Universidade Federal do Rio Grande – FURG
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Potencial disponibilidade de metais traço em sedimentos em áreas de estaleiros no sudeste e sul do Brasil

ASTOLFO ENRIQUE VALERO SORIANO

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

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A-B-C

Au – Ouro (Gold)

Ba – Bário (Barium)

C_{DGT} – Concentração de metal lábil na água intersticial (Concentration of the labile metal in the porewater)

Cd – Cadmio (Cadmium)

C_L – Concentração de metal lábil na fase sólida do sedimento (Concentration of the labile metal in the solid phase of sediments)

Cr – Cromo (Chromium)

Cu – Cobre (Copper)

CuS – Sulfeto de cobre (Copper sulfide)

D-E-F

DGT – Gradiente Difusivo de Fina Membrana (Diffusive Gradients in Thin Films)

Eh – Potencial redox (Redox potential)

Fe – Ferro (Iron)

G-H-I

GF-AAS – Espectrometria de Absorção Atômica com Forno de Grafite (Graphite Furnace Atomic Absorption Spectrometry)

GS – Estaleiro G (G Shipyard)

H_2S – Sulfeto de hidrogênio (Hydrogen sulfide)

HCl – Ácido clorídrico (Hydrochloric acid)

Hg – Mercúrio (Mercury)

HgS – Sulfeto de Mercúrio (Mercury sulfide)

HNO_3 – Ácido Nítrico (Nitric acid)

HVO_4^{-2} – Íon Vanadato (Vanadate ion)

ICP-MS – Espectrometria de Massa com Plasma Indutivamente Acoplado (Inductively Coupled Plasma Mass Spectrometry)

ICP-OES – Espectrometria de Emissão Ótica com Plasma Indutivamente Acoplado (Inductively Coupled Plasma Optical Emission Spectrometry)

M-N

MI – Ilha dos Marinheiros; Área de referência (Marinheiros Island, Reference area)

Mn – Manganês (Manganese)

N_2 – Nitrogênio (Nitrogen)

$NaNO_3$ – Nitrato de sódio (Sodium nitrate)

NE – Nordeste (Northeast)

Ni – Níquel (Nickel)

O-P-Q

O_2 – Oxigênio dissolvido (Dissolved oxygen)

Pb – Chumbo (Lead)

PS – Estaleiro P (P Shipyard)

R-S-T

RJ – Estado Rio de Janeiro (Rio de Janeiro state)

RS – Estado Rio Grande do Sul (Rio Grande do Sul state)

S – Enxofre (Sulfur)

S – Sul (South)

S_1 – Período amostral 1 (Sampling period 1)

S_2 – Período amostral 2 (Sampling period 2)

SC – Estado de Santa Catarina (Santa Catarina state)

Sn – Estanho (Tin)

SO_4^{2-} – Íon sulfato (Sulfate ion)

SQGs – Diretrizes de Qualidade dos Sedimentos (Sediment Quality Guidelines)

SW – Sudoeste (Southwest)

TMS – Estaleiro TM (TM Shipyard)

TOC – Carbono Orgânico Total (Total Organic Carbon)

U-V-W

V – Vanádio (Vanadium)

VO^{+2} – Íon Vanadyl (Vanadyl ion)

X-Y-Z

Zn – Zinco (Zinc)

RESUMO

A especiação e fracionamento dos metais traço, da fase sólida à líquida dos sedimentos, controlam sua potencial disponibilidade e, assim, seu risco ecológico para os organismos. Portanto, para obter uma avaliação de risco mais abrangente, é necessário acoplar metodologias capazes de avaliar a mobilidade de metais no sedimento. Neste estudo, a técnica de Gradientes Difusivos de Fina Membrana (DGT) e métodos clássicos de extração química para estabelecer a biodisponibilidade de metais traço em sedimentos, juntamente com sensores voltamétricos de estado sólido, foram acoplados com o objetivo de avaliar a mobilidade e potencial disponibilidade de Cr, Cu, Ni, Pb, V e Zn em água intersticial e sedimentos de áreas de estaleiros do sudeste e sul do Brasil. As maiores concentrações de metais lábeis foram determinadas quando maior quantidade de embarcações foram reparadas e em estaleiros com um maior tempo de operação. Além disso, a distribuição dos metais na água intersticial e na fase sólida dos sedimentos (metais móveis) e as relações significativas entre os metais permitiram distinguir a contribuição dos componentes das tintas anti-incrustante e produtos derivados do petróleo. O fluxo difusivo de cada metal para a interface água-sedimento indicou que o $Cu_{\mathbf{DGT}}$ apresentou o maior fluxo difusivo (3,66E-03 $mmol.m^{-2}.d^{-1}$) no estaleiro com o maior tempo de operação. Portanto, um enriquecimento foi observado para Cu, Pb e Zn nos sedimentos e um possível risco ecológico de Effects Range Median para Apparent Effects Threshold para a biota aquática. Isto, independentemente das condições físico-químicas e hidrodinâmicas de cada ambiente. Finalmente, o acoplamento destas metodologias permitiu uma avaliação abrangente das propriedades geoquímicas do sedimento e a potencial biodisponibilidade e risco ecológico dos metais traço em sistemas estuarinos onde há entrada contínua e específica desses elementos. Assim como o uso da técnica de DGT no sedimento, pela primeira vez, em distintos sistemas estuarinos demonstrou seu potencial para ser aplicado em futuros programas de monitoramento.

Palavras-Chave: Metais traço, especiação, DGT, água intersticial, sedimentos.

ABSTRACT

Speciation and partitioning of trace metals, from solid to solution phases of sediments, control their potential availability and thus, their potential ecological risk to organisms. Therefore, in order to obtain a broad evaluation of their risk, it is necessary to couple methodologies which are able to assess metal mobility in the sediment. In this study, the Diffusive Gradients in Thin Films (DGT) technique and classic chemical extraction methods of trace metal availability in sediments, together with solid-state voltammetric sensors, were coupled with the objective of assessing mobility and potential availability of Cr, Cu, Ni, Pb, V and Zn in sediment porewaters and sediments in southeastern and southern Brazilian shipyard areas. The highest labile metal concentrations were determined where great vessel repairs were carried out and in shipyards with the longest operating time. In addition, trace metals distribution in solution phase and solid phase of sediments (mobile metals) and significant relations among metals enabled to distinguish the contribution of antifouling paint components and petroleum products. The diffusive flux of every metal to the sediment-water interface indicated that $Cu_{\mathbf{DGT}}$ had the highest flux (3.66E-03 $mmol.m^{-2}.d^{-1}$) in the shipyard with the longest operating time. Therefore, enrichment was observed for Cu, Pb and Zn in sediments and a possible ecological risk of Effects Range Median to Apparent Effects Threshold for aquatic biota. This was observed regardless of the physicochemical and hydrodynamic conditions of each environment. Finally, coupling of these methodologies allowed a comprehensive evaluation of the geochemical properties of the sediment and the potential bioavailability and ecological risk of trace metals in estuarine systems where there is continuous and specific input of these elements. The use of the DGT technique in the sediment, for the first time, in distinct estuarine systems demonstrated its potential to be applied to future network programs.

Keywords: Trace metals, speciation, DGT, porewater, sediments

CAPÍTULO I:

Introdução

Introdução

Nas últimas décadas tem ocorrido maior entrada de metais traço em ambientes estuarinos, propiciada por atividades antrópicas; as quais se concentram nas margens dos grandes sistemas aquáticos (Machado *et al.*, 2016). Isto pode representar um grande risco ecológico devido aos metais serem tóxicos para os organismos quando ultrapassam níveis críticos; além de resultar altamente persistentes e invariáveis em compartimentos ambientais como os sedimentos (Loska & Wiechula, 2003; Sun *et al.*, 2018).

Contudo, o sedimento - incluindo a água intersticial- também pode representar uma fonte potencial de contaminação; devido a uma série de processos (adsorção, precipitação, difusão e advecção, ação de maré e ondas e bioturbação) e oscilações regulares da interface redox (Du Laing *et al.*, 2009; Machado *et al.*, 2016), geram um incremento no fluxo difusivo dos metais e das taxas de reação. Isto aumenta o seu risco ambiental em curto prazo, já que uma vez dissolvidos, são mais facilmente biodisponíveis para os organismos (McClain *et al.*, 2003; Song *et al.*, 2018). Não obstante, a aplicação das Diretrizes de Qualidade de Sedimentos e Índices de Poluição para avaliar o possível risco ecológico desses poluentes, realiza-se utilizando a fração total do sedimento, a qual não reflete a mobilidade e reatividade dos metais (MacDonald *et al.*, 2000; Saleem *et al.*, 2015).

Portanto, para avaliar tal risco em áreas com atividades antrópicas localizadas, torna-se necessário aplicar metodologias que permitam inferir o comportamento geoquímico dos metais através do estudo do fracionamento e possível biodisponibilidade dos metais no sedimento e água intersticial (Tessier *et al.*, 1979; Forstner *et al.*, 1986; Du Laing *et al.*, 2009). No entanto, técnicas de especiação para metais no sedimento, e técnicas químicas clássicas para sua determinação na água intersticial podem não resultar precisas. Os principais problemas ocorrem devido a mudanças nas condições físico-químicas ambientais e, portanto mudanças na especiação de alguns metais, que podem ser geradas durante coleta, transporte e tratamento das amostras (Hooda & Zhang, 2008; Stockdale *et al.*, 2009).

Portanto, tem se desenvolvido técnicas mais precisas para o estudo da disponibilidade dos metais traço, como é a aplicação de amostradores passivos de Gradientes Difusivos de Fina Membrana (DGT; siglas em inglês), os quais são capazes de acumular quantitativa e simultaneamente espécies metálicas lábeis na água intersticial com alta resolução espacial (Zhang & Davison, 1995; Zhang *et al.*, 1995). Estes amostradores passivos atuam de forma dinâmica fornecendo uma medida que reflete a concentração na fase líquida do sedimento, a taxa de reabastecimento para a solução e a taxa de transporte dos íons metálicos através do sedimento. (Hooda & Zhang, 2008; Stockdale *et al.*, 2009). Isto permite avaliar as taxas de fluxo difusivo e os processos que atuam entre a fase sólida e líquida para tornar os metais disponíveis (Zhang & Davison, 1995; Zhang *et al.*, 1995; Zhang *et al.*, 2014). Adicionalmente, diversos autores indicam que a técnica DGT em combinação com técnicas de avaliação do conteúdo de metais no sedimento permitem uma determinação mais abrangente do risco potencial destes contaminantes (Parker *et al.*, 2017; Song *et al.*, 2018; Wang *et al.*, 2019).

Da mesma forma, a voltametria em estado sólido permite fazer medições contínuas *in situ* e em tempo real de múltiplos íons na água intersticial, de forma simples e com alta sensibilidade em microescala (Brendel & Luther, 1995; Olson *et al.*, 2017). A aplicação desta técnica permite obter uma visão das espécies químicas sensíveis às variações redox no sedimento e, portanto dos processos geoquímicos atuantes tanto na interface água-sedimento, como entre as fases sólida-líquida ao longo de um perfil sedimentar (Taillefert *et al.,* 2007). A técnica DGT e da voltametria em estado sólido são complementares, e estudos acoplando estas ferramentas podem gerar resultados mais robustos na avaliação da especiação de metais traço no sedimento. Embora, estudos acoplando estas técnicas são praticamente inexistentes atualmente, especialmente em sistemas estuarinos. Adicionalmente, o acoplamento permitir uma melhor avaliação de locais com presença de uma fonte continua de metais traço ou *hotspots*. Exemplo disto podem ser os estaleiros, responsáveis pela construção e reparação de embarcações de diverso porte, e amplamente distribuídos ao longo de toda a costa brasileira.

Nestas áreas, desenvolvem-se processos industriais como: aplicação de pintura e revestimentos, aplicação de óleos e lubrificantes, e corte e soldagem de peças metálicas (Celebi & Vadar, 2008). Consequentemente, partículas de tintas anti-incrustantes - de nova geração- que são aplicadas para inibir a incrustação de organismos nos casos das embarcações, apresentam altas concentrações de Cu e Zn; além de conter Ba, Cd, Cr, Ni, Pb e Sn em menor proporção (Turner, 2010; Huntingford & Turner, 2011; Costa *et al.*, 2016; Soroldoni *et al.*, 2018). Metais como Ni, Pb e V podem ser gerados da queima de combustíveis fosseis e aplicação de outros produtos derivados de petróleo como graxas e diesel naval (Cheng & Hu, 2010; Pereira *et al.*, 2018). Ademais, a presença de embarcações abandonadas representa um passivo ambiental de metais como Cu, Zn e Pb (Rees *et al*., 2014; Turner, 2014; Pereira *et al.*, 2018).

Adicionalmente, Pereira *et al.* (2018) mostraram que em um sistema hidrodinâmico complexo como o estuário da Lagoa dos Patos (RS), as próprias condições que caracterizam as áreas de estaleiros (circulação restrita, baixa energia de transporte, margens modificadas pelo homem e aporte contínuo) permitem obter relações interelementares significativas para traçar metais provenientes de produtos derivados de petróleo e tintas anti-incrustantes. Isto permite concluir que aplicação de ferramentas geoquímicas como o uso destas relações, permite identificar a possível proveniência dos metais traço em áreas com presença de *hotspot*; e assim discernir entre o aporte antrópico e o possível enriquecimento natural (Prabakaran *et al.*, 2019).

