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TESE DE DOUTORADO

**CONDIÇÕES SAZONAIS E ESPACIAIS PARA EXPLICAR
O COMPORTAMENTO GEOQUÍMICO DE METAIS
TRAÇO EM ZONAS ESTUARINAS NA BAÍA DE TODOS
OS SANTOS, BAHIA, BRASIL**

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SALVADOR

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Tese de Doutorado apresentada ao Programa de Pós-Graduação em Geologia do Instituto de Geociências da Universidade Federal da Bahia como requisito parcial à obtenção do Título de Doutor em Geologia, Área de Concentração: Geologia Ambiental, Hidrogeologia e Recursos Hídricos.

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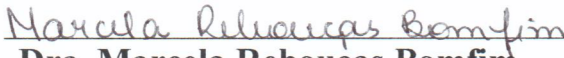
**“CONDIÇÕES SAZONAIS E ESPACIAIS PARA EXPLICAR
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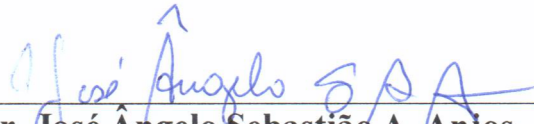
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A toda minha família, aos grandes amigos e a todos aqueles que contemplam a natureza.

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RESUMO

Ambientes estuarinos e suas florestas de manguezal tem uma grande importância ecológica por servir como habitat para muitas espécies. Devido suas condições naturais, esses ecossistemas são muito especiais, fazendo deles sensíveis a perturbações. Devido sua dinâmica, os metais traço, elementos importantes no ambiente, tem sua geoquímica influenciada por diversos fatores, como pH, Eh, matéria orgânica, salinidade, etc., tanto nos sedimentos quanto nas águas superficiais. Tais fatores podem variar ao longo do ano, principalmente por conta dos diferentes índices pluviométricos entre as estações do ano, bem como de acordo com as características locais. A Baía de Todos os Santos, localizada no Recôncavo Baiano, é uma área com diversos ecossistemas e com uma grande diversidade de fauna e flora que requer cada vez mais estudos que possam ajudar a entender sua dinâmica. Este estudo teve como objetivo determinar a concentração espacial e temporal de metais traço (Zn, Fe, Ni e Cu) em 3 diferentes áreas de manguezal na Baía de Todos os Santos. Foram realizadas análises da concentração de metais na água e no sedimento. A biodisponibilidade dos metais traço foram estimadas medindo-se a concentração nos tecidos de ostras *Crassostrea rhizophorae* (Guildin, 1828). Analisando também parâmetros físico-químicos na água e no sedimento, cálculos de especiação podem ser feitos para estimar possíveis flutuações na disponibilidade de metais traço em diferentes localidades da baía. Os parâmetros físico-químicos bem como as concentrações de metais traço das águas superficiais, sedimentos e das concentrações internas na ostra *C. rhizophorae* ao longo da Baía de Todos os Santos mostrou variações espaciais e temporais. Tais variações estão relacionadas as diferentes características dos locais de amostragem como também das condições meteorológicas, que mudam o volume de chuva e a penetração da água do mar para dentro dos rios. Parâmetros como pH e condutividade nas águas superficiais bem como matéria orgânica e granulometria nos sedimentos se mostraram fundamentais para compreender a variação espaço-temporal das concentrações de metais traço nas regiões estudadas. Estudos sazonais e espaciais foram importantes para determinar os efeitos dos parâmetros físico-químicos sobre as concentrações de metais na água, sedimento e biota, uma vez que correlações realizadas mostraram que as concentrações de metais responderam as mudanças dos parâmetros. Verificou-se também que não somente isoladamente, mas um conjunto desses parâmetros tem forte influência sobre o comportamento dos metais. As concentrações de metais no sedimento e na água no geral estiveram abaixo dos limites estabelecidos pelas leis brasileiras. As concentrações na ostras em geral também foram abaixo dos limites, contudo, excederam os limites em alguns casos. Isto, entretanto, não significa que os níveis encontrados são perigosos pois alguns elementos são essenciais para os organismos. A biodisponibilidade, representada pela atividade livre dos íons, mostrou que não necessariamente a concentração total de um elemento químico estará disponível para os organismos no ambiente, mas somente uma fração desta concentração. Pesquisas adicionais precisam ser realizadas para obter mais informações detalhadas sobre a especiação dos metais nestes ambientes estuarinos e investigar o risco para os organismos. Isso pode dar um suporte apropriado para a avaliação de risco da poluição de metais na Baía de Todos os Santos.

Palavras-chave: Parâmetros Físico-químicos; Metais; Sazonalidade.

