continental runoff on RSCP, washouts can represent up to 28% of the Patos Lagoon estuary's outflow and be more significant than the Mampituba River and Tramandaí Lagoon outflows.

Despite having groundwater and rain as freshwater sources, and different spatial and temporal dynamics compared to other coastal plains flow vectors, washouts can play an important role in the structure of sandy beaches, environments dependent on allochthonous sources of organic material and nutrients. Based on the Redfield molar ratio, dissolved elements fluxes through the washouts can support a potential primary productivity of 18.0 gC m^{-2} y^{-1}, considering the entire RSCP surf zone.

Washouts showed a strong interaction with the underground environment on the beaches where they are located. The profiles drawn with GPR indicate that this interaction can reach 1.0 km in length and approximately 3.0 m in depth. Variables such as the wind regime, coastal drift and rainfall rates are key factors for the migration of the washouts mouths and for their interaction with the aquifer, in a portion we called the active washout migration zone. GPR is a very useful tool for the understanding of these complex systems. We chose a simple and low-cost methodology compared to more modern and expensive techniques. However, it proved to be quite effective for the washouts. As it is the first study with these approaches, we introduced the knowledge about the importance of washouts as vectors for the fluxes of some chemical components to the coastal ocean of southern Brazil. And we showed the background of these compounds' concentrations in the washouts.

This study shows that the washouts of the RSCP should be considered as an important source of continental freshwater and dissolved elements to the coastal ocean, and should be included on the regional biogeochemical cycles. Future studies should consider it as an integrated environment (aquifer-washout), and consider these water bodies on the submarine groundwater discharge (SGD) studies, widespread in the region.

Acknowledgements
The authors wish to acknowledge all the people who helped in field sampling and analyzes. This study was financed in part by the *Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil* (CAPES) – Finance Code 001.

Capítulo V:

Síntese de Resultados e Discussões

Síntese de resultados e discussões

Este estudo é uma contribuição para o entendimento das fontes e dos fluxos alternativos de elementos dissolvidos na interface continente-oceano da planície costeira do Rio Grande do Sul, e que muitas vezes são negligenciados nos ciclos biogeoquímicos regionais e globais.

No primeiro manuscrito foi avaliado o sistema de aquíferos costeiros da barreira arenosa que separa a Lagoa dos Patos do oceano Atlântico como fonte de nutrientes para as águas costeiras adjacentes. Dá-se a hipótese de que a LP, por representar um importante corpo hídrico na região de estudo, tanto em extensão quanto em volume, tem forte relação com a variação dos nutrientes na água subterrânea, uma vez que representa a principal fonte de recarga dos aquíferos costeiros. A precipitação pluviométrica, além de fonte de recarga direta, tem importância na recarga de toda a bacia de drenagem da LP e, consequentemente, na variação do seu nível de água. Devido a sedimentologia da barreira apresentar alta permeabilidade, os aquíferos costeiros neste ambiente comportam-se como um sistema aberto, onde as variáveis climáticas (precipitação pluviométrica, regime de ventos) e hidrogeológicas (nível da LP, permeabilidade) influenciam fortemente neste sistema. Em razão da extensa série de nove anos de dados de nutrientes, os fluxos desses elementos foram investigados em cenários de alto e baixo nível da LP.

Os dados de condutividade hidráulica mostraram que a permeabilidade da barreira é bastante variável, com os menores valores nos poços próximos à LP comparados com os poços próximos ao oceano. Os resultados refletiram a evolução dos diferentes estágios morfodinâmicos da PCRS e influenciaram diretamente nos fluxos subterrâneos do sistema de aquíferos da barreira. As maiores taxas de fluxos (Q) foram encontradas nos poços adjacentes ao oceano, onde o solo é arenoso e mais permeável, e na região norte da barreira, onde a LP fornece um maior gradiente hidráulico pelo aumento do seu nível de água, pois recebe mais de 50% de toda a bacia de drenagem do Estado. Ambas as variáveis resultaram em maiores taxas de fluxos subterrâneos em direção à costa.

A descarga de água subterrânea (DAS) é uma ferramenta usualmente utilizada para estimar os fluxos de elementos dissolvidos na interface continente-oceano. A DAS é resultado da soma de uma componente continental (Q_{fw}) e outra componente marinha (Q_{sw}). A primeira foi calculada utilizando um método inédito para a região de estudo a partir da Lei de Darcy, que descreve o fluxo de um fluido em um meio poroso a partir de dados de condutividade hidráulica. E Q_{sw} foi calculado a partir de do balanço salino através de dados de salinidade no estuário subterrâneo (ES), região de mistura entre a água doce continental e a água marinha recirculada nos sedimentos.