No entanto, estudos mostrando se estas relações podem ser observadas para os metais traço que estejam presentes na água intersticial do sedimento destes locais são inexistentes. Portanto, no presente estudo foram selecionadas instalações de estaleiros (médio a grande porte) localizadas em áreas estuarinas com condições hidrodinâmicas diferentes. O estudo dessas áreas permitiu a formulação de duas hipóteses: (1) o aporte de metais traço nos sedimentos é localizado o suficiente para permitir estabelecer relações entre as frações lábeis, apesar das diferentes hidrodinâmicas de cada local e (2) o acúmulo de metais traço no sedimento dessas áreas é elevado o suficiente para permitir observar a mesma relação entre metais potencialmente disponíveis na água intersticial, como geralmente é observado na fase sólida.

Consequentemente, este estudo visou: (1) Avaliar a mobilidade e biodisponibilidade de diversos metais traço (Cr, Cu, Ni, Pb, V & Zn) em sedimentos de áreas de estaleiros e sua relação com as possíveis fontes antrópicas (tintas anti-incrustantes e produtos derivados de petróleo) em diferentes condições hidrodinâmicas e (2) mostrar o acoplamento de diversas técnicas (ataque ácido, exposição de amostradores passivos DGT e aplicação *in situ* de sensores voltamétricos) como uma ferramenta para avaliação da disponibilidade e possível risco de metais traço em locais com fonte localizada de aporte antropogênico.

CAPÍTULO II:

Objetivos

Objetivos

1. Geral

Avaliar a potencial disponibilidade de Cr, Cu, Ni, Pb, V & Zn nos sedimentos superficiais de áreas de estaleiros da costa sudeste e sul do Brasil e estabelecer a sua relação com as suas possíveis fontes antrópicas em diferentes condições hidrodinâmicas.

2. Específicos

- ✓ Determinar as concentrações lábeis de Cr, Cu, Ni, Pb, V e Zn e se ocorrem diferenças entre as mesmas presentes na fase líquida e sólida dos sedimentos superficiais dos estaleiros TMS (Niterói, RJ), PS (Navegantes, SC) e GS (Rio Grande, RS).

- ✓ Comparar a relação entre a concentração lábil dos metais na água intersticial com a fracção lábil na fase sólida em função dos processos que atuam nos sedimentos superficiais de cada local de estudo.

- ✓ Verificar se a granulometria, as condições físico-químicas, os teores de carbono orgânico total e sulfetos no sedimento possuem uma correlação com os metais em estudo.

- ✓ Estabelecer se nas áreas de estudo ocorre correlação semelhante entre os elementos metálicos, e relação com as suas possíveis fontes (tintas anti-incrustantes e derivados de petróleo).

CAPÍTULO III:

Resultados e Discussões

Para a obtenção do título de Mestre pelo Programa de Pós-Graduação em Oceanologia, é requerido que o discente realize a submissão de pelo menos um artigo científico como primeiro autor em periódico com corpo indexado. Desse modo, os resultados da pesquisa desenvolvida durante o período de mestrado e a discussão dos resultados serão apresentados em forma de artigo neste Capítulo. O manuscrito, de autoria de Astolfo Valero, Karelys Umbría-Salinas, Mônica Wallner-Kersanach, Carlos Ferreira de Andrade, Maria Josefa Santos Yabé, Leonardo Contreira-Pereira, Julio Cesar Wasserman, Katia Kuroshima e Hao Zhang, é intitulado **"Potential availability of trace metals in sediments in southeastern and southern Brazilian shipyard areas by the DGT technique and chemical extraction methods"** e foi submetido para publicação e encontra-se sub revisão no periódico ***"Science of The Total Environment"***.

Potential availability of trace metals in sediments in southeastern and southern Brazilian shipyard areas by the DGT technique and chemical extraction methods

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Abstract

Speciation and partitioning of trace metals, from solid to solution phases of sediments, control their bioavailability and thus, their potential ecological risk to organisms. Therefore, in order to obtain a broad evaluation of their risk, it is necessary to couple methodologies which are able to assess metal mobility in the sediment. In this study, the Diffusive Gradients in Thin Films (DGT) technique and classic chemical extraction methods of trace metal bioavailability in sediments, together with solid-state voltammetric sensors, were coupled with the objective of assessing mobility and potential availability of Cr, Cu, Ni, Pb, V and Zn in sediment porewaters and sediments in southeastern and southern Brazilian shipyard areas. The highest labile metal concentrations were determined where great vessel repairs were carried out and in shipyards with the longest operating time. In addition, trace metals distribution in porewater and solid phase of sediments (labile metals) and significant relations among metals enabled to distinguish the contribution of antifouling paint components. The diffusive flux of every metal measured at the surface of the sediment indicated that $Cu_{\mathbf{DGT}}$ had the highest flux (3.66E-03 $mmol.m^{-2}.d^{-1}$) in the shipyard with the longest operating time. Therefore, enrichment was observed for Cu, Pb and Zn in sediments and a possible ecological risk of Effects Range Median to Apparent Effects Threshold. Finally, coupling of these methodologies allowed a comprehensive evaluation of potential bioavailability and ecological risk of trace metals in aquatic systems where there is continuous and specific input of these elements. The use of the DGT technique in the sediment, for the first time, in distinct estuarine systems demonstrated its potential to be applied to future network programs.

Keywords: DGT; trace metals; shipyards; porewater; availability; microelectrodes.

1. Introduction

Recently, there has been great input of trace metals into estuarine environments as the result of anthropogenic activities, which concentrate in the margins of large aquatic systems (Machado *et al.,* 2016). These elements become toxic to organisms when they exceed critical levels, besides being highly persistent in environmental compartments, such as sediments (Loska & Wiechula, 2003; Sun *et al.,* 2018). However, sediment –including porewater – may represent a potential source of pollution, since certain processes, such as precipitation or dissolution of mineral phases, biological activity, groundwater discharge and tidal variations (Du Laing *et al.,* 2009; Machado *et al.,* 2016), drive diffusive flux of trace metals from solid to solution phases, and, once dissolved, they become more easily available to organisms (Song *et al.,* 2018).

Consequently, the application of Sediment Quality Guidelines and Pollution Index to ecological risk assessment of these pollutants, which are applied to the total metal concentration in the sediment, do not fully reflect the mobility and reactivity of trace metals (Long & MacDonald, 1998). Therefore, to assess such risk more accurately, it is necessary to apply methodologies that enable geochemical behavior and bioavailability of trace metals to be inferred in sediment and porewater (Forstner *et al.,* 1986; Du Laing *et al.,* 2009). Nevertheless, these methodologies may not be accurate, due to changes in physicochemical conditions and thus, changes in speciation of some metals during sampling, transport and sample treatment (Hooda & Zhang, 2008; Stockdale *et al.,* 2009). Therefore, more precise techniques have been developed to study potential availability of trace metals, such as Diffusive Gradients in Thin Films (DGT) which is able to accumulate, quantitatively and simultaneously, labile metal species in sediments with high spatial resolution (Zhang & Davison, 1995; Zhang *et al.,* 1995).

DGT provides a measure which is able to reflect labile metal concentrations at the interface of DGT probe and the sediment, as well as the resupply rate from solid phases to the porewater; which are important to a more comprehensive understanding of processes involving available metal species (Hooda & Zhang, 2008; Stockdale *et al.,* 2009). In addition, the combination of the DGT technique and other methodologies for the evaluation of trace metal contents in sediment is useful for a more accurate assessment of their potential risks (Song *et al.,* 2018).

Likewise, solid-state voltammetry enables continuous in situ and real-time measurements of multiple ions in porewater, in a simple way and with high sensitivity at microscale (Brendel & Luther, 1995; Olson *et al.,* 2017). The application of this technique enables chemical species which are sensitive to redox variations to be found in the sediment. Therefore, geochemical processes at the sediment-water interface and between solid-solution phases along a sedimentary profile can be observed. Since the DGT and solid-state voltammetry techniques are complementary, studies that couple them may yield useful results in the evaluation of metal species in sediments. However, there are almost no studies of this topic, especially in locations with a continuous source of trace metals. Examples are the poorly studied Brazilian shipyard sites which are widely distributed along the coast and responsible for ship building and repair.

During vessel maintenance, new-generation antifouling paints, which are rich in Cu and Zn, generate particles that end up in the water; to a lesser extent, they also contain other metals, such as Ba, Cd, Cr, Ni, Pb and Sn (Turner, 2010; Costa *et al.,* 2016; Soroldoni *et al.,* 2018). Additionally, trace metals, such as Ni, Pb and V, can be generated by the burning of fossil fuels and the application of other petroleum products, such as diesel oil and grease (Pereira et al., 2018). Studies on sediments in shipyard areas showed that abandoned vessels contribute many trace elements, such as Cu, Pb and Zn (Rees *et al.,* 2014) to the surrounding environment. Characteristics of shipyard areas (restricted circulation, low transport energy, modified margins and continuous supply of metals) lead to significant relations among metals (derived from conventional acid extraction) in the sediment solid phase, which can be used as contamination tracers of petroleum products and antifouling paints in different locations (Pereira *et al.,* 2018). However, no studies have shown whether such relations among metals can be found in the solution phase (porewater) of sediments of shipyard areas.

Therefore, in this study, shipyard facilities (from medium to large ones) located in estuarine systems with different hydrodynamic conditions were selected. The study of these areas permitted the formulation of two hypotheses: (1) the input of trace metals from shipyard activities to the sediments is localized enough that allow to stablish relationships among the labile fraction of them, despite the variations in the hydrodynamics of each site and (2) the trace metals accumulation in the sediment of these areas is elevated enough that allow to observe the same relationship among potentially bioavailable metals in the porewater as generally is observed in the solid phase. Thus, this study aimed: (1) to evaluate the mobility and potential bioavailability of Cr, Cu, Ni, Pb, V and Zn in sediments in shipyard areas and their relations with anthropogenic sources (antifouling paints and petroleum products) under different hydrodynamic conditions; and (2) to couple diverse methodologies (acid leaching, DGT technique for labile metals and in situ application of voltammetric sensors for O_2 and H_2S) as a frame of multiple tools to evaluate potential bioavailability and possible risk of trace metals in places with specific sources of anthropogenic input.

2. Materials and Methods

2.1. Study Area

The study was carried out in three different shipyard facilities situated in port areas of economic importance in estuaries of the southeastern and southern coast of Brazil, specifically, the Guanabara Bay (RJ), the Itajaí-Açu River (SC) and the Patos Lagoon estuary (RS), between February and September 2018 (Figure 1). In the Patos Lagoon estuary, a reference site without any shipyard facility was also selected.

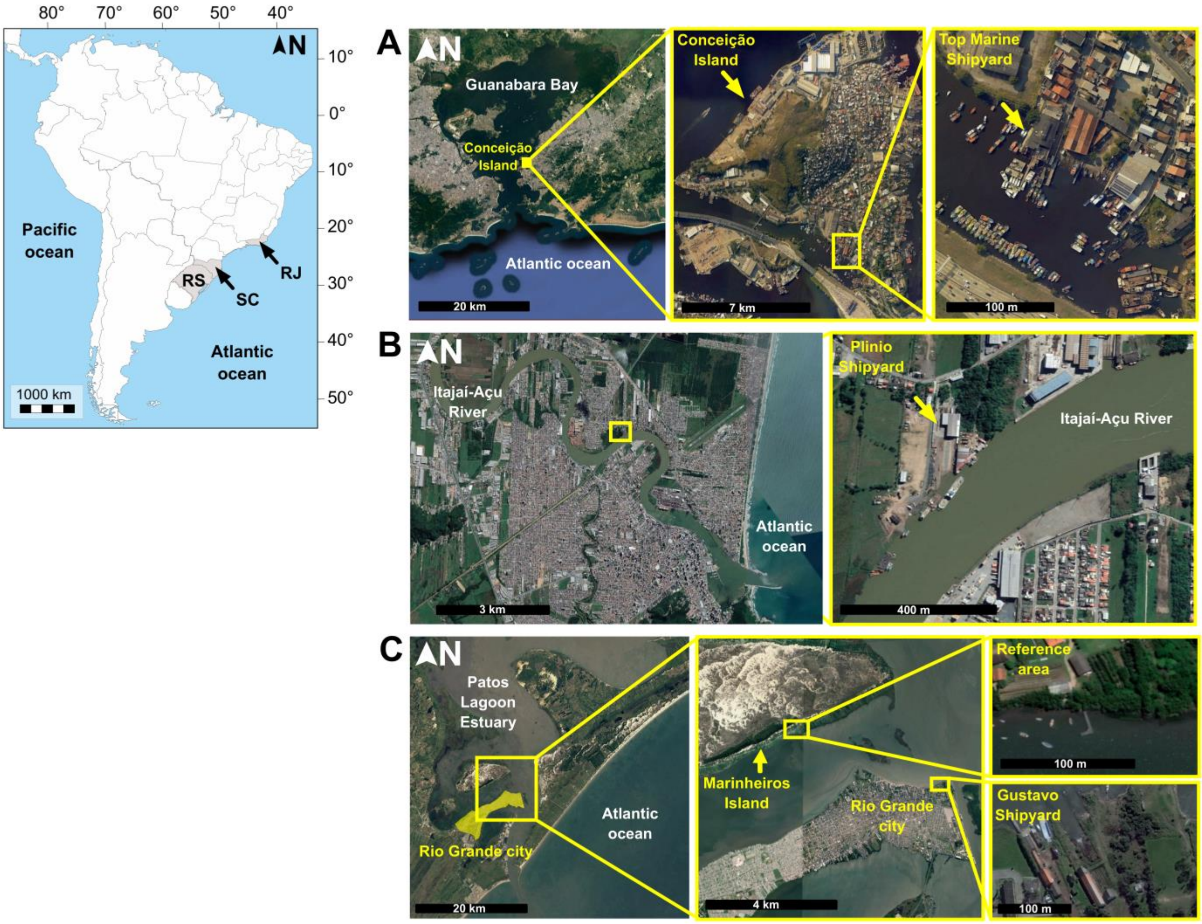

Figure 1. Study sites in estuarine areas in the southeastern and southern coast of Brazil, specifically: A) the TM Shipyard located in the Conceição Island in the margins of the Guanabara Bay (RJ); B) the P Shipyard located in the margins of the Itajaí-Açu River (SC); and C) the G Shipyard (GS) and a Reference Area, with not shipyard facilities (MI) located in the southern region of the Patos Lagoon estuary (RS). Satellite images were extracted from Google Earth® in 2019 July.