ABSTRACT

Estuarine environments and its mangrove forests have large ecological importance by serving as habitat for many species. Due their natural conditions, these ecosystems are very special, making them also sensitive to disturbances. Due to its dynamics, trace metals, important elements in the environment, have their geochemistry influenced by several factors, such as pH, Eh, organic matter, salinity, etc., both in sediments and in surface waters. These factors can vary throughout the year, mainly due to the different rainfall indices between the seasons of the year, as well as according to the local characteristics. The Todos os Santos Bay is located in the Rencôncavo Baiano region and is a unique area that has many ecosystems with a large fauna and flora biodiversity which needs studies that can help to understand its dynamic. This study aimed to determine the spatial and temporal exposure with metals (Zn, Fe, Ni and Cu) of three different mangrove areas in the Todos os Santos Bay. This involved analyzing metal concentrations in surface water and sediment. Metal bioavailability was estimated by measuring concentrations in soft tissues of the oyster *Crassostrea rhizophorae* (Guildin, 1828), popularly known as mangrove oyster. And by analyzing also physicochemical parameters in water and sediment, speciation calculations could be made to estimate possible fluctuations in available metal concentrations at different points in the bay. The physicochemical parameters and the metal concentrations of surface waters, sediments and the internal metal concentrations in the oyster *C. rhizophorae* along the Todos os Santos bay showed spatial and temporal variations. These variations are related with the different characteristics of sampling location as well as the meteorological conditions, which change the input of rain and the penetration of seawater into the rivers. Parameters such as pH and conductivity in surface waters as well as organic matter and grain size in the sediments were shown to be fundamental for understanding the spatio-temporal variation of trace metal concentrations in the studied regions. Seasonal and spatial studies were important to determine the effects of physicochemical parameters on the concentrations of metals in water, sediment and biota, since correlations showed that the concentrations of metals responded to changes in the parameters. It has also been found that not only in isolation, but a set of these parameters has a strong influence on the behavior of the metals. Metal concentrations in the sediment and water generally were below limits established by the Brazilian regulations. Concentrations in the oysters in general were below the limits, although they did exceed the limits in a few cases. This, however, doesn't mean that levels found are dangerous as some elements are essential to the organisms. The bioavailability, represented by the free activity of the ions, showed that not necessarily the total concentration of a chemical element will be available to the organisms in the environment, but only a fraction of this concentration. Further research is needed to obtain more detailed information on metal speciation in these estuarine environments and to investigate their actual risk to organisms. This may support a proper risk assessment of metal pollution in the Todos os Santos Bay.

Keywords: Physicochemical Parameters; Metals; Seasonality.

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CAPÍTULO 1 - INTRODUÇÃO GERAL

Os estuários são corpos d'água costeiros, semi-fechados, que apresentam uma livre conexão com o mar aberto e dentro do qual a água salgada é diluída gradativamente pela água doce proveniente da drenagem terrestre. Também podem ser definidos como ecossistemas de transição entre o continente e o oceano, áreas de encontro dos rios com o mar.

As áreas estuarinas têm grande importância na perpetuação das espécies, que além de servir como habitat para inúmeros organismos, diversos animais encontram ali seus alimentos.

Os estuários com suas florestas de mangue servem de habitat para diversos animais desde formas microscópicas até grandes peixes, aves, répteis e mamíferos e apresentam condições ideais para alimentação, proteção e reprodução de representantes de todos os elos da cadeia alimentar, sendo assim zonas de grande produtividade biológica (Campana et al. 2005).

Nos estuários, as condições ambientais são muito especiais e adversas, o que os torna altamente vulneráveis, podendo ser destruídos se houver alterações abruptas em alguns dos seus parâmetros ambientais. A dinâmica dos estuários é particularmente complexa, devido às influências de cheias e vazantes das marés.

Nestes ambientes encontram-se diversos elementos químicos que são de extrema importância para a manutenção de condições favoráveis para os meios bióticos e abióticos, os metais traço. Esses elementos são bons condutores de eletricidade e possuem alta densidade. O termo "traço" é utilizado para caracterizar os metais encontrados em baixas concentrações no ambiente, e que em concentrações ideais contribuem para diversas atividades de vários organismos (Pekey et al. 2004). Os metais estão presentes nos ambientes aquáticos e terrestres como resultado de processos naturais e antropogênicos. Concentrações background de metais em ambiente natural, devido a processos de intemperismo de rochas deposição atmosférica como fontes, são relativamente baixas quanto as concentrações que podem ser encontradas em lugares contaminados (Alloway, 1995). Além dos níveis de background, elevadas concentrações de metais no ambiente são principalmente causadas por atividades humanas (Bak et al., 1997). Tais concentrações de metais liberadas no ambiente por fontes antrópicas podem alcançar os ecossistemas terrestres e aquáticos através de várias rotas: diretamente (despejo, vazamento e derramamento), emissões atmosféricas seguidas deposições e via efluentes domésticos, essa introdução pode modificar as concentrações naturais, acarretando sérios problemas ao ecossistema (Da Costa 2007).