Os fluxos dos nutrientes inorgânicos dissolvidos associados a DAS foram calculados com base no modelo conceitual de Niencheski et al. (2007). Esse sistema de fluxos inclui: o fluxo dos nutrientes dos aquíferos da barreira (água doce continental) para o estuário subterrâneo (F1); o fluxo de água subterrânea do ES para a zona de surfe (F2); o fluxo de água marinha recirculada nos sedimentos do ES (F3); e o fluxo da zona de surfe para a plataforma. Além das estimativas médias, também foram calculados os fluxos dos nutrientes considerando um cenário de menor nível de água da LP e um cenário de maior nível de água da LP.

Os resultados mostraram que os aquíferos costeiros da barreira tiveram as taxas dos nutrientes controladas, principalmente, pelas flutuações do nível de água da LP e, consequentemente, pelo processo de diluição em períodos de maiores taxas pluviométricas. Os aquíferos podem estar conectados a ciclos climáticos mais longos, como o El Niño e La Niña, devido à influência desses fenômenos nas taxas pluviométricas da região sul do país, e que ainda não haviam sido avaliados em relação aos estudos da DAS na PCRS.

A aplicação da Lei de Darcy para estimar os fluxos de água doce subterrânea, uma das componentes da DAS, foi bastante efetivo no ambiente de estudo, uma barreira arenosa caracterizada pela presença de sedimentos permeáveis. Os processos de remoção e adição dos nutrientes ocorreram com maior intensidade na zona de mistura entre a água doce continental e marinha do estuário subterrâneo. Os fluxos dos nutrientes foram fortemente controlados pela variação do nível de água da LP e pelo processo de diluição em períodos de mais alta pluviosidade, principais fontes de recarga dos aquíferos. No cenário de alto nível da LP, a concentração nos fluxos de silicato foram 75% menores quando comparados com as concentrações em cenário de baixo nível. O mesmo padrão foi observado para o fosfato, com uma diminuição de até 78%. Em períodos de maior nível de água da LP, ocorre uma maior influência das águas superficiais da LP nos aquíferos e causaram a diluição dos teores desses nutrientes. No caso do fosfato, este nutriente foi rapidamente removido das águas subterrâneas na interface continente-oceano através da adsorção a óxidos/hidróxidos de ferro ou pela coprecipitação com alguns elementos dissolvidos em sua fase mineral. Os resultados corroboraram e enfatizaram a forte correlação negativa entre o fosfato e o nível de água da LP, e entre o fosfato e as taxas pluviométricas em toda a série de dados.

O aporte dos nutrientes para as águas costeiras através da DAS é um processo contínuo e que contribuiu significativamente para a produtividade primária dessas águas. A descarga de água doce continental mostrou ser o fluxo de maior relevância e dependente das periodicidades climáticas antes de aportar na zona de mistura do estuário subterrâneo. Esses fluxos podem variar em relação a razão molar N/P e, dessa forma, causar mudanças nas comunidades fitoplanctônicas ao longo do ano. Com base nos resultados encontrados, o fósforo foi o nutriente limitante na zona de surfe adjacente aos aquíferos, podendo suportar uma produtividade primária potencial de cerca de 2735 gC m^{-2} ano^{-1}, considerando os 90 km de linha de costa da região norte da barreira e 100 m de zona de surfe.

No segundo manuscrito, avaliou-se de forma inédita a disponibilidade dos nutrientes, carbono e ferro dissolvidos nos sangradouros e a contribuição desses corpos d’água em termos de concentração para o oceano costeiro adjacente à PCRS. Os sangradouros são canais de escoamento que fazem parte da drenagem da planície costeira e estão intimamente interligados com os aquíferos costeiros da região de praia. A água subterrânea e a chuva representam as principais fontes de água para a manutenção e formação dos sangradouros. Portanto, devido à forte interação hidrogeológica entre o ambiente subterrâneo e superficial, este estudo também forneceu os primeiros passos no entendimento da conexão entre esses dois compartimentos, a influência de água doce dos sangradouros nos aquíferos rasos de praias arenosas e a extensão dessa interação.

A vazão de água doce pelos sangradouros foi sazonalmente influenciada pelas taxas de precipitação pluviométrica. A vazão média no período de mais alta pluviosidade pode ser quase 90% maior que a vazão em período de baixa pluviosidade. Comparados com outros vetores da drenagem continental da PCRS, os sangradouros podem representar até 28% da vazão do estuário da Lagoa dos Patos e serem mais significativos que a vazão do rio Mampituba e da Lagoa de Tramandaí.

Apesar de terem como fontes de água doce o lençol freático e a chuva, e diferentes dinâmicas espacial e temporal se comparados com outros vetores de fluxos das planícies costeiras, os sangradouros podem desempenhar um importante papel na estrutura de praias arenosas, ambientes dependentes de fontes alóctones de material orgânico e nutrientes. Com base na razão molar de Redfield, os fluxos de elementos dissolvidos pelos sangradouros podem sustentar uma produtividade primária potencial de 18,0 gC m^{-2} ano^{-1}, quando considerado 50 metros de zona de surfe e toda a PCRS.