The TM Shipyard (TMS; 22°52'32"S, 43°6'59"W) has operated for about 20 years in a total area of 1.500m² located in the Guanabara Bay (22°52'32"S, 43°6'59"W), specifically on the Conceição Island (Niterói, RJ). The shipyard is located in a small inlet where water circulation is restricted; besides, several other shipyards, a port and a large number of active and abandoned vessels can be found in its surrounding waters (Kjerfve *et al.,* 1997). The Guanabara Bay includes several islands and is considered one of the most prominent coastal zones in Brazil; it is shallow near Niterói with a mean depth of 5.7m (Amador, 1997). It is a highly eutrophic environment, which is driven mainly by mixed and semi-diurnal tidal currents and whose tidal amplitude is 0.3m (Kjerfve *et al.,* 2001). This environment is partially stratified with the surficial waters supersaturated with oxygen, while anoxic conditions are found in the water near the bottom (Kjerfve *et al.,* 1997).

The P Shipyard (PS; 26°51'55"S, 48°42'23"W) is located in one of the meanders of the Itajaí-Açú River (Navegantes, SC). It stretches over 2,589m² and has been operating since 1999, providing repair services, transportation and launching of ferry boats, fishing boats and from medium to large vessels. Saltwater input in the estuarine basin depends on the discharge regime of the river, i.e., under low discharge conditions penetration of seawater can reach approximately 18km upstream the river mouth (Schettini, 2002). In addition, the tidal regime is characterized by mixed semi-diurnal micro-tides and is influenced by local meteorological factors, whose main agents are atmospheric pressure and wind shear stress (Schettini, 2002). This estuary has great economic importance, not only because it is the largest national fishing center, but also due to several industrial units along the river banks (Schettini, 2002). However, these industries contribute to the inputs of organic compounds and metals throughout the river basin (Pereira Filho *et al.,* 2010).

The G Shipyard (GS), located in the southern region of the Patos Lagoon estuary (32°01.77"S, 52°04.91"W) (Rio Grande, RS) has been repairing vessels for more than one century. It is also an important location where city vessels are supplied with diesel oil (Costa *et al.,* 2016; Pereira *et al.,* 2018). In addition, a reference area at the Marinheiros Island (MI) was selected because there are no shipyard facilities there. The Patos Lagoon estuary has complex hydrodynamics, driven mainly by wind strength and, to a lesser extent, by the tidal regime, with amplitude of 0.47m (Möller *et al.,* 1996; Fernandes *et al.,* 2002). The estuary also exhibits a seasonal wind pattern from September to April, which is characterized by strong activity of northeast (NE) winds, while southwest (SW) to south (S) winds predominate from May to September (Möller *et al.,* 1996). NE winds impulse the discharge of fresh water of the lagoon, while S and SW winds favor the entry of seawater into the estuary (Costa *et al.,* 1988). In addition, climatological events, such as "El Niño", generally cause an intense discharge of fresh water to the ocean through the estuary, while "La

Niña" events produce periods of drought and high entrance and permanence of seawater inside the estuary (Pasquini *et al.,* 2012).

2.2. DGT sampler preparation

All reagents used for the preparation of DGT samplers and chemical analyses were of analytical grade, whilst ultra-pure water (Milli-Q®, 18.2MΩcm) was also used. Cleaning of plastic materials and glassware used for trace metal determination was performed by immersion in 10% (v/v) nitric acid (HNO_3) solution for at least 24 h.

DGT devices consist of a plastic base, an ionic exchange resin gel (thickness and composition depending on the desired analyte), polyacrylamide diffusive gel (0.8mm thick), a membrane filter of cellulose nitrate (0.45μm porosity) and a plastic holder with a circular (3.14cm^2) exposure window (Zhang *et al.,* 1995). Plastic holders of the DGT devices were obtained from DGT Research Ltd (Lancaster, UK) and prepared with diffusive gel (0.8mm thick) and two types of ion exchange resin: (1) Chelex-100 (0.4mm) for the determination of Cr, Cu and Ni, as described by Zhang *et al.* (1995); and (2) precipitated ferrihydrite (0.5mm) for the determination of V, as described by Luo *et al.* (2010). Gels were made with the help of polystyrene spacers of the required thickness and resulting thickness was tested by a 1000X resolution digital microscope.

Once prepared, DGT devices were immersed in a metal free sodium nitrate ($NaNO_3$) and deoxygenated solution, prior to field deployment, for 16 hours by continuous bubbling of N_2 (Lin *et al.,* 2017). Samplers were kept refrigerated in zip-lock® bags until deployment. All procedures were performed in a laminar flow hood to minimize contamination by metals. Two devices for blanks were submitted to the same procedures and taken to the field without being deployed.

2.3. DGT deployment and sediment sampling

Sampling was carried out in every shipyard facility in two sampling periods in 2018. One (S_1) was conducted between February and March, which represent the rainy season at the Guanabara Bay and the Itajaí-Açu River and the dry season at the Patos Lagoon estuary. The second one (S_2), was carried out between July and September, representing the rainy season at the Patos Lagoon estuary and the dry season at the Guanabara Bay and the Itajaí-Açu River. It should be noted that, in the rainy season, sampling in the Patos Lagoon estuary was more intensive, since previous studies show that, in periods with high fluvial discharge, trace metal concentration tends to be higher in both the water column and the sediment (Costa *et al.,* 2016, Pereira *et al.,* 2018).

DGT devices were deployed in situ on the superficial sediment (0-2cm depth), by using between 5 and 9 units of two types of binding gels (Chelex-100 and precipitated ferrihydrite). They were deployed in the intertidal area (during low tide) of the shipyards for 48 hours. Each DGT device was gently pressed onto the surface of the sediment, ensuring full contact between the device exposure window and the sediment surface. It was conducted with the support of an acrylic structure which allows the fixation of the devices to the sediment. At the end of deployment, DGT devices were rinsed with ultrapure water to remove any particle retained on the filter, then stored and transported under refrigeration to the laboratory. Afterwards, binding gels were transferred to eppendorf tubes and eluted in 1mL suprapur® HNO_3 (1M) for at least 24 hours before analysis (Zhang & Davison, 1995).

The following physicochemical parameters were determined: temperature (DataLogger, OnSet) was measured at every sampling hour during the 48-hour deployment and the sensor was inserted in the sediment in the same DGT structure; and pH (MP120, Mettler Toledo) and Eh (ROX-500, Analion) were measured directly in the sediment at the beginning and the end of the deployment. Besides, salinity was measured in the water column. Additionally, a sediment core (10cm) was collected both at the G Shipyard and Marinheiros Island, during the S_2 period, between July and September. The choice of the GS site was due to its high sediment contamination (Costa *et al.,* 2016; Pereira *et al.,* 2018) while the MI site was picked because of the absence of inputs from shipyards. Sampling took place during flood tide and the supernatant water in the upper core was maintained for the subsequent in situ qualitative determination of dissolved O_2 and H_2S. Core sampling occurred on days influenced by NE winds and constant precipitations that allowed greater discharge of fresh water into the estuary. Finally, in the first and second sampling periods, 3 and 9 samples of superficial sediments (0-5cm depth) were collected by triplicate, respectively, to determine the content of trace metals, Total Organic Carbon (TOC) and granulometry. In the laboratory, sediment samples were lyophilized (Liotop-model L101) for approximately 72h and, subsequently, disaggregated and homogenized with a mortar and pestle.

2.4. Analytical procedures

2.4.1. Granulometry and Total Organic Carbon

The granulometric analysis was performed according to the method described by Suguio (1973). The TOC content was determined by the method described by Zimmermann *et al.* (1997), i.e., 1g sediment was decarbonated under concentrated HCl vapor for a 24h period. After that, samples were dried again and the analysis was performed by a CHNS/O Elemental Analyzer (2400 series, Perkin Elmer®). In order to determine the accuracy of the method, three Certified Reference Materials were analyzed: acetanilide and Marine Sediment Certified Reference Material for Trace Metals (MESS-1 and MESS-3; National Research Council, Canada). Variations in mean percentage recoveries (n = 3) of the materials was below ± 10%.

2.4.2. *In situ* voltammetric method of porewater analyses

Qualitative determination of dissolved O_2 in the water column (1cm above the sediment) and the sediment-water interface, as well as dissolved H_2S determination in the porewater, was performed as described by Brendel & Luther (1995). All measurements were performed in situ and in the first 30 minutes after core sampling. Measurements were carried out by a solid micro-electrode of Au/Hg amalgam, constructed as described by Luther *et al.* (2008) and connected to a potentiostat (μStat 400 Bipotentiostat, Metrohm). Voltammetric scans were performed using cyclic voltammetry across a potential range from -0.10 to -1.80V at a scan rate of $1000 mV.s^{-1}$. Besides, -0.9V conditioning was applied to the beginning of every scan for electrochemical conditioning of the electrode to avoid interference of HgS formed on the sensor surface. Measurements were performed in duplicate, thus generating profiles of dissolved H_2S in depth (cm) in the sediment.

2.4.3. Trace metal labile fraction (C_{DGT})

Determination of labile metal concentrations (CDGT), at the interface of DGT and sediment, was carried out according to Zhang *et al.* (1995). Firstly, the mass of every metal retained in resin gels (M) was calculated by the following equation:

$$M = \frac{Ce\,(V_{HNO_3} + V_{gel})}{fe} \qquad \text{Equation 1}$$

Where the concentration measured in the elution solution (Ce), the gel volume (V_{gel}), the total volume of the acid (V_{HNO_3}) and the elution factor (fe) are considered. Based on the metal mass, $C_{\mathbf{DGT}}$ can be calculated by the equation:

$$C_{DGT} = \frac{M\Delta g}{DtA} \qquad \text{Equation 2}$$

Where the terms include thicknesses of the diffusive gel and of the filter (Δg), the diffusion coefficient of the metal retained in the diffusive gel (D), the deployment time (t) and the sampler window area (A). Diffusion coefficients were obtained from DGT Research Ltd (www.dgtresearch.com).

The flux of every trace metal (F) from sediment to DGT device was determined by the equation described by Gao *et al.* (2009):

$$F = \frac{M}{At} \qquad \text{Equation 3}$$

As DGT devices were directly deployed on the surface of the sediment, the DGT fluxes can be treated as potential metal fluxes from sediment to overlying water.

Cr (Cr_{DGT}), Cu (Cu_{DGT}) and Ni (Ni_{DGT}) contents were analyzed by Graphite Furnace Atomic Absorption Spectrometry (GF-AAS, Shimadzu model AA-7000), whereas V_{DGT} was analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Varian model 820MS). Analytical and instrumental control of the analysis was carried out by the River Water Certified Reference Material for Trace Metals (SLRS-6; National Research Council, Canada). Resulting recoveries (n = 3) were: Cr (138%); Cu (98%); and Ni (94%). The highest recovery percentages of Cr are associated with low concentrations of the element in the Certified Reference Material (0.252 ± 0.012 $\mu.L^{-1}$), which was closer to the Detection Limit calculated for the technique ($0.1733\mu.L^{-1}$). Analyses were carried out individually for every sampling period; Detection Limits (3σ) of C_{DGT} in the first and second sampling periods were 0.04-0.07 $\mu g.L^{-1}$ for Cr, 0.04-0.10 $\mu g.L^{-1}$ for Cu, 0.10-0.11 $\mu g.L^{-1}$ for Ni and 0.08 $\mu g.L^{-1}$ for V.

2.4.4. Leachable trace metal concentrations in the solid phase of sediments (C_L)

Concentrations of the leachable trace metals in the solid phase of sediments (C_L) were measured in the total granulometric fraction (<1000μm) in order to maintain high representation of the dominant granulometry at most study sites. C_L concentration was obtained by the application of 0.1M HCl acid leaching, as described by Costa *et al.* (2016). Resulting solutions were individually filtered through a quantitative Whatman (No. 44; 3μm porosity) filter, filled up to 25mL with 0.1M HCl solution and stored at 4°C prior analysis. This methodology allows the determination of the fraction of weakly adsorbed metals associated with poorly crystalline Fe/Mn oxyhydroxides and iron monosulfides (Canfield, 1989).