Os metais normalmente alcançam o estuário através das marés em duas formas, incorporados na matéria em suspensão ou dissolvidos e podem ser incorporados na fase sólida (sedimentos) e na fase aquosa (na coluna d'água) (Jesus et al. 2003).

No ambiente aquático os metais traço podem estar distribuídos entre as fases aquosas da coluna de água, na água intersticial dos sedimentos, na fase sólida suspensa e sedimentada, em organismos aquáticos e em plantas. Normalmente os sedimentos estuarinos e costeiros são o destino final da descarga dos elementos metálicos no ambiente aquático (Szefer et al. 1995), sendo que as pequenas velocidades das correntes, comuns em ambientes lacustres, permitam com que as partículas mais finas dos sedimentos se acumulem no fundo do corpo aquático (Souza 2007).

Alguns processos físico-químicos como temperatura, oxigênio dissolvido, salinidade e granulometria corroboram para as altas capacidades de sorção/acumulação de espécies orgânicas e inorgânicas nos sedimentos. Além dos fatores abióticos, fatores bióticos controlam a toxicidade e a bioacumulação dos vários contaminantes nos ambientes aquáticos (Jesus et al. 2003).

Mudanças nas condições do ambiente, marés, ou variações na acidificação exercem um papel importante na dinâmica dos sedimentos, e também na distribuição dos metais nos mesmos.

Os metais presentes nos sedimentos podem acabar voltando para a interface sedimento-água por difusão, resuspensão do sedimento (Souza 2007; Torres et al. 2008) ou atividade biológica (Wilson and Chang, 2000). Fazendo com que estes elementos se tornem biodisponíveis para a biota. O termo Biodisponibilidade é usado para se referir a fração da concentração total de um elemento químico em cada reservatório abiótico que pode ser captado pelos organismos (Vincente-Martorell et al. 2009), ou seja, é a medida do potencial que um elemento químico tem para ser absorvido pelos seres vivos, estando diretamente relacionada com a forma química deste composto no ambiente (Guimarães e Sígilo, 2008). Tal termo também foi introduzido e é utilizado como um conceito que considera a fração de um total de um elemento químico que causa efeitos tóxicos. O conhecimento sobre biodisponibilidade portanto pode aprimorar a precisão de uma avaliação de risco. A biodisponibilidade tem sido considerada um processo dinâmico no qual a disponibilidade ambiental de um metal cause exposição, resultando na assimilação (biodisponibilidade) e consequentemente efeitos devido a interação dos metais com alvos biológicos (Van Straalen et al., 2005).

Estando disponíveis, esses elementos podem ser incorporados pelos organismos, já que muitos metais traço são essenciais para diversas funções vitais. Pelo fato de que atualmente as ações antrópicas têm interferido bastante nas concentrações naturais, os animais estão sujeitos a incorporar maiores concentrações do que possam precisar para sua sobrevivência.

O estudo da biodisponibilidade de metais traço permite verificar a concentração destes elementos nas matrizes abióticas do ambiente, água e sedimento, por exemplo, e através dos resultados podem-se estimar níveis de toxicidade e determinar se existe uma possível contaminação/poluição numa área específica (Campana et al. 2005).

Até os dias atuais os procedimentos referentes a avaliação de risco de metais ainda são predominantemente baseadas nas concentrações totais dos metais. Contudo, estudos tem mostrado que a relação entre a concentração total de um metal e o seu efeito tóxico sobre a biota não é direto (Van Gestel et al., 1995). Nos ecossistemas, a ecotoxicidade aquática e terrestre não varia somente entre as espécies mas as características ambientais também influenciam muito o efeito da concentração dos metais (Plette et al., 1999; Lock et al., 2000; Lock and Janssen, 2001). Portanto, a concentração total de um metal por si só não é considerada como sendo um indicador confiável para potencial efeitos adversos (Janssen et al., 2000). Somente a fração biodisponível pode realmente ser captada pelos organismos e conseqüentemente induzir a efeitos adversos (Peijnenburg et al., 2002). Ao invés de tentar definir biodisponibilidade em uma forma genérica, uma estratégia mais proveitosa pode ser desenvolver um série de indicadores, tais como a atividade livre de íons metálicos e a concentração do metal no corpo dos organismos.

Metais e estuários

Normalmente, as concentrações dos metais traço nos ambientes estuarinos são mais altas a montante dos rios e diminuem em direção a foz (Rocha et al. 2012). Entretanto, os ambientes estuarinos são altamente dinâmicos, sofrendo grande influência dos regimes das marés e das descargas pluviais, fazendo com que as variáveis físico-químicas sejam constantemente modificadas e com isso, podem ocorrer variações do comportamento dos metais traço neste ambiente (Onofre et al. 2007).