Os sangradouros mostraram forte interação com o ambiente subterrâneo nas praias onde estão inseridos. Os perfis traçados com o GPR indicam que essa interação pode chegar a 1,0 km de extensão e aproximadamente 3,0 m de profundidade. Variáveis como o regime de ventos, deriva litorânea e as taxas de precipitação pluviométricas são fatores-chave na migração da desembocadura dos sangradouros e na sua interação com o aquífero, em uma porção chamada de zona ativa de migração do sangradouro. O uso do GPR constituiu uma ferramenta de grande utilidade para o entendimento desses complexos sistemas. Foi escolhida uma metodologia simples e de baixo custo em comparação com técnicas mais modernas e custosas, porém, que se mostrou bastante eficaz para os sangradouros. Como é o primeiro estudo com essas abordagens, introduzimos o reconhecimento da importância dos sangradouros como vetor nos fluxos de alguns componentes químicos para o oceano costeiro sul do Brasil. E mostramos o *background* das concentrações desses compostos nos sangradouros.

Este estudo mostrou que tanto os aquíferos costeiros, quando os sangradouros da PCRS devem ser considerados como fonte importante de água doce continental e elementos dissolvidos para o oceano costeiro, e devem ser incluídos nos ciclos biogeoquímicos regionais e globais. Estudos futuros devem considerar o ambiente de forma integrada (aquífero-sangradouro) e considerar os sangradouros como parte do sistema nos estudos de descarga de água subterrânea (SGD), já difundidos na região.

Referências Bibliográficas

Alves, D. C. L. 2020. Hidrogeomorfologia e efeitos da subida do nível do mar no balneário Cassino, RS - Brasil. Ph.D. Thesis. Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil, 182 p.

Aminot, A.; Chaussepied, M. Manuel des analyses chimiques en milieu marin. Brest, E: C.N.E.X.O**.,** 1983. 395 p.

Andrade, C. F. F.; Niencheski, L. F. H.; Attisano, K. K.; Milani, M. R.; Santos, I. R.; Milani, I. C. 2012. Fluxos de nutrientes associados às descargas de água subterrânea para a Lagoa Mangueira (Rio Grande do Sul, Brasil). *Quim. Nova*, 35, 5-10.

Annan, A. 2005. GPR methods for hydrogeological studies. *Hydrogeophysics* 50: 185-213. https://doi.org/10.1007/1-4020-3102-5_7.

Annan, A. P. 2002. GPR-history, trends and future developments. *Subsurface Sensors Technology Applied*, 3: 253-270. https://doi.org/10.1023/A:1020657129590.

APHA (AMERICAN PUBLIC HEALTH ASSOCIATION). 2012. Standard methods for the examination of water and wastewater. 22 ed. Washington: United States, 1496p.

Babu, D. S.; Sahai, A. K.; Noernberg, M. A.; Marone, E. 2008. Hydraulic response of a tidally forced coastal aquifer, Pontal do Paraná, Brazil. *Hydrogeol. J.*: 16, 1427.

Barboza, E. G., Tomazelli, L. J., Dllenburg, S. R., Rosa, M. L. C. C. 2009. Planície costeira do Rio Grande do Sul, erosão em longo período. *Sociedad Uruguaya de Geologia*, n. 15, 94 – 97.

Benitez-Nelson, C. R. 2000. The biogeochemical cycling of phosphorus in marine systems. *Earth Science*, 51, 109–135. doi:10.1016/S0012-8252(00)00018-0.

Billerbeck, M.; U. Werner; K. Bosselmann; E. Walpersdorf; M. Huettel (2006), Nutrient release from an exposed intertidal sand flat, *Mar. Ecol. Prog. Ser*., 316, 35–51, doi:10.3354/meps316035.

Bowen, J. I.; Kroeger, K. D.; Tomasky, G.; Pabich, W. J.; Cole, M. I.; Carmichael, R. H.; Valiela, I. (2007). A review of land-sea coupling by groundwater discharge of nitrogen to New England estuaries: mechanisms and effects. *Appl. Geochem.* 22, 175- 191.

Burford M. A.; Rothlisberg, P. C. 1999. Factors limiting phytoplankton production in a tropical continental shelf ecosystem. *Est. Coas. Shelf Sci*., 48: 541-549.

Burnett, W. C. & Dulaiova, H. 2003. Estimating the dynamics of groundwater input into the coastal zone via continuous radon-222 measurements. *Journal of Environmental Radioactivity*. v. 69(1-2), 21-35. doi.org/10.1016/S0265-931X(03)00084-5.

Burnett, W. C. et al., 2006. Quantifying submarine groundwater discharge in the coastal zone via multiple methods. *Science of the Total Environment*. v. 367 (2–3), 498–543. doi.org/10.1016/j.scitotenv.2006.05.009.