Cr_L, Cu_L, Ni_L, Pb_L, V_L and Zn_L contents were measured by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Perkin Elmer, model 2100 DV). In the analytical quality control, the Method of Detection Limit was based on the analysis of a sample (n=10) of every metal. Additionally, in order to determine the accuracy of the analytical method, blanks and samples with aliquots of known metal concentrations (spike, n=3) were submitted to the same analytical procedure. The following recoveries were obtained: Cr (99%); Cu (140%); Ni (82%); Pb (105%); V (103%); and Zn (141%). Detection Limits of the Method (3σ) were 0.05 $mg.kg^{-1}$ for CrL, 2.03 $mg.kg^{-1}$ for Cu, 0.05 $mg.kg^{-1}$ for Ni, 0.08 $mg.kg^{-1}$ for Pb, 0.05 $mg.kg^{-1}$ for V and 1.27 $mg.kg^{-1}$ for Zn.

2.5. Statistical analysis

Normality of data distribution was evaluated by the Shapiro-Wilk test at 95% significance level, showing a normal distribution; data were log(x) transformed for C_L and log(x+1) transformed for C_{DGT}. Differences between sampling periods and among sites were evaluated by the t-test ($p<0.05$). In addition, Pearson's correlation coefficients (r; $p<0.05$) were calculated to evaluate associations among variables, i.e., C_{DGT} and C_L concentrations, physicochemical properties of the sediment and TOC content of all sampling sites in the second sampling period. This period was selected for the determination of the correlation coefficients due to their high n (36), which enabled correlations with great robustness and accuracy to be obtained. Data processing was performed with the Software R Core Team (2016).

3. Results and discussion

3.1. Sediment parameters

Predominantly, coarse granulometric fractions of fine sands (>63µm) were found at the TMS site and fine fractions (<63µm) were observed at the PS site in the Itajaí-Açu River (Table 1). Both values reflect sedimentary characteristics of each system, as well as seasonal variations resulting from the high water flow in the rainy season in these regions. Such seasonal variations in summer and winter (southern hemisphere) were also observed in temperature values in sediment and salinity in the water column. Exception was found at the TMS; that may be associated with the facts that the Guanabara Bay is highly influenced by salt water and that the shipyard is located in an area with restricted water renewal. In general, all sediment showed a dark color, with redox potential (Eh) and pH values similar to those found in other estuarine sediments (Wang & Wang, 2017); and in agreement with values reported at marine and shipyard sites in the Patos Lagoon estuary (Costa *et al.,* 2016; Pereira *et al.,* 2018) and at the Niterói port (Wasserman, unpublished data). The lowest pH and salinity values observed at the PS site were due to the fact that in the week before sampling, strong precipitations had occurred and fresh water greatly influenced the estuary.

The TOC content is consistent with values which have already been reported in the Patos Lagoon estuary (Pereira *et al.,* 2018) and in the area of the Niterói port (Wassermann, unpublished data). These values are directly related to the granulometric fraction of every site, i.e., sites rich in sands (GS and MI) exhibit low TOC contents, because systems with predominance of fine material allow the preservation of organic material. It is related to: a) low rate of oxygenation in the system, and b) generation of processes of physical protection of TOC due to its interaction with mineral grains with great surficial area (Coppola *et al.,* 2007). In addition, these values also agree with the conditions of every environment under study; for example, hypoxia conditions in the water column of the Guanabara Bay (TMS) provide high preservation of the organic matter in more anoxic sediments (Kjerfve *et al.,* 2001).

Table 1. Mean values of the physical and chemical parameters of the water column and sediments in every study area. S_1 = rainy season at the Guanabara Bay and the Itajaí-Açu River; dry season at the Patos Lagoon estuary. S_2 = rainy season at the Patos Lagoon estuary; dry season at the Guanabara Bay and the Itajaí-Açu River.

Study Areas	**Temperature (°C)**		**Salinity**		**pH**		**Eh (mV)**		**TOC (%)**		**Dissolved Sulfides (µM)**	**Granulometry fine sands (%)**		**Granulometry silt and clay (%)**	
	S_1	**S_2**	**S_1**	**S_2**	**S_1**	**S_2**	**S_1**	**S_2**	**S_1**	**S_2**	**S_2**	**S_1**	**S_2**	**S_1**	**S_2**
TM Shipyard (TMS), Guanabara Bay	30.2	23.5	30.13	31.7	7.40	7.90	-340	-420	2.20	2.47	-	16.1	24.0	14.4	11.9
P Shipyard (PS), Itajaí-Açu River	24.2	18.0	0.11	18.2	6.20	7.00	-	-200	1.95	1.33	-	5.9	19.7	87.1	76.9
G Shipyard (GS), Patos Lagoon Estuary	27.5	16.5	33.85	1.0	7.20	7.10	-290	-290	0.61	0.77	6.06	58.4	51.6	12.9	20.4
Marinheiros Island (MI), Patos Lagoon Estuary	26.0	24.5	27.3	1.60	7.40	6.93	-270	-20	0.33	0.20	39.89	95.6	92.6	2.5	4.6

To understand such conditions, a semi-quantitative range of the dissolved O_2 and H_2S in the sediment may be established, by the comparison of the electric current values found by this study and the ones of the voltammograms reported by Luther *et al.* (2008). Therefore, H_2S values shown in Table 1 represent a mean value of all depths measured in the sedimentary profiles of GS and MI in the Patos Lagoon estuary. The lowest H_2S values obtained at the GS (6.06μM) were similar to the reported ones (0.1-6.0μM) in estuarine sediments with influence of anthropogenic activities (Wang & Wang, 2017), while the highest H_2S values on the MI were similar to those found (0-80μM) in sandy sediments from coastal wetlands (Kankanamge *et al.,* 2017).

In the sediment-water profiles of the GS and MI sites during S_2 (rainy season at Patos Lagoon estuary), decrease in dissolved O_2 was observed at the sediment-water interface from the water column to the first cm depth into surface sediments (Figure 2). Consequently, increasing concentrations of dissolved H_2S from this depth were detected to the deepest cm of the collected cores. Thus, estimated concentrations, in a range from 5 to 40μM in surface sediments (<15cm), agree with data that has been recently found in marsh areas in the same estuary (Bem; unpublished data). This author also reports that, in summer conditions (southern hemisphere), decrease in the dissolved H2S content can be expected. Additionally, similar distributions are reported by Kankanamge *et al.* (2017), who also show sedimentary profiles with high values of H_2S (80-90μM) in the first 2-4cm.

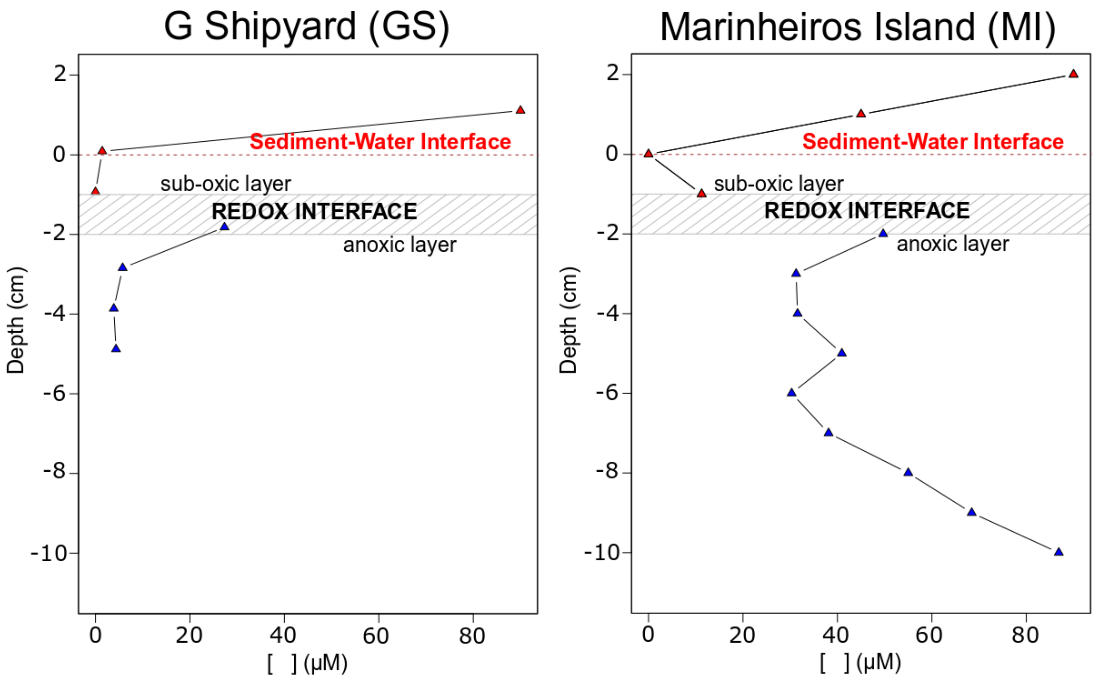

Figure 2. Semi-quantitative concentrations of dissolved O_2 and H_2S (μM; derived by voltammograms reported by Luther *et al.,* 2008) at 5-10cm in depth determined by solid estate Au/Hg voltammetric microelectrodes in the second sampling in the Patos Lagoon estuary at the G Shipyard (left) and the Marinheiros Island (right), as a reference site. Red and blue triangles represent O_2 and H_2S concentrations, respectively.

Thus, floods in intertidal areas of permeable sandy sediments (e.g., the Patos Lagoon estuary and the Guanabara Bay margins) allows vertical infiltration of superjacent oxygenated waters in the first cm of surface sediment (<10cm; Rush *et al.,* 2000). Therefore, increase in the rate of advection enables the porewater rich in chemical species (trace metals and nutrients) to meet surface water rich in oxidizing species, a fact that leads to changes in the redox interface along the sedimentary profile (Santos *et al.,* 2012). Dissolved H_2S reduces Fe(III) oxyhydroxides, and together with precipitation of authigenic mineral phases of Fe sulfides, directly influences concentrations of dissolved Fe(II) in the porewater, resulting in an important process of retention (sediment solid phase) or mobilization (porewater) of trace metals (Kostka & Luther, 1994; Du Laing *et al.,* 2009).

3.2. Trace metal labile fraction (C_{DGT})

Cr_{DGT}, Cu_{DGT} and Ni_{DGT} concentrations, in the first sampling (S_1), exhibited the following decreasing order at all sites: PS ≥ GS > TMS > MI. While V_{DGT} showed the decreasing order: GS > MI > PS > TMS (Figure 3).

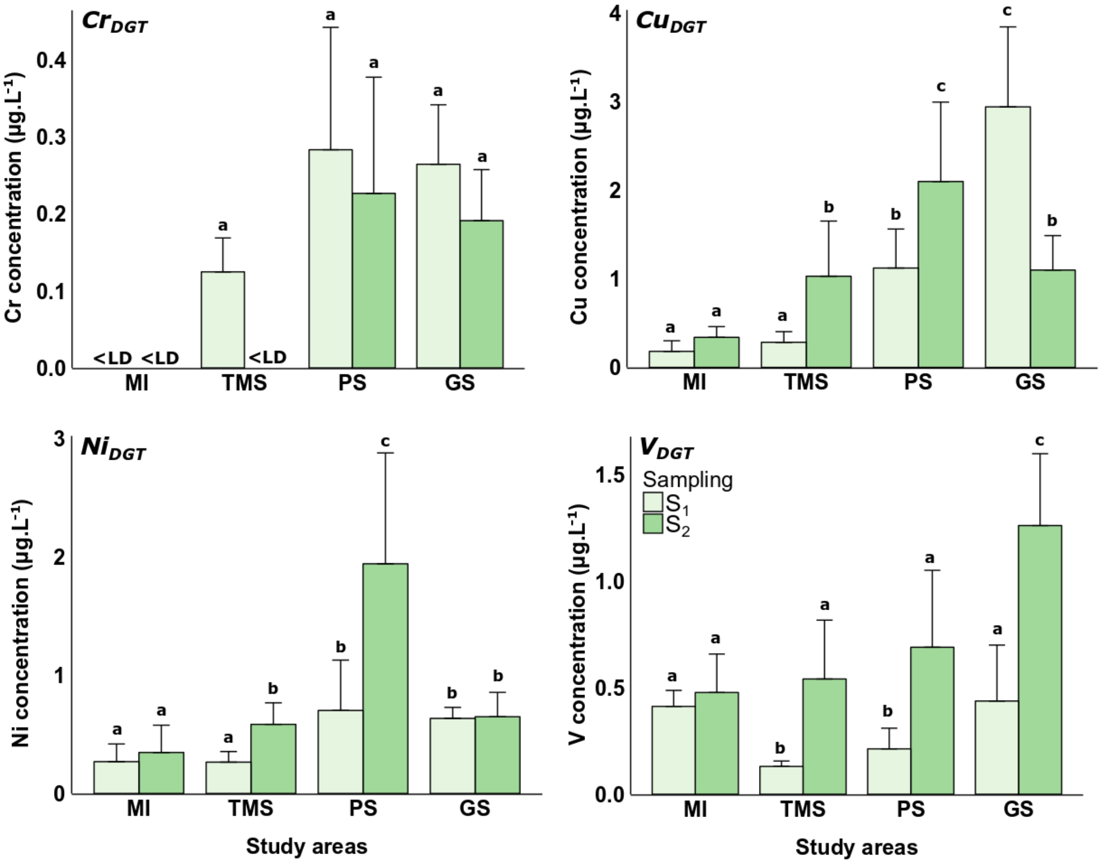

Figure 3. DGT labile metals (C_{DGT}) of Cr, Cu, Ni and V (µg.L-1) in the first (light green) and second (dark green) sampling periods on the Marinheiros Island (MI), the TM Shipyard (TMS), P Shipyard (PS) and G Shipyard (GS). Data are represented by mean±SD, n=5-9. Same letters above bars represent that there was no significant difference ($p<0.05$) whereas different letters represent significant difference ($p>0.05$) and <DL means below detection limit.