Calliari, L. J. & Klein, A. H. F. 1993. Características morfodinâmicas e sedimentológicas das praias oceânicas entre Rio Grande e Chuí, RS. *Pesquisas em Geociências*. 20(1): 48-56.

Calliari, L. J.; Klein, A. H. F; Barros, F. C. R. 1996. Beach differentiation along the Rio Grande do Sul coastline (Southern Brazil). *Revista Chilena de Historia Natural*. 69, 485-493.

Calliari, L. J.; Speransk, N.; Bukareva, I. 1998. Stable Focus of Wave Rays as a Reason of Local Erosion at the Southern Brazilian Coast. *Journal of Coastal Research*. 26, 19-23.

Campbell, E. E. The global distribution of surf accumulations. *Rev. Chil. Hist. Nat.* 69, p. 495-501, 1996.

Carmouze, J. P. *O metabolismo dos ecossistemas aquáticos - Fundamentos teóricos, métodos de estudo e análises químicas*: Editora FAPESP. 1994. 253 p.

Carvalho, L. M. V.; Jones, C.; Liebmann, B. 2004. The south Atlantic convergence zone: intensity, form, persistence, and relationships with intraseasonal to interannual activity and extreme rainfall. *Journal of Climate*. 17, 88-108.

Carvalho, T. M. 2008. Técnicas de medição de vazão por meios convencionais e não convencionais. *Rev. Bras. Geogr. Fís*. 1(1): 73-85. doi: doi.org/10.1175/1520-0442(2004)017<0088:TSACZI>2.0.CO;2.

Carvalho, V. C. & Rizzo, H. *A zona costeira brasileira – subsídios para uma avaliação ambiental. Brasília*: Ministério do Meio Ambiente, dos Recursos Hídricos e da Amazônia Legal – MMA, Secretaria de Coordenação de Assuntos de Meio Ambiente –SCA. p.211, 1994.

Castelão, R. M. & Moller Jr. O. O. 2003. Sobre a circulação tridimensional forçada por ventos na lagoa dos Patos. *Atlântica*, Rio Grande, v. 25 (2), 91-106.

Castello, J. P. & Moller Jr. O. O. 1977. Sobre as condições oceanográficas no Rio Grande do Sul. *Atlântica*. v. 2(2), 25-35.

Charette, M. A. & Sholkovitz, E. R. 2002. Oxidative precipitation of groundwater-derived ferrous iron in the subterranean estuary of a coastal bay. *Geophysical Research Letters*. v. 29 (10), 85-100.

Charette, M. A. & Sholkovitz, E. R. 2006. Trace element cycling in a subterranean estuary: Part 2. Geochemistry of the pore water. *Geochimica et Cosmochimica Acta.* 70, 811–826.

Cho, H.-M.; Kim, G.; Kwon, E. Y.; Moosdorf, N.; Orellana, J. G; Santos, I. R. 2018. Radium tracing nutrient inputs through submarine groundwater discharge in the global ocean. *Scientific Reports,* 8:2439. doi: 10.1038/s41598-018-20806-2.

Christian, G.D. 1994. Analytical Chemistry. John Wiley & Sons. 832p.

Colombini, I. & Chelazzi, L. 2003. Influence of allochthonous input on sandy beach communities. *Oceanogr. Mar. Biol. Ann. Rev*. 41: 115-159.

Couturier, M.; Tommi-Morin, G.; Sirois, M.; Rao, A.; Nozais, C.; Chaillou, G. 2017. Nitrogen transformations along a shallow subterranean estuary. *Biogeosciences* 14, 3321–3336. doi.org/10.5194/bg-2016-535.

CPRM. Serviço Geológico Brasileiro. *Determinação de altitudes da estação de Ipanema –Rio Guaíba*. (Relatório Interno), 1985.

Cunha, N. G. da. *Caracterização dos solos de São José do Norte, Tavares e Mostardas - RS*. Pelotas, RS: EMBRAPA/CPACT, Ed. UFPel, 1997. 47 p. il. (Documentos CPACT; 7/94) 2ª edição.

D’Aquino, C. A.; Andrade Neto, J. S.; Barreto, G. A. M.; Schettini, C. A. F. 2011. *Revista Brasileira de Geofísica.* 29(2): 217-230.

Diaz, A. F.; Studzinski, C. D.; Mechoso, C. R. 1998. Relationship between precipitation anomalies in Uruguay and Southern Brazil and sea surface temperature in the Pacific and Atlantic oceans. *J. Clim*. 11: 251-271.

Dillenburg, S. R.; Roy, P. S.; Cowell, P. J.; Tomazelli, L. J. 2002. Influence of Antecedent Topography on Coastal Evolution as Tested by the Shoreface Translation–Barrier Model (STM). *J. Coast. Res*. v. 16, 71–81.

Dorsett, A.; Cherrier, J.; Martin, J. B.; Cable, J. E. 2011. Assessing hydrologic and biogeochemical controls on pore-water dissolved inorganic carbon cycling in a subterranean estuary: a 14C and 13C mass balance approach. *Mar. Chem*. 127, 76–89. doi: 10.1016/j.marchem.2011.07.007.

Essam, D.; Ahmed, M.; Abouelmagd, A.; Soliman, F. 2020. Monitoring temporal variations in groundwater levels in urban áreas using ground penetrating radar. *Science and the Total Environment*, 703: 134986. doi: 10.1016/j.scitotenv.2019.134986.

Esteves, F. A. 1950. Fundamentos de limnologia. 2ª ed. Rio de Janeiro: Interciência, 1998.

Fernandes, E. H. L.; Dyer, K. R..; Moller, O. O.; Niencheski, L. F. 2002. The Patos Lagoon hydrodynamics during an El Niño event (1998). *Continental Shelf Research*, 22, 1699-1713. doi: 10.1016/S0278-4343(02)00033-X.

Fernandes, E. H. L.; Niencheski, L. F. Um modelo de caixas simplificado para o estudo dos processos de transporte na região estuarina da Lagoa dos Patos (RS-Brasil). *Atlântica*. v.20, p. 73-85, 1998.

Fetter, C. W. 2001. *Applies Hydrogeology*. New Jersey, Prentice-Hall, Inc.

Figueiredo, S. A. & Calliari, L. J. 2005. Sangradouros: distribuição espacial, variação sazonal, padrões morfológicos e implicações no gerenciamento costeiro. *Gravel*. 3: 47-57.

Figueiredo, S. A. & Calliari, L. J. 2006. Washouts in the central and northern littoral of Rio Grande do Sul state, Brazil: distribution and implications. J. Coast. Res. 39(SI): 366-370.

Figueiredo, S. A.; Cowell, P.; Short, A. D. 2007. Intermittent backbeach discharge to the surfzone: modes and geomorphologic implications. Journal of Coastal Research, SI 50: 610-614.

Gallucci, F. & Netto, S. A. 2004. Effects of the passage of cold fronts over a coastal site: an ecosystem approach. *Mar. Ecol. Prog. Ser*. 281: 79-92.

Gandara-Martins, A. L; Borzone, C. A.; Guilherme, P. D. B.; Vieira, J. V. 2014. Spatial effects of a washout on sandy beach macrofauna zonation and abundance. *J. Coast. Res*. 31(6): 1459-1468.

Gianuca, K. S. & Tagliani, C. R. A. 2012. Análise em um Sistema de Informação Geográfica (SIG) das alterações na paisagem em ambientes adjacentes a plantios de pinus no Distrito do Estreito, município de São José do Norte, Brasil. *Revista da Gestão Costeira Integrada*. 12(1):43-55.

Godoy, J. M.; Souza, T. A.; Godoy, M L. D.; Moreira, I.; Carvalho, Z. L.; Lacerda, L. D.; Fernandes, F. C. 2013. Groundwater and surface water quality in a coastal bay with negligible fresh groundwater discharge: Arraial do Cabo, Brazil. *Mar. Chem*. 156, 85-97.

Godoy, J. M.; Souza, T. A.; Godoy, M. L. D.; Moreira, I.; Carvalho, Z. L.; Lacerda, L. D.; Fernandes, F. C. 2013. Groundwater and surface water quality in a coastal bay with negligible fresh groundwater discharge: Arraial do Cabo, Brazil. *Mar. Chem.* 156, 85.

Gonzaga, B. A.; Leal Alves, D.; Albuquerque, M. G.; Espinoza, J. M. A.; Almeida, L. P.; Weschenfelder, J. 2020. Development of a low-cost ultrasonic sensor for groundwater monitoring in coastal environments: validation using field and laboratory observations. *Journal of Coastal Research*, 95(SI), XXX-XXX. Doi: 10.2112/SI95-0XX1.

Grimm, A. M.; Barros, V. R.; Doyle, M. E. 2000. Climate variability in Southern South America associated with *El Niño* and *La Niña* events. *J. Clim.* 13, 35-58.

Han, D.; Cao, G.; McCallum, J.; Song, X. 2015. Residence times of groundwater and nitrate transport in coastal aquifer systems: Daweijia area, northeastern China. *Sci. Total Environ*. 538, 539–554. doi.org/10.1016/j.scitotenv.2015.08.036.

Harari, Z. 1996. Ground-penetration radar (GPR) for imaging stratigraphic features and groundwater in sand dunes. *Journal of Applied Geophysics*, 36, 43-52.

Herz, R. 1997. Circulação das águas de superfície da Lagoa dos Patos. Ph.D. Thesis. Universidade de São Paulo, São Paulo, Brazil.

Instituto Brasileiro de Geografia e Estatística (IBGE). Censo demográfico, 2000. Available in <www.ibge.gov.br> Accessed in April, 2020.