In the second sampling (S_2), such order was similar: PS ≥ GS > TMS > MI. Additionally, in both periods, Cu_{DGT} and V_{DGT} showed significant differences ($p<0.05$) between periods at all sites except for MI. Whereas Ni_{DGT} showed significant differences ($p<0.05$) only at the PS and MI sites. However, Cr did not exhibit any significant differences in any period.

Low concentrations of Cr_{DGT} observed at all sites, without any significant difference ($p>0.05$), are related to the ion exchange resin of Chelex-100 which was used in the DGT devices. It is capable of retaining only Cr(III) -a less toxic and mobile species than Cr(VI)- in the form of $Cr(OH)_3^0$ in aquatic environments at pH values close to neutral (Markiewcz et al., 2015). It is also known that Cr(VI) can be reduced to Cr(III) in sediments with sulfides (Di Toro, 1990), which can occur at the GS and MI sites in the first cm of the sediment, where the highest content of H_2S was detected.

Cu_{DGT} and Ni_{DGT} were found to have strong correlation ($p<0.05$) (Table 2) when all data are considered. It indicates that both elements have similar behavior in the sediment and the same source of contamination. The highest concentrations of both elements were measured at the PS and GS sites, where the highest contents of silt and clay fractions were found (Table 1). The smallest grains have larger surface area and reactive electric charges on their surfaces, which are capable of retaining metal ions, as opposed to sandy material (Horowitz, 1991). Thus, under varying physicochemical conditions, metals are desorbed from the grains and, once dissolved in the porewater, they are more readily available, and, therefore, easily retained in the DGT units (Song et al., 2018). However, no significant correlation ($p>0.05$) was observed for any metal with the dominant granulometric fraction of every study site.

Table 2. Pearson correlation matrix among mean trace metal labile concentrations (C_{DGT}) and Total Organic Carbon (TOC) content in the sediment in the second sampling (S_2) in the study areas.

	Cu DGT	**Cr DGT**	**NI DGT**	**V DGT**	**TOC**
Cu DGT	1				
Cr DGT	0.77	1			
NI DGT	0.77*	0.20	1		
V DGT	0.12	0.05	0.10	1	
TOC	0.20	0.29	0.08	-0.24	1

* above numbers means significant correlation ($p<0.05$)

In both periods, significant differences ($p<0.05$) between Cu_{DGT} and V_{DGT} (except at the MI site) were observed, whereas for Ni_{DGT}, differences were observed at the TMS and PS sites, but not at the GS and MI sites. However, no differences in Cr_{DGT} levels were observed at any site. It suggests that, in addition to sedimentary characteristics of every site, variations in environmental physicochemical conditions (e.g. temperature, salinity, pH, Eh) also influence concentration of Cu_{DGT}, Ni_{DGT} and V_{DGT}, especially at the TMS and PS sites. Previously mentioned factors, together with hydrodynamic conditions and the TOC content, are important to the mobilization of trace metals on surface layers of sediments in intertidal areas (Du Laing *et al.,* 2009). Nevertheless, no significant correlations ($p<0.05$) of TOC contents were found in the sediment with C_{DGT} (Table 1) at any site, mainly considering their low levels (TOC<1%) at the GS and MI sites. It occurred because TOC contents were quantified in the bulk sediment, whereas trace metals in the porewater are complexed with the dissolved organic matter. Therefore, integration with the dissolved organic carbon content should provide more significant relations.

Additionally, the largest variations among sediment parameters (Table 1) were related to temperature and pH, as well as to the salinity in the water column. These parameters have been reported as driving factors of the potential bioavailability of C_{DGT} in the water column of hydrodynamically complex estuaries, such as the Patos Lagoon (Wallner-Kersanach, 2009; Costa & Wallner-Kersanach, 2013). The highest values of pH and salinity at the TMS and PS sites were determined in the second sampling (S_2), which took place in the dry season in these estuaries, when concentrations of Cu, Ni and V were significantly ($p<0.05$) higher than the ones found in the first period. This is in agreement with previous studies of the DGT in waters from the Patos Lagoon estuary (Wallner-Kersanach *et al.,* 2009), but it must be considered that some variation in the diffusion coefficients is expected (c.a. 8%) during changes between fresh and seawater (Zhang & Davison, 1995). Variations in pH concentrations in estuarine sediments can also affect mobility of trace metals, which may be controlled by the interaction between these elements and certain processes, such as reduction of Fe, Mn and SO_4^{2-}, generated by the presence of H_2S (Paquin *et al.,* 2003).

These interactions control the remobilization of metals from the solid phase (mineral) of the sediment to the solution phase (porewater); and as a result, the sediment ability to accumulate those (Olson *et al.,* 2017). Such interactions would then control the labile concentration of Cu_{DGT} and Ni_{DGT}, because they can be released from authigenic oxyhydroxides during Fe and Mn reduction (Shaw *et al.,* 1990). Therefore, Cu_{DGT} and Ni_{DGT} exhibited a very significant correlation ($p<0.01$), but not correlation with the TOC content, suggesting that similar geochemical processes control the labile concentrations of these elements in porewater and the sediment. In addition, high Cu_{DGT} and Ni_{DGT} concentrations are in agreement with the ones from other estuarine surface sediments, with parameters (pH, Eh and dissolved H_2S) similar to those measured by this study, with high C_{DGT} in superficial layers (2-4cm) of the sediment (Gao *et al.,* 2009; Wang & Wang, 2017).

In addition, Paradas & Amado Filho (2007) suggest that Zn-rich compounds found in the composition of antifouling paints used at shipyard sites are highly persistent. Although Zn_{DGT} was not determined by the present study, this element is expected to have higher values than Cu_{DGT} (0.12 ± 0.12 - 3.78 ± 1.71µg.L^{-1}). It has been observed for Zn_{DGT} in sediments from estuaries whose input of metal pollutants has anthropic origin (Wang & Wang, 2017).

V_{DGT} concentrations showed no significant correlation with other C_{DGT}. It indicates that other geochemical processes, different from Cu_{DGT} and Ni_{DGT}, control the mobility of this metal. The highest concentrations of V_{DGT}, which were observed at the GS site in the second sampling (S_2), were significantly different ($p<0.05$) from the ones found at the other sites. It could occur due to the permeability of sediments in the Patos Lagoon estuary (predominantly sandy) and contrasting salinity changes in this system, which could facilitate the entry of more oxygenated waters loaded with vanadate ions (HVO_4^{-2}) in the anoxic conditions of the sediment, thus, generating reduction to vanadyl ions (VO^{+2}; Beck et al., 2008). The latter is a more reactive species, which can easily complex with the dissolved organic matter and remain in the porewater (Beck *et al.,* 2008; Olson *et al.,* 2017).

In general, C_{DGT} concentrations exhibited a similar decreasing order of Cu>Ni>V>Cr in both sampling periods at the shipyard sites, although their hydrodynamics and geochemical characteristics were different. However, at the MI site, the decreasing order was V>Cu>Ni>Cr. Sediments from shipyard areas have been reported to have high levels of Cu, Ni and V (Baptista-Neto *et al.,* 2006; Costa *et al.,* 2016; Pereira *et al.,* 2018). It suggests that, besides environmental factors that control mobility of trace metals in the porewater, continued and specific contribution of these pollutants to the local, as well as their accumulation in the sediment, influences potential bioavailability of trace metals. It was observed for Cu_{DGT} that high values found at the GS site are consistent with previous studies that reported high values of labile Cu fraction in the sediment (Costa *et al.,* 2016).

Remobilization flux of metals from the porewater and sediment to the sink induced by DGT uptake is generated through the molecular diffusion (from the highest concentration to the lowest one) and exchange between solid phase and solution phase of trace metals. As the devices were deployed directly on the surface of the sediment, they can be considered as the potential fluxes from the sediment to overlying water. Cr_{DGT} flux was higher in the first sampling (S_1) in each estuary, mainly at the PS and GS sites (Table 3), regardless of salinity (Table 1). Cu_{DGT} flux exhibited variable flux, depending on the site; it increased when salinity was high at the TMS, GS and PS sites. However, Ni_{DGT} flux was higher in both sampling periods at the PS and GS sites. V_{DGT} flux was generally higher during the second sampling period (S_2) for TMS, PS and GS sites and the first sampling (S_1) for MI.

Table 3. Mean calculated remobilization fluxes ($mmol.m^{-2}.d^{-1}$) of Cr, Cu, Ni and V measured by the deployment of DGT devices in the sediment water interface in the study areas: Marinheiros Island (MI), TM Shipyard (TMS), P Shipyard (PS) and G Shipyard (GS). S_1 = sampling in rainy season at the Guanabara Bay and Itajaí-Açu River; dry season at the Patos Lagoon estuary. S_2 = sampling at rainy season in the Patos Lagoon estuary and dry season at the Guanabara Bay and the Itajaí-Açu River.

Element	Sampling	MI	TMS	PS	GS
Cr	S_1	6,46E-05	8,08E-05	1,65E-04	2,04E-04
	S_2	4,21E-05	1,47E-05	7,71E-05	7,45E-05
Cu	S_1	1,33E-04	1,22E-03	6,04E-04	3,66E-03
	S_2	3,01E-04	8,91E-04	1,39E-03	9,26E-04
Ni	S_1	2,15E-04	1,71E-04	4,65E-04	5,01E-04
	S_2	2,35E-04	4,77E-04	1,49E-03	5,01E-04
V	S_1	9,53E-04	1,43E-04	1,79E-04	4,33E-04
	S_2	5,88E-04	6,29E-04	6,11E-04	1,39E-03

Cr_{DGT} flux was lower than the one of other metals due to the fact that DGT devices only measure Cr (III) specie in aquatic environments. The Cr_{DGT} and NiDGT fluxes were lower than those found in marine sediments from the North Sea by Gao *et al.* (2009), while Cu_{DGT} was an exception, presenting higher fluxes at the TMS, PS and GS sites, where high labile concentration of this element were measured. High Cu flux in the shipyard areas allows us to infer that once this metal is mobilized to the porewater, it is neither easily retained in another mineral phase nor complexed with organic matter. This mobilization increased at sites, such as the GS and the TMS, where the influence of seawater and bioturbation processes favors the oxygenation in the sediment and metal release (He *et al.,* 2017). In addition, the highest V_{DGT} fluxes at the MI and GS sites reinforce the idea of high mobilization of this element in the porewater due to high sediment permeability at these sites.

3.3. Leachable trace metal concentrations in the solid phase of sediments (C_L)

Concentrations of leachable trace metals in the solid phase of the sediments (C_L) were significantly different ($p<0.05$) between periods for Cu_L and Zn_L at all study sites except for GS site. While for Cr_L significant differences between periods were observed at all the sites. The Ni_L showed significant differences at all the study sites except for MI. In contrast, for V_L only TMS site exhibit significant differences between periods, while Pb_L not showed significant differences ($p>0.05$) between periods at all study sites. But Pb_L concentrations were significantly different in the GS, by comparison with the other sites.