Instituto Nacional de Meteorologia do Brasil – INMET. Normais Climatológicas (2011). Brasília-DF, 2011.

Kjerfve, B. 1986. Comparative oceanography of coastal lagoons. In: Wolde, D.A. (Ed.), Estuarine Variability Academic Press, New York, pp. 63–81.

Kroeger K. D. & Charette, M. A. 2008. Nitrogen biogeochemistry of submarine groundwater discharge. *Limnol. Oceanogr*. 53(3), 1025–1039

Krusche, N.; Saraiva, J. M. B.; Reboita, M. S. 2003. Normais climatológicas provisórias de 1991 a 2000 para Rio Grande, RS. Rio Grande: Editora FURG. 84p.

Marques, W. C.; Stringari, C. E.; Eidt, R. T. 2014. The exchange processo of the Patos Lagoon estuary – Brazil: A typical El Niño year versus a normal meteorological conditions year. *Advances in Water Resource and Protection*. 2.

Martin, J. M., Meybeck, M. 1979. Elemental mass-balance of material carried by world major rivers. *Mar. Chem*. 7, 173–206.

Moller, O. O.; Castaing, P.; Salomon, J.C.; Lazure, P. 2001. The influence of local and non-local forcing effects on the subtidal circulation of Patos Lagoon. *Estuaries*. 24 (2), 297–311.

Moller, O. O.; Lorenzetti, J. A.; Stech, J. L.; Mata, M. M. 1996. The Patos Lagoon summertime circulation and dynamics. *Continental Shelf Research*, 16, 35–351. doi.org/10.1016/0278-4343(95)00014-R.

Moore, W. S. 1999. The subterranean estuary: a reaction zone of ground water and seawater. *Marine Chemistry.* v. 65: 111–125. doi.org/10.1016/S0304-4203(99)00014-6.

Moore, W. S. 2010. The effect of submarine groundwater discharge on the ocean. *Annu. Rev. Mar. Sci*. 2, 59–88. doi: 10.1146/annurev-marine-120308-081019.

Moore, W.S. 1996. Large groundwater inputs to coastal waters revealed by ^{226}Ra enrichments. *Nature*, 380, 612-614.

Mulligan, A. E. & Charette, M. A. 2006. Intercomparison of submarine groundwater discharge estimates from a sandy unconfined aquifer. *Journal of Hydrology*, **327**, 411-425. doi: 10.1016/j.jhydrol.2005.11.056.

Mulligan, A. E. & Charette, M. A. 2009. Groundwater flow to the coastal ocean. In: Steele JH, Thorpe SA and Turekian KK (eds) The Coastal Ocean, 2010. Oxford, The United Kingdom, 143-152. doi: doi.org/10.1016/B978-012374473-9.00645-7.

National Water Agency – BRAZIL (ANA). **Hidroweb:** sistemas de informações hidrológicas. Online: http://hidroweb.ana.gov.br/.

Niencheski, L. F. H. & Windom, H. L. 1994. Nutrient flux and budget in Patos Lagoon estuary. *The Science of the Total Environment*. 149, 53-60. doi.org/10.1016/0048-9697(94)90004-3.

Niencheski, L. F. H., Windom, H. L., Moore, W. S.; Jahnke, R. A. 2007. Submarine groundwater discharge of nutrients to the ocean along a coastal lagoon barrier, Southern Brazil. *Mar. Chem*. v. 106 (3-4), 546-561. https://doi.org/10.1016/j.marchem.2007.06.004.

Null, K. A., Dimova, N. T., Knee, K. L., Esser, B. K., Swarzenski, P. W., Singleton, M. J., Stacey, M., Paytan, A. 2012. Submarine groundwater discharge-derived nutrient loads to San Francisco Bay: implications to future ecosystem changes. *Estuar. Coasts.* 35, 1299–1315.

Odebrecht, C.; Du Preez, D. R.; Abreu, P. C.; Campbell, E. E. 2013. Surf zone diatoms: a review of the drivers, patterns and role in sandy beach food chains. *Est. Coast. Shelf Sci*.150, 24-35.

Oehler, T.**;** Tamborski, J.; Rahman, S.; Moosdorf, N.; Ahrens, J.; Mori, C.; Neuholz, R.; Schnetger, B.; Beck, M. 2019. DSi as a Tracer for Submarine Groundwater Discharge. *Frontiers in Marine Science*, *6*, 563.

Pai, S. C.1988. Pre-concentration efficiency of Chelex-100 resin for heavy metals in seawater: Part 2. Distribution of heavy metals on a Chelex-100 column and optimization of the column efficiency by a plate simulation method. *Anal. Chim. Acta*, 211: 271-280.

Paiva, M. & Niencheski, L. F. H. 2018. Advances of submarine groundwater discharge studies in South America. *Journal of the Brazilian Chemical Society*, 29: 916-924.

Paiva, M. L.; Baumgarten, M. G. Z.; Wally, M. K. 2012. Especiação do ferro em águas subterrâneas: otimização do método espectrofotométrico na região da luz visível. *Revista Analytica*, 57, 60-66.

Pasquini, A. I.; Niencheski, L. F. H.; Depetris, P. J. 2012. The ENSO signature and other hydrological characteristics in Patos and adjacent coastal lagoons, south-eastern Brazil. *Estuarine Coast. Shelf Sci*. doi.org/10.1016/j.ecss.2012.07.004.

Paz, C.; Alcalá, F. J.; Carvalho, J. M.; Ribeiro, L. 2017. Current uses of ground penetrating radar in groundwater-dependent ecossystems research. *Science and the Total Environment*, 595, 868-885. http://dx.doi.org/10.1016/j.scitotenv.2017.03.210.

Pereira da Silva, R. 1998. Ocorrência, distribuição e características morfodinâmicas dos sangradouros na zona costeira do Rio grande do Sul: trecho Rio Grande - Chuí, RS. Porto Alegre. 146p. Dissertação de Mestrado em Geociências, Instituto de geociências, Universidade Federal do Rio grande do Sul.

Pereira da Silva, R.; Calliari, L. J.; Tozzi, H. A. M. 2003. The influence of washouts on the erosive susceptibility of Rio Grande do Sul between Cassino and Chuí beaches, Southern Brazil. *Journal of Coastal Research*, SI 35: 332-338.

Pereira da Silva, R.; Calliari, L. J.; Tozzi, H. A. M. 2003. The influence of washouts on the erosive susceptibility of Rio Grande do Sul between Cassino and Chuí beaches, Southern Brazil. *Journal of Coastal Research*, SI 35: 332-338.

Pereira, P. S.; Calliari, L. J. Barletta, R. C. 2010. Heterogeneity and homogeneity of Southern Brazilian beaches: A morphodynamic and statistical approach. *Cont. Shelf Res.* 30, 270-280.

Piedras, F. R. & Odebrecht, C. 2012. The response of surf-zone phytoplankton to nutrient enrichment (Cassino Beach, Brazil). *J. Exp. Mar. Biol. Ecol*., 432 –433, 156–161, http://dx.doi.org/10.1016/j.jembe.2012.07.020.

Piola, A. R.; Matano, R. P.; Palma, E. D.; Möller, O. O.; Campos, E. J. D. 2005. The influence of the Plata River discharge on the western South Atlantic shelf. *Geophys. Res. Letters*, 32, L01603.

Press, F., Siever R., Grotzinger, J. & Jordan, T. H. 2006. Para Entender a Terra. Tradução Rualdo Menegat, 4 ed. – Porto Alegre: bookman, 656 p.: il.

Redfield, A. C.; Ketchum, B. H.; Richards, F. A. 1963. The influence of organisms on the composition of seawater. *The Sea*. M. N. Hill. New York, Interscience Pub. 2, 26-77.

Robinson, C. E., Xin, P., Ssantos, I. R., Charette, M. A., Li, L., Barry, D. A. 2018. Groundwater dynamics in subterranean estuaries of coastal unconfined aquifers: Controls on submarine groundwater discharge and chemical inputs to the ocean. *Advances in Water Resources*. 115, 315-331. doi: 10.3389/fenvs.2019.00141.

Rodellas, V.; Garcia-Orellana, J.; Tovar-Sánchez, A.; Basterretxea, G.; López-Garcia, J. M.; Sánchez-Quiles, D.; Garcia-Solsona, E.; Marqué, P. 2014. Submarine groundwater discharge as a source of nutrients and trace metals in a Mediterranean bay (Palma Beach, Balearic Islands). *Mar. Chem*. 160, 56–66. doi.org/10.1016/j.marchem.2014.01.007.

Rodrigues, M. L. G.; Franco, D.; Sugahara, S. 2004. Climatologia de frentes frias no litoral de Santa Catarina. *Rev. Bras. Geofís*. 22(2): 135-151.

Ruttenberg, K.C. 2005. The Global Phosphorus Cycle, in Schlesinger, W.H. (ed), *Treatise of Biogeochemistry*, Elsevier, 8: 585-643. doi:10.1016/B0-08-043751-6/08153-6.

Santos, I. R.; Burnett, W. C.; Dittmar, T.; Suryaputra, I. G. N. A.; Chanton, J. 2009. Tidal pumping drives nutrient and dissolved organic matter dynamics in a Gulf of Mexico subterranean estuary. *Geochim. Cosmochim. Acta*. 73(5): 1325-1339.

Santos, P. J. P. 1991. Morphodynamical influence of a temporary freshwater stream on the population dynamics of Scolelepis gaucha (Polychaeta: Spionidae) on a sandy beach in Southern Brazil. *Bull. Mar. Sci*. 48(3): 657-664.