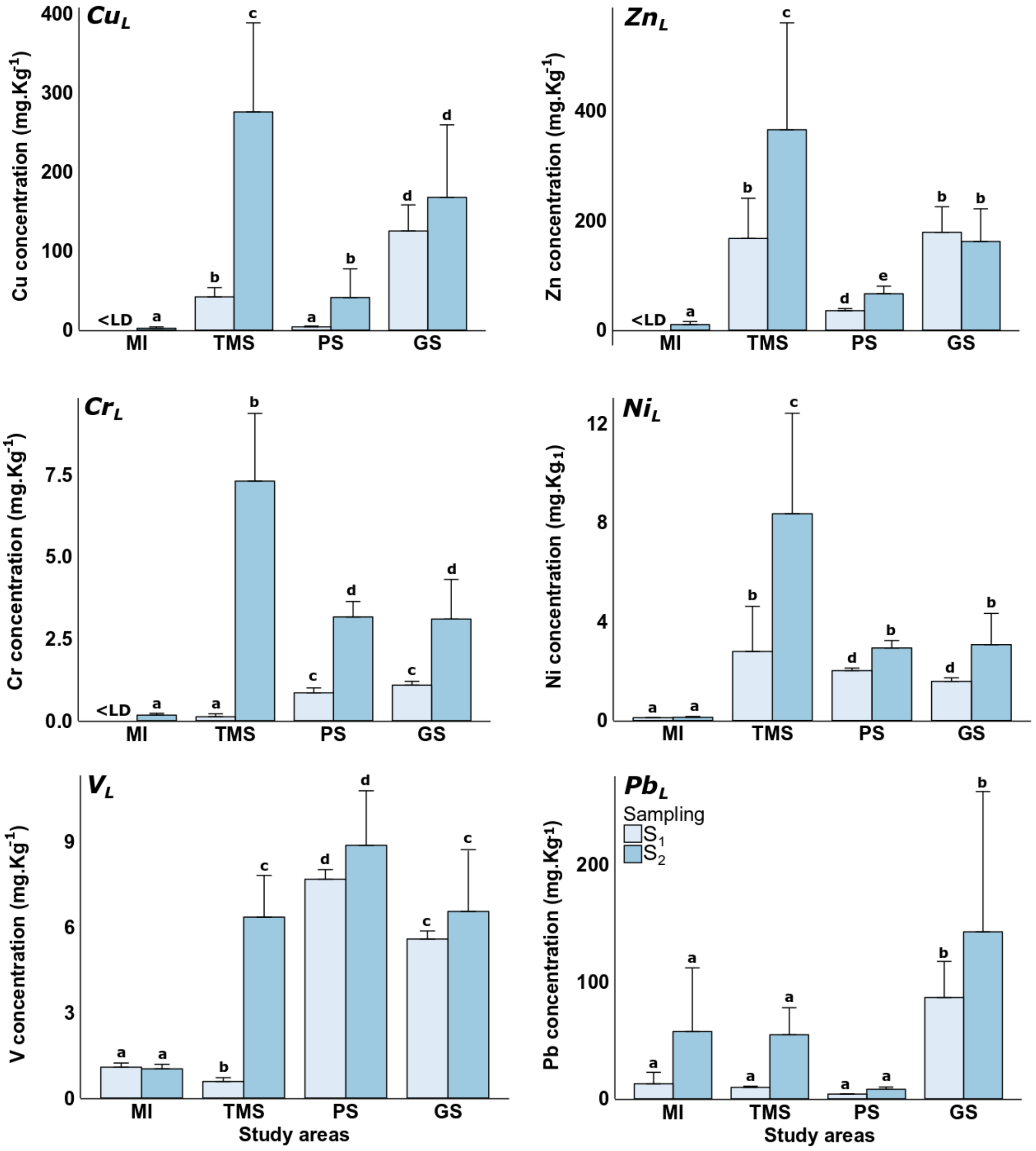

Figure 4. Leachable metal (C_L) concentrations ($mg.kg^{-1}$ dry weight) of Cr, Cu, Ni, Pb, V and Zn in the first (light gray) and the second (dark gray) sampling periods at the following sites: the Marinheiros Island (MI), TM Shipyard (TMS), P Shipyard (PS) and G Shipyard (GS). Data are represented by mean±SD, n=3-9. Same letters over bars mean that differences are not significant ($p<0.05$) whereas different letters represent significant difference ($p>0.05$); <DL means below detection limit.

These significant differences correspond to variations in sediment properties (pH, Eh, particle size) and salinity in the water column at every study site, as described for C_{DGT}. However, at the PS site, low trace metal content was observed (except for V), although higher accumulation of metals was expected due to its silt-clay (75%) and TOC contents (2%). Therefore, variations in the contribution of trace metals are also expected as a function of the working intensity of every site. The most active shipyards are the TMS and the PS, by comparison with the GS. Despite being more than one century old, the GS does not have the same working intensity as the others, besides having had low demand since 2008 (Costa *et al.,* 2016; Soroldoni *et al.,* 2018).

In addition, C_L, in general, was higher in the second period (S_2), which is in agreement with data observed for C_{DGT} by previous studies carried out in the Patos Lagoon estuary (Costa *et al.,* 2016; Pereira *et al.,* 2018). Significant variations could also be related with the fact that, in this period, intense maintenance of vessels was observed at all sites. This fact would be able to continuously increase supply of these metals to the water column and then, to the sediment. Therefore, antifouling paint particles can act as a direct source of metal pollutants in the sediment (Soroldoni *et al.,* 2017).

In general, C_L concentrations had similar decreasing order to the one described for C_{DGT}, i.e., it was Zn>Cu>Pb>Ni>V>Cr in both periods of study. However, the MI site showed a distribution of Pb>V>Ni>Zn>Cu>Cr. More specifically, distributions described for Cu_L and Zn_L allow us to infer that the supply of these elements is controlled by activities developed in these places and their intensity. Therefore, these elements exhibit a very significant correlation ($p<0.01$, Table 4), which suggests that these metals come from a common anthropic source. Thus, residues from the application of antifouling paints have been previously reported as a source of Cu and Zn by several studies worldwide (Turner, 2010; Rees *et al.,* 2014) and in southern Brazil (Costa *et al.,* 2016; Pereira *et al.,* 2018). Costa *et al.* (2016) also reported significant correlations in this C_L fraction at other shipyard installations in the Patos Lagoon estuary, which are in agreement with the composition of the antifouling paints applied in this estuary, containing Cu and Zn (%), as well as

Cr, Ni and Pb (μg.g^{-1}). Consequently, Cu_L showed a significant relation ($p<0.05$) with Cr_L and Pb_L, whilst Zn_L showed a significant relation with Cr_L and Ni_L.

Table 4. Pearson correlation matrix among mean leachable trace metal concentrations (C_L) and the Total Organic Carbon content in sediments in the second sampling (S_2) in the study areas.

	Cu	**Zn**	**Cr**	**Ni**	**V**	**Pb**	**TOC**
Cu	1						
Zn	0.92*	1					
Cr	0.58*	0.73*	1				
Ni	0.49	0.69*	0.85*	1			
V	-0.60	-0.43	-0.28	-0.02	1		
Pb	0.82*	0.21	0.30	0.28	-0.45	1	
TOC	-0.34	0.46	0.01	0.15	0.29	-0.23	1

* means significant relation ($p<0.05$)

Consequently, the highest Cu_L and Zn_L concentrations were found at the TMS site, which is a small place with short operating time (<20 years), where a large number of vessels were repaired in the second sampling (S_2) period and which has accumulation of vessels in its vicinity. Likewise, the second highest values of Cu_L and Zn_L were found at the GS site, which has operated for more than one century and has allowed great accumulation of these metals in the surface sediments over time; they can be equally released in both periods.

The significant ($p<0.05$) high concentrations of Cr_L and Ni_L determined at the TMS site, especially in the second sampling period, allow to infer an anthropic contribution of these metals. That may be related to the type of vessels that are reformed at the TMS and PS sites. These shipyards maintain vessels of various materials, unlike what occurs at shipyards located in the Patos Lagoon estuary, that tend to build and maintain vessels of wood and fiberglass. Cr and Ni are commonly found in stainless steel alloys, which constitute the hull of vessels and the propeller of engines. Consequently, Cr_L and Ni_L showed a significant correlation ($p < 0.05$).

The highest concentrations of V_L were observed at the PS site, but it did not show significant differences ($p > 0.05$) between both sampling periods. In this place, during samplings, large vessels were being repaired and anchored directly in the margin of the shipyard. Like Cr and Ni, V is also commonly used in stainless steel alloys for the construction of metallic parts which are resistant to high temperatures. In addition, high concentrations were also determined at the GS site, where a diesel oil filling station is installed. Thus, V could also be related to petroleum products, as described by Pereira *et al.* (2018) in their study of the Patos Lagoon estuary.

Pb_L in general, did not exhibit significant differences ($p > 0.05$) regarding seasonal periods and study sites. It leads to the observation that Pb potential bioavailability is mainly controlled by natural sediment processes at all sites under study. However, concentrations of Pb at the GS site, which has worked on vessel maintenance for about 100 years, were significantly ($p < 0.05$) higher; thus, they may be related to antifouling paints (Rees *et al.,* 2014) and derivatives of oil, due to the presence of an area of oil supply for vessels (Pereira *et al.,* 2018).

The comparison of data on background values (Table 6) and C_L values found by this study at the TMS and GS shipyard sites shows that Cr_L and Ni_L exhibit background values which are similar to the ones found in sites located in the Patos Lagoon estuary and the Guanabara Bay, whilst Cu_L, Pb_L and Zn_L had values above background. When concentrations obtained at the TMS, PS and GS sites were compared to the concentrations of MI (reference site), Cr_L values were 10-40-fold higher, Ni_L were10-100-fold higher and Zn_L were 50-fold higher, although Pb_L showed similar contents. Enrichment in these elements was found to be related to the continued input of metals resulting from shipyard activities, as has been reported elsewhere (Turner, 2010; Rees et al., 2014; Pereira et al., 2018). However, Pereira et al. (2018) reported total concentrations of V in sediments from shipyard areas in the Patos Lagoon estuary; these values (2.0 - 70.0 mg.kg^{-1}) were up to 8-fold higher than those determined for the leachable fraction in this area. Contents of Cr_L Cu_L, Ni_L Pb_L and Zn_L are in the same range as leachable concentration values previously reported in sediments from marine, port and shipyard areas in the Patos Lagoon estuary (Costa et al., 2016).

Table 5. Leachable metals concentrations (mg.kg^{-1} in dry weight, minimum and maximum) in sediments of shipyard areas of the present study compared with different locations. S_1 = sampling in rainy season at the Guanabara Bay and Itajaí-Açu River; dry season at the Patos Lagoon estuary. S_2 = sampling in rainy season at the Patos Lagoon estuary and dry season at the Guanabara Bay and Itajaí-Açu River.

Area (Shipyard)		**Granulometry**	**Acid Leaching**	**Cr**	**Cu**	**Ni**	**Pb**	**V**	**Zn**	**Reference**
TM Shipyard (TMS), Guanabara Bay, Brazil	S_1	<1000µm	0.1M HCl	0.06-0.22	30.40-53.74	1.60-4.88	9.16-10.83	0.45-0.72	103.42-246.89	**Present study**
	S_2			4.11-10.23	149.43-489.53	5.13-17.12	9.35-87.89	3.78-8.34	225.93-824.81	
PShipyard (PS), Itajaí-Açu River, Brazil	S_1	<1000µm	0.1M HCl	0.71-1.01	3.15-5.23	1.90-2.10	3.99-4.02	7.32-7.99	32.87-39.64	
	S_2			2.59-3.99	9.25-101.42	2.43-3.19	7.26-10.94	5.38-10.78	45.18-85.62	
G Shipyard (GS), Patos Lagoon Estuary, Brazil	S_1	<1000µm	0.1M HCl	1.01-1.22	100.29-162.75	1.43-1.70	62.89-121.21	5.28-5.84	149.58-231.68	
	S_2			1.35-4.82	83.78-258.20	1.44-5.14	38.01-339.27	3.22-9.53	96.64-258.23	
Marinheiros Island (MI), Patos Lagoon Estuary, Brazil	S_1	<1000µm	0.1M HCl	0.04-0.06	<DL	0.11	10.95-23.34	0.94-1.23	<DL	
	S_2			0.10-0.29	0.50-5.68	0.09-0.17	7.77-141.52	0.76-1.33	4.50-18.75	
Shipyards, marinas and port areas, Patos Lagoon estuary, Brazil		<1000µm	0.1M HCl	0.86-3.3	3.1-768	1.1-6.8	6.1-178.0	-	16.1-578.0	Costa *et al.* 2016
Saltwater Barullus Lake, Egypt			1M HCl	15.09-40.85	37.02-109.75	48.04-68.06	31.70-69.85	-	30.53-84.69	El Nemr (2003)
Rías Baixas bays, Spain		<63µm	1M HCl	1.00-31.2	0.17-84.3	-	146.0	-	0.69-84.40	Villares *et al.* (2003)
Suez Gulf, Red Sea, Egypt		<63µm	1M HCl	6.76-40.29	4.46-55.02	38.14-61.25	31.45-63.40	-	27.95-72.19	El Nemr *et al.* (2006)

<DL means below the Detection Limit

Similarly, the highest values of CuL, PbL and ZnL at shipyard sites were higher than those reported for estuarine sediments in highly urbanized regions in the Mediterranean Sea (El Nemr *et al.,* 2006) and in the northwestern coast of Spain (Villares *et al.,* 2003). However, values of CrL and NiL found by this study were lower than those reported in the Suez Gulf in the Red Sea (El Nemr *et al.,* 2006), sites with refineries and shipyards.

When CL concentrations are compared with the NOAA Screening Quick Reference Tables (2008, Table 6) for marine sediments, CrL NiL and VL did not exceed any level indicated in tests of toxicity with organisms. However, CuL and PbL concentrations reached Probable Effects Levels, while ZnL values reached Effects Range-Low for the biota in the first sampling period. Nevertheless, in the second sampling period, PbL values presented Effects Range Median, whereas CuL and ZnL concentrations reached Apparent Effects Threshold for Oysters larvae (Mollusca) and infaunal community impacts, respectively. It is noteworthy that, regardless of the site and its characteristics, these elements are the ones that are more easily enriched in sediments and can exhibit high availability and, therefore, great risk to organisms.