Serpa, C. G. 2013. Morfodinâmica praial relacionada à presença de corpos de água intermitentes em duas praias da costa do Rio Grande do Sul, Brasil. Ph.D. Thesis. Universidade Federal do Rio Grande, Rio Grande, Brazil.

Silva, A. F.; Toldo Jr, E. E.; Weschenfelder, J. 2016. Morfodinâmica da desembocadura da Lagoa de Tramandaí (RS-Brasil). *Pesquisas em Geociências*, 44 (1): 155-166.

Silveira, A. L. L. Ciclo Hidrológico e a Bacia Hidrográfi ca. In TUCCI, C. E. M. *Hidrologia: ciência e aplicação*. Porto Alegre: Edusp / ABRH, 1997, 35-51p.

Slomp, C. P. & Van Cappellen, P. 2004. Nutrient inputs to the coastal ocean through submarine groundwater discharge: controls and potential impact. *Journal of Hydrology.* 295 (1-4), 64 - 86.

Soares, I. & Möller, O. 2001. Low-frequency currents and water mass spatial distribution on the southern Brazilian shelf. *Continental Shelf Research* 21(16-17): 1785-1814.

Song, J. M. 2010. Biogeochemical Processes of Biogenic Elements in China Marginal Seas. *Springer, Berlin Heidelberg*, 676p. doi: 10.1007/978-3-642-04060-3.

Sospedra, J.; Niencheski, F. H.; Falco, S.; Andrade, C. F. F.; Attisano, K. K.; Rodilla, M. 2018. Identifying the main sources of silicate in coastal waters of the Southern Gulf of Valencia (Western Mediterranean Sea). *Oceanologia* 60 (1), 52-64. doi.org/ 10.1016/j.oceano.2017.07.004.

Spiteri, C.; Slomp, C. P.; Tuncay, K.; Meile, C. (2008) Modeling biogeochemical processes in subterranean estuaries: the effect of flow dynamics and redox conditions on submarine groundwater discharge. *Water Resour*. Res. 44, W02430. doi:10.1029/ 2008WR006997.

Strickland, J. D. & Parsons, T. R. A pratical handbook of seawater analysis**.** Fish Res.Board. Can. Bull. v.163, 310p, 1972.

Todd, D. K. *Hidrologia de águas subterrâneas*. Trad. sob direção de Araken Silveira e Evelyna Bloem Souto Silveira. São Paulo, EDGARD. 319p, 1959.

Tomazelli, L. J. & Villwock, J. A. 2000. O Cenozóico no Rio Grande do Sul: Geologia da Planície Costeira. In: Holz, M. & De Ros, L. F. eds. Geologia do Rio Grande do Sul. Edição CIGO/UFRGS, Porto Alegre, p. 375-406.

Ullman, W. J.; Chang, B.; Miller, D. C. Madsen, J. A. (2003). Groundwater mixing, nutrient diagenesis, and discharges across a sandy beachface, Cape Henlopen, Delaware (USA). *Estuar. Coast. Shelf Sci.* 57, 539-552.

Vieira, E. F. 1984. Rio Grande do Sul: geografia física e vegetação. Porto Alegre: Sagra. 256p.

Villwock, J. A. & Tomazelli, L. J. Planície Costeira do Rio Grande do Sul: gênese e paisagem atual. 2007. In: Becker, F. G.; Ramos,R. A.; Moura,L. A. (Org.). Biodiversidade. Regiões da Lagoa do Casamento e dos Butiazais de Tapes, planície costeira do Rio Grande do Sul. 1ª ed. Brasília: Ministério do Meio Ambiente/SBF, 2007, p. 1-388.

Windom, H. & F. Niencheski. 2003. Biogeochemical processes in a freshwaterseawater mixing zone in permeable sediments along the coast of Southern Brazil. *Mar. Chem*. v. 83(3-4), 121 - 130. doi.org/10.1016/S0304-4203(03)00106-3.

Windom, H., Moore, W. S., Niencheski, L. F., Jahnke, R. 2006. Submarine groundwater discharge: a large, previously unrecognized source of dissolved iron to the South Atlantic Ocean. *Mar. Chem*. v. 102, 252 - 266. doi.org/10.1016/j.marchem.2006.06.016.

Zabel, M.; Dahmke, A.; Schulz, H. D. 1998. Reginal distribution of diffusive phosphate and silicate fluxes through the sediment-water interface: the eastern south Atlantic. *Deep-Sea Research Part I*, 45, 277–300. doi:10.1016/S0967-0637(97)00073-3.

Zhuang, W.; Gao, X.; Zhang, Y.; Xing, Q.; Tosi, L.; Qin, S. 2014. Geochemical characteristics of phosphorus in surface sediments of two major Chinese mariculture áreas: The Laizhou Bay and the coastal Waters of the Zhangzi Island. *Marine Pollution Bulletin*, 83: 343-351. doi: 10.1016/j.marpolbul.2014.03.040.