Table 6. NOAA Screening Quick Reference values (mg.kg-1) of Cr, Cu, Ni, Pb, V and Zn for marine sediments (Buchman, 1999) and background values (mg.kg-1) of trace metals for sediments of the Patos Lagoon estuary (Niencheski *et al.,* 2002) and Guanabara Bay (Baptista-Neto *et al.,* 2000) by total chemical extraction.

	Cr	**Cu**	**Ni**	**Pb**	**V**	**Zn**
Threshold Effect Level (TEL)	52.30	18.70	15.9	30.24	-	124.00
Effects Range Low (ERL)	81.0	46.70	20.90	46.70	-	150.0
Probable Effects Level (PEL)	160.0	108.0	42.8	112.0	-	271.0
Effects Range Median (ERM)	370.0	270.0	51.60	218.0	-	410.0
Apparent Effects Threshold (AET)	62.0	390.0	110.0	400.0	57.00	410.0
Guanabara Bay Background	40.5	9.0	27.0	24.4	-	58.4
Patoos Lagoon estuary Background	7.83	7.82	-	4.75	-	33.01

3.4. Potential Cu availability in the Patos Lagoon estuary

Cu is the element with the highest percentage in paints; it represents a great risk due to its toxicity to aquatic organisms. High labile concentrations in both Cu_{DGT} and C_L fractions, as well as high calculated Cu_{DGT} fluxes at the GS site, indicate that a significant Cu pool of the solid phase of the sediment occurs and that it can be easily mobilized into the porewater phase of the sediment under variation in physicochemical conditions (Förstner et al., 1986).

When Cu_{DGT} values were compared with those reported for estuarine sediments with similar physicochemical parameters, maximum Cu_{DGT} values found by this study were lower. It allows to infer that Cu in the upper layers of surface sediments is being immobilized at the places under study in the Patos Lagoon estuary due to active diagenetic processes. It could be a product of CuS precipitation, thus retaining free Cu present from desorption of Fe/Mn oxyhydroxides or the remineralization of the organic matter, which has been reported as processes capable of decreasing Cu concentration in the porewater (Burton *et al.,* 2006). Thus, conditions of pH and measured Eh (Table 1) and concentrations of up to 20μM of dissolved H_2S in the first 2cm (Figure 2), as well as low TOC content in the Patos Lagoon estuary, would be adequate for it to occur, as a function of the mineral stability data for Cu, Fe and S described by Sato (1992). Additionally, his diagram shows that when there is decrease in Eh, as related on the MI (-20mV, Table 1) in the second sampling period, Fe also influences Cu mobilization.

Despite this fact, it would be necessary to determine concentrations of dissolved Fe or Mn in the porewater to allow better understanding of the mobilization process of Cu and other elements. Therefore, the influence of diagenetic factors on the bioavailability of metal species at the study sites for the sediment porewater should be studied in the future. However, taking into account that the sites under study exhibit restricted hydrodynamics that limit more constant renewal of their waters, the flux of Cu at the GS would represent a continuous source of Cu free ions from the sediment to the sediment-water interface. It highlights the risk represented by this element to benthic communities, resulting in potential bioavailability in sediments from shipyard sites.

4. Conclusions

Results of this study indicated the availability of trace metals in areas with specific and continuous sources of these elements, such as shipyard areas, which are controlled by physicochemical and geochemical factors in the sediment. Additionally, sources of trace metals from shipyards should be considered, since they vary according to the period and intensity of vessels repairs, persistence of the activity over time, type of composition of vessel hulls and the composition of generated antifouling paints.

At the sites under study, application of DGT technique capable of determining labile metals in the sediment and chemical extraction technique able of measuring the weakly adsorbed metals to minerals found in the sediment allowed to distinguish the same decreasing order of metals concentration for both phases. It shows that the solid phase supplies the porewater directly, making it important not only to study one of the phases to establish the mobility of the metals, but also to establish the possible risk associated with these elements. Consequently, these orders reflected the constituent metals of antifouling paints and oil derivatives in shipyard areas and were in agreement with the previously established hypothesis of this study.

Regardless of the environmental characteristics and individual activities of every shipyard, they have enriched sediments with respect to background values and with high labile fractions of Cu, Pb and Zn, leading to an environmental risk to some aquatic organisms at the level of Effects Range Median to Apparent Effects Threshold. Special attention should be given to Cu, which exhibits the highest concentrations in the potentially available species (labile) and higher diffusive in the sediment, especially in sandy permeable sediments, such as the Patos Lagoon estuary. Despite this fact, Cu in such an estuary may be immobilized by diagenetic processes, such as authigenesis of Fe/Mn oxyhydroxides or metal sulfides.

The results obtained in this study by DGT passive samplers and classical chemical techniques, together with voltammetric microelectrodes, established physical and chemical conditions and geochemical properties of the sediment. These procedures enabled a more comprehensive assessment of the mobility, speciation and risk of potentially toxic metals in aquatic systems with the presence of continuous and specific input of metals.

Results represent only a first insight into possible factors involved in the early diagenesis in the intertidal areas in the estuaries under study. Further studies should be conducted to understand the influence of these processes on potential availability of metal species in porewater, with special attention to Fe and Mn, and the dissolved organic carbon content. Additionally, the application of the DGT technique to the sediment demonstrated that it is a robust procedure for the quantification of labile metals in distinct estuarine systems for the first time and that it can be used as monitoring network for data comparison.

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CAPÍTULO IV:

Síntese da Discussão e Conclusões

Síntese da discussão e conclusões

Este estudo visava avaliar a mobilidade e potencial biodisponibilidade de Cr, Cu, Ni, Pb, V & Zn nos sedimentos superficiais de áreas de estaleiros e estabelecer a sua relação com as possíveis fontes antrópicas (tintas anti-incrustantes e produtos derivados de petróleo) em diferentes condições hidrodinâmicas. Consequentemente, os resultados obtidos indicam, que a biodisponibilidade dos metais traço em áreas com fontes específicas e contínuas desses elementos são controladas por fatores físico-químicos e geoquímicos no sedimento. No entanto, as fontes localizadas de metais nos estaleiros devem ser consideradas na avaliação ambiental destes locais, uma vez que as concentrações lábeis tendem a variar de acordo com o período e a intensidade na reparação de embarcações, a persistência da atividade ao longo do tempo, tipo de composição dos cascos dos navios e composição das tintas anti-incrustantes.

Consequentemente, nos locais em estudo, a aplicação de amostradores passivos DGT capazes de determinar metais potencialmente disponíveis na água e técnicas químicas capazes de extrair os metais mais reativos e fracamente adsorvidos aos minerais encontrados no sedimento permitiu distinguir a mesma ordem decrescente de concentração de metais para ambas as fases. Isso mostra que, nos sedimentos em estudo, a fase sólida supre diretamente a água intersticial, sendo importante não apenas estudar uma das fases para estabelecer a mobilidade dos metais e o possível risco associado a esses elementos. Essas ordens refletiram os metais presentes na composição das tintas anti-incrustantes e de derivados de petróleo utilizados em áreas de estaleiros. Portanto os resultados foram concordantes com as hipóteses previamente estabelecidas para este estudo, de que o aporte localizado e acumulação de metais traço nestes locais são suficiente para permitir estabelecer relações entre os metais em estudo e as atividades antrópicas em ambas as fases do sedimento.

Por outra parte, de forma geral os sedimentos de todas as áreas de estaleiros mostraram estar enriquecidos, em relação aos valores *background*, com importantes concentrações lábeis de Cu, Pb e Zn. Isto ocorre independentemente das próprias características físico-químicas e hidrodinâmicas de cada ambiente e das atividades desenvolvidas em cada estaleiro. Portanto, foi reportado um risco ambiental para organismos bentônicos de nível Effects Range Median para Apparent Effects Threshold. Da mesma forma, atenção deve ser dada ao Cu, que apresentou as maiores concentrações na fração potencialmente biodisponível na água intersticial e um maior fluxo difusivo para a interface água-sedimento. Isto resulta especialmente importante em sedimentos permeáveis, como o estuário da Lagoa dos Patos e as proximidades de Niterói na Baía de Guanabara.

Consequentemente, mediante o acoplamento dos resultados (parâmetros do sedimento, sensores voltamétricos, amostradores passivos DGT e extração convencional de metais em meio ácido do sedimento) obtidos foi realizado uma primeira avaliação da potencial biodisponibilidade do Cu nos sedimentos do estuário da Lagoa dos Patos. Os resultados demonstraram que este elemento parece ser imobilizado por processos diagenêticos, como a autogênese de oxihidróxidos de Fe/Mn ou sulfetos metálicos. Os resultados representam apenas um primeiro *insight* sobre os possíveis fatores envolvidos na diagênese precoce nas áreas intermarés neste estuário. Outros estudos devem ser conduzidos para entender a influência desses processos no comportamento das espécies lábeis dos metais traço na água intersticial. Adicionalmente, deve ser dada especial atenção para o conteúdo Fe e Mn e as fases minerais do sedimento e o teor de carbono orgânico dissolvido na água intersticial.

Finalmente, os resultados deste estudo relacionados à aplicação de amostradores passivos DGT e técnicas químicas clássicas, juntamente com microelétrodos voltamétricos em estado sólido ou outros sensores, permitiram estabelecer as condições físico-químicas e as propriedades geoquímicas do sedimento. Por conseguinte, permitiu uma avaliação mais abrangente da mobilidade, partição e risco de metais potencialmente tóxicos em sistemas aquáticos, com a presença de um aporte contínuo e específico de metais. Adicionalmente, a aplicação da técnica de DGT ao sedimento demonstrou pela primeira vez que é um procedimento robusto para a quantificação de metais lábeis em distintos sistemas estuarinos e que pode ser utilizado como rede de monitoramento para comparação de dados.

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Anexos

Anexo 1. Parâmetros físico-químicos do sedimento (pH e Eh) e da água (temperatura e salinidade) durante fevereiro de 2018 (S_1) e julho de 2018 (S_2).

Local	Coordenadas	Amostragem	Tempo de Exposição DGT (s)	Maré	Temperatura (°C)	Salinidade	pH	Eh (mV)
TM Shipyard (TMS) - Baia de Guanabara (RJ)	22°52'32"S 43°06'59"W	S_1 (Inicio)	171480	Enchente	29,5	30,3	7,5	-270
		S_1 (Final)		Vazante	30,2	30,3	7,2	-414
		S_2 (Inicio)	171600	Vazante	23,0	31,1	7,8	-431
		S_2 (Final)		Vazante	24,0	32,2	8,1	-422
P Shipyard (PS) - Rio Itajaí-Açu (SC)	26°51'55"S 48°42'23"W	S_1 (Inicio)	172035	Enchente	24,4	0,1	*nd*	*nd*
		S_1 (Final)		Vazante	24,5	0,1	6,2	*nd*
		S_2 (Inicio)	175234	Vazante	20,0	*nd*	7,1	*nd*
		S_2 (Final)		Vazante	18,0	*nd*	7,0	-177
G Shipyard (GS) - Estuário da Lagoa dos Patos (RS)	32°01'45"S 52°04'57"W	S_1 (Inicio)	173838	Vazante	26,0	33,5	7,3	-286
		S_1 (Final)		Vazante	25,0	34,2	7,1	-288
		S_2 (Inicio)	169855	Enchente	16,0	1,9	7,1	-279
		S_2 (Final)		Enchente	17,0	0,1	7,1	-287
Área de Referencia - Marinheiros Island (MI) (RS)	32°00'50"S 52°07'53"W	S_1 (Inicio)	172753	Vazante	26,0	28,0	6,9	-293
		S_1 (Final)		Vazante	26,0	26,6	7,9	-255
		S_2 (Inicio)	171818	Enchente	25,0	2,7	6,8	-40
		S_2 (Final)		Enchente	24,0	0,5	7,1	-44

Anexo 2

Concentrações de O_2 e H_2S no sedimento de GS e MI durante setembro de 2018 (S_2).

G Shipyard (GS) - Estuário da Lagoa dos Patos (RS)

Espécie	Profundidade (cm)	Perfil$_1$ (µA)	Perfil$_1$ (µM)	Perfil$_2$ (µA)	Perfil$_2$ (µM)	MEDIA (µM)
O_2	1	0,18	56,88	0,15	47,81	52,34
	0	0,01	4,06	0,01	3,75	3,91
	-1	0,01	3,13	0,09	28,13	3,13
H_2S	-2	0,09	27,81	0,03	8,44	18,13
	-3	0,01	2,19	0,02	5,31	3,75
	-4	0,01	1,56	0,01	3,44	2,50
	-5	0,01	2,19	0,01	3,44	2,81

Marinheiros Island (MI) - Estuário da Lagoa dos Patos (RS)

Espécie	Profundidade (cm)	Perfil$_1$ (µA)	Perfil$_1$ (µM)	Perfil$_2$ (µA)	Perfil$_2$ (µM)	MEDIA (µM)
O_2	1	0,07	23,13	0,07	21,56	22,34
	0	0,07	20,63	0,05	16,56	18,59
	-1	0,06	18,13	0,07	20,94	18,13
	-2	0,06	18,75	0,06	17,50	17,50
H_2S	-3	0,16	49,69	0,13	40,31	45,00
	-4	0,10	31,25	0,15	47,19	39,22
	-5	0,10	31,56	0,17	51,56	41,56
	-6	0,13	40,94	0,21	65,31	53,13
	-7	0,10	30,31	0,20	62,50	46,41
	-8	0,12	38,13	0,20	63,75	50,94
	-9	0,18	55,00	-	-	27,50
	-10	0,22	68,44	-	-	34,22
	-11	0,28	86,88	-	-	43,44

Anexo 3

Determinação da concentração de carbono orgânico total (COT) no sedimento em fevereiro de 2018 (S_1),

Local	Amostra	%C
Área de Referencia - Marinheiros Island (MI) (RS)	MI_1	0,32
	MI_2	0,33
	MI_3	0,35
TM Shipyard (TMS) - Baía de Guanabara (RJ)	TMS_1	1,98
	TMS_2	1,66
	TMS_3	1,44
P Shipyard (PS) - Rio Itajaí-Açu (SC)	PS_1	2,10
	PS_2	1,91
	PS_3	1,83
G Shipyard (GS) - Estuário da Lagoa dos Patos (RS)	GS_1	0,73
	GS_2	0,61
	GS_3	0,50
Material Certificado de Referencia MESS-3	MRC_1	2,22
	MRC_2	2,23
	MRC_3	2,13

Anexo 4

Determinação da concentração de carbono orgânico total (COT) no sedimento entre julho-setembro de 2018 (S_2).

Local	Amostra	%C
Área de Referencia - Marinheiros Island (MI) (RS)	$MI_{1.1}$	0,15
	$MI_{1.2}$	0,16
	$MI_{1.3}$	0,21
	$MI_{2.1}$	0,19
	$MI_{2.2}$	0,20
	$MI_{2.3}$	0,21
	$MI_{3.1}$	0,21
	$MI_{3.2}$	0,20
	$MI_{3.3}$	0,30
TM Shipyard (TMS) - Baía de Guanabara (RJ)	$TMS_{1.1}$	1,24
	$TMS_{1.2}$	1,37
	$TMS_{1.3}$	1,23
	$TMS_{2.1}$	0,90
	$TMS_{2.2}$	1,73
	$TMS_{2.3}$	1,46
	$TMS_{3.1}$	4,70
	$TMS_{3.2}$	4,74
	$TMS_{3.3}$	4,85
P Shipyard (PS) - Rio Itajaí-Açu (SC)	$PS_{1.1}$	1,26
	$PS_{1.2}$	1,42
	$PS_{1.3}$	1,91
	$PS_{2.1}$	1,37
	$PS_{2.2}$	1,17
	$PS_{2.3}$	1,16
	$PS_{3.1}$	1,03
	$PS_{3.2}$	0,78
	$PS_{3.3}$	0,85
G Shipyard (GS) - Estuário da Lagoa dos Patos (RS)	$GS_{1.1}$	1,14
	$GS_{1.2}$	0,89
	$GS_{1.3}$	1,73
	$GS_{2.1}$	0,98
	$GS_{2.2}$	0,66
	$GS_{2.3}$	0,61
	$GS_{3.1}$	0,73
	$GS_{3.2}$	1,88
	$GS_{3.3}$	0,41
Material Certificado de Referencia MESS-1	MRC_1	2,81
	MRC_2	2,55
	MRC_3	2,59
	MRC_4	2,71

Anexo 5

Concentrações de metais fracamente sorvidos no sedimento em Fevereiro de 2018 (S_1).

Local	Amostra	Cu (mg.kg-1)	Cr (mg.kg-1)	Ni (mg.kg-1)	Pb (mg.kg-1)	V (mg.kg-1)	Zn (mg.kg-1)
Área de Referencia - Marinheiros Island (MI) (RS)	MI_1	<2,03	0,04	0,11	10,95	0,94	<1,27
	MI_2	<2,03	0,04	0,05	3,94	1,08	< 1,27
	MI_3	<2,03	0,06	0,11	23,34	1,23	<1,27
TM Shipyard (TMS) - Baía de Guanabara (RJ)	TMS_1	30,40	0,22	4,88	9,16	0,45	246,89
	TMS_2	41,91	0,07	1,87	9,22	0,56	103,42
	TMS_3	53,74	0,06	1,60	10,83	0,72	150,24
P Shipyard (PS) - Rio Itajaí-Açu (SC)	PS_1	3,15	0,71	2,04	4,02	7,74	33,56
	PS_2	4,03	0,83	1,90	3,99	7,32	32,87
	PS_3	5,23	1,01	2,10	6,19	7,99	39,64
G Shipyard (GS) - Estuário da Lagoa dos Patos (RS)	GS_1	113,08	1,02	1,61	62,89	5,84	149,58
	GS_2	162,75	1,22	1,70	121,21	5,62	231,68
	GS_3	100,29	1,01	1,43	74,99	5,28	153,07

Anexo 6.

Concentrações de metais fracamente sorvidos no sedimento entre julho-setembro de 2018 (S$_2$).

Local	Amostra	Cu (mg.kg-1)	Cr (mg.kg-1)	Ni (mg.kg-1)	Pb (mg.kg-1)	V (mg.kg-1)	Zn (mg.kg-1)
Área de Referencia - Marinheiros Island (MI) (RS)	MI$_{1.1}$	<2,03	0,10	0,17	7,77	1,13	14,23
	MI$_{1.2}$	<2,03	0,17	0,14	10,47	1,05	7,14
	MI$_{1.3}$	<2,03	0,11	0,09	16,84	1,01	4,50
	MI$_{2.1}$	<2,03	0,15	0,11	123,74	0,97	16,86
	MI$_{2.2}$	<2,03	0,19	0,16	119,70	0,98	8,56
	MI$_{2.3}$	<2,03	0,15	10,16	141,52	0,76	5,15
	MI$_{3.1}$	5,68	0,29	5,40	30,20	1,33	10,89
	MI$_{3.2}$	<2,03	0,17	0,11	30,22	0,88	18,75
	MI$_{3.3}$	<2,03	0,18	0,80	35,13	1,10	4,63
TM Shipyard (TMS) - Baía de Guanabara (RJ)	TMS$_{1.1}$	489,53	5,90	5,96	60,84	5,96	388,09
	TMS$_{1.2}$	164,81	1,27	11,40	9,35	0,33	268,53
	TMS$_{1.3}$	1149,47	4,11	10,35	44,08	3,78	824,81
	TMS$_{2.1}$	345,14	8,78	8,69	78,13	8,34	346,13
	TMS$_{2.2}$	221,10	6,72	17,12	35,90	5,91	201,47
	TMS$_{2.3}$	324,62	8,22	5,69	59,20	8,25	492,59
	TMS$_{3.1}$	211,71	10,23	5,13	87,89	6,67	255,88
	TMS$_{3.2}$	149,43	5,54	5,91	55,12	5,73	225,93
	TMS$_{3.3}$	301,35	8,94	4,85	60,63	6,16	280,46
P Shipyard (PS) - Rio Itajaí-Açu (SC)	PS$_{1.1}$	15,79	2,83	3,09	7,80	9,56	57,36
	PS$_{1.2}$	14,08	2,59	2,86	7,28	9,27	54,45
	PS$_{1.3}$	9,25	2,72	3,06	7,26	10,45	45,18
	PS$_{2.1}$	23,12	3,19	3,19	8,22	10,20	64,57
	PS$_{2.2}$	21,53	2,85	2,43	8,43	10,78	60,92
	PS$_{2.3}$	23,52	3,13	2,43	8,97	10,19	64,58
	PS$_{3.1}$	68,58	3,46	2,97	9,71	7,11	82,26
	PS$_{3.2}$	93,35	3,70	3,17	10,94	5,38	80,58
	PS$_{3.3}$	101,42	3,99	3,14	3,92	6,92	85,62
G Shipyard (GS) - Estuário da Lagoa dos Patos (RS)	GS$_{1.1}$	258,20	2,82	3,10	207,75	5,94	228,67
	GS$_{1.2}$	726,68	4,82	4,62	325,50	6,15	258,23
	GS$_{1.3}$	3458,39	3,32	5,14	339,27	5,95	1761,70
	GS$_{2.1}$	154,44	4,62	3,84	114,90	5,35	170,63
	GS$_{2.2}$	102,19	1,35	1,44	64,34	3,22	102,63
	GS$_{2.3}$	330,02	2,10	2,37	97,59	4,94	183,49
	GS$_{3.1}$	139,57	4,15	2,98	41,84	8,96	130,33
	GS$_{3.2}$	83,78	2,23	1,80	38,01	8,92	96,64
	GS$_{3.3}$	107,26	2,47	2,25	52,11	9,53	120,70

Anexo 7

Concentrações de metais lábeis na água intersticial retidos nas unidades DGT em fevereiro de 2018 (S_1).

Local	Amostra	Cu ($\mu g\ L^{-1}$)	Cr ($\mu g\ L^{-1}$)	Ni ($\mu g\ L^{-1}$)	V ($\mu g\ L^{-1}$)
Área de Referencia - Marinheiros Island (MI) (RS)	MI_1	<0,040	<0,040	0,218	1,026
	MI_2	<0,040	<0,040	0,131	0,409
	MI_3	0,070	<0,040	<0,100	0,489
	MI_4	0,306	<0,040	0,480	0,339
	MI_5	0,170	<0,040	0,247	1,612
TM Shipyard (TMS) - Baía de Guanabara (RJ)	TMS_1	0,231	<0,040	0,168	0,135
	TMS_2	4,862	0,1513	0,283	0,118
	TMS_3	0,272	0,1492	0,344	0,164
	TMS_4	0,178	0,0740	<0,100	<0,080
	TMS_5	0,454	<0,040	<0,100	0,105
P Shipyard (PS) - Rio Itajaí-Açu (SC)	PS_1	0,669	<0,040	0,211	0,289
	PS_2	1,547	0,4428	0,975	<0,080
	PS_3	0,064	<0,040	<0,100	<0,080
	PS_4	1,148	0,1244	0,918	0,104
	PS_5	0,054	0,2836	<0,100	0,247
G Shipyard (GS) - Estuário da Lagoa dos Patos (RS)	GS_1	12,369	0,3311	0,768	0,381
	GS_2	5,4505	0,3311	0,512	0,369
	GS_3	3,842	<0,040	0,610	0,897
	GS_4	2,037	0,2120	0,663	0,277
	GS_5	2,940	0,1849	0,617	0,262

Anexo 8

Concentrações de metais lábeis na água intersticial retidos nas unidades DGT entre julho-setembro de 2018 (S$_2$).

Local	Amostra	Cu (µg L^{-1})	Cr (µg L^{-1})	Ni (µg L^{-1})	V (µg L^{-1})
Área de Referencia - Marinheiros Island (MI) (RS)	MI$_{1.1}$	0,432	<0,070	0,895	0,771
	MI$_{1.2}$	0,279	<0,070	0,191	0,886
	MI$_{1.3}$	0,385	<0,070	0,368	0,952
	MI$_{2.1}$	0,185	<0,070	0,392	0,288
	MI$_{2.2}$	0,220	<0,070	0,155	0,500
	MI$_{2.3}$	0,573	<0,070	0,288	0,614
	MI$_{3.1}$	0,278	<0,070	0,446	0,297
	MI$_{3.2}$	0,290	<0,070	0,174	0,281
	MI$_{3.3}$	0,410	<0,070	0,210	0,276
TM Shipyard (TMS) - Baía de Guanabara (RJ)	TMS$_{1.1}$	1,649	<0,070	0,829	0,771
	TMS$_{1.2}$	0,345	<0,070	0,514	0,886
	TMS$_{1.3}$	2,060	<0,070	0,517	0,952
	TMS$_{2.1}$	0,136	<0,070	0,453	0,288
	TMS$_{2.2}$	0,289	<0,070	0,487	0,500
	TMS$_{2.3}$	0,840	<0,070	0,946	0,614
	TMS$_{3.1}$	0,639	<0,070	0,410	0,297
	TMS$_{3.2}$	1,238	<0,070	0,498	0,281
	TMS$_{3.3}$	1,171	<0,070	0,605	0,276
P Shipyard (PS) - Rio Itajaí-Açu (SC)	PS$_{1.1}$	1,776	<0,070	3,401	0,334
	PS$_{1.2}$	2,727	<0,070	2,535	0,425
	PS$_{1.3}$	0,043	<0,070	1,345	0,390
	PS$_{2.1}$	2,215	0,3779	2,974	1,212
	PS$_{2.2}$	0,746	0,0758	2,009	0,776
	PS$_{2.3}$	0,256	<0,070	1,049	1,157
	PS$_{3.1}$	3,350	<0,070	0,969	0,376
	PS$_{3.2}$	1,772	<0,070	1,243	1,039
	PS$_{3.3}$	0,155	0,2269	5,094	0,495
G Shipyard (GS) - Estuário da Lagoa dos Patos (RS)	GS$_{1.1}$	1,393	<0,070	0,504	0,635
	GS$_{1.2}$	3,6958	0,1767	0,720	1,515
	GS$_{1.3}$	1,003	0,2400	0,582	1,554
	GS$_{2.1}$	0,749	<0,070	0,646	1,274
	GS$_{2.2}$	1,646	<0,070	0,990	0,951
	GS$_{2.3}$	1,342	0,1035	0,910	1,475
	GS$_{3.1}$	0,907	<0,070	0,681	1,632
	GS$_{3.2}$	0,460	<0,070	0,398	1,329
	GS$_{3.3}$	1,288	0,2454	0,404	0,978