As variáveis que podem controlar as concentrações dos metais traço em ambientes estuarinos e que estão sujeitas a dinâmica deste ambiente são: a salinidade, temperatura, o pH, Eh, matéria orgânica, a concentração de material particulado em suspensão (Ruelas-Inzunza and Páez-Osuna 2000; Campana et al. 2005) e também as fontes antrópicas (Varma et al. 2011).

É importante ressaltar um fator fundamental para a pesquisa sobre biodisponibilidade, a sazonalidade. Durante o ano, a depender da região do estudo, pode ocorrer variações climáticas que terão influência sobre os índices pluviométricos e conseqüentemente sobre a temperatura das águas. Variações nesses parâmetros podem causar modificações sobre as outras variáveis físico-químicas e então alterar a distribuição e concentração dos metais nas matrizes ambientais (Vicente-Martorell et al. 2009), tal fato pode ser observado na Figura 1.1.

Date	Sampling station	Zn (mg kg ⁻¹)	Cd (mg kg ⁻¹)	Pb (mg kg ⁻¹)	Cu (mg kg ⁻¹)	As (mg kg ⁻¹)
October 2004	1	602.94	3.43	136.76	1115.70	85.15
	2	1506.68	4.84	246.15	2099.49	198.79
	3	1327.12	3.87	343.25	2325.75	237.74
April 2005	1	1736.95	33.20	1166.67	3333.63	615.43
	2	738.41	5.11	358.38	1470.11	284.29
	3	1489.18	8.93	879.06	2469.38	599.81
October 2005	1	1308.01	15.99	817.35	2157.68	375.03
	2	1161.15	18.30	974.95	1513.77	530.39
	3	1569.12	14.04	1028.15	2652.79	486.77
May 2006	1	966.92	5.08	238.87	1829.17	246.24
	2	1054.66	5.41	404.33	2505.34	343.86
	3	1337.25	1.50	269.64	1412.51	211.98

Figure 1.1 Concentração de metais nos sedimentos de 3 diferentes rios na Huelva, Espanha: (1) Odiel river; (2) Tinto river; (3) Canal del Padre Santo em quatro diferentes tempos amostrais. Fonte: (Vicente-Martorell et al. 2009)

Atividade livre dos íons

Além destas variáveis, a forma química como cada elemento se encontra na natureza também irá indicar a sua biodisponibilidade e o possível grau de contaminação/poluição. Isso ocorre, pois os

organismos estão sujeitos a assimilarem os metais de acordo com a forma como estes se encontram no ambiente. Os íons metálicos livres são considerados como as espécies mais disponíveis/ativos em soluções água/solo uma vez que metais traço são principalmente transportados para dentro de células biológicas em formas iônicas devido ao fato de que os canais iônicos estão envolvidos (Ahlf et al., 2009). A variedade observada em toxicidade pode ser parcialmente explicada pela atribuição do efeito tóxico do metal nas diferentes soluções nas atividades de íons livres (Sauvé et al., 1998; Slaveykova and Wilkinson, 2002). Como a especiação de metais tem forte influência em relação a sua biodisponibilidade, qualquer fator ambiental que mude a relativa distribuição de um metal traço sobre suas diferentes espécies irá causar um efeito em sua disponibilidade e toxicidade. A especiação de metais traços em sistemas aquáticos é principalmente dependente do pH e nos quais complexos ligantes estejam presentes (Pagenkopf, 1983; Van Gestel and Koolhaas, 2004). Carbono orgânico dissolvido (COD) e ligantes inorgânicos pode reduzir o toxicidade de um metal pela complexação com metais e reduzindo o montante dos íons metálicos livres (Playle et al., 1993; Heijerick et al., 2003). Programas de Software como WHAN (Tipping, 1994) e MINEQL (www.mineql.com) tem sido desenvolvidos para calcular as atividades de íons livres de metais a partir de concentrações de metais dissolvidos e a incorporação de um conjunto de parâmetros químicos (pH, COD, e outros cations).

Diferentes organismos respondem de forma diferenciada as fontes de metais biodisponíveis (Ruelas-Inzunza and Páez-Osuna 2000). Devido a tal situação, muitas vezes para se realizar uma completa descrição da biodisponibilidade de metais em um ambiente estuarino se faz necessário a utilização de um conjunto de organismos para refletir a biodisponibilidade nas variadas formas de um elemento químico.

Os metais traço podem estar presentes no ambiente em diversas formas físico-químicas (solúveis, adsorvidos na superfície dos minerais, relacionados com a matéria orgânica, precipitado ou aprisionado em fases minerais) sendo que as formas trocáveis usualmente são consideradas como espécies imediatamente biodisponíveis (Li et al. 2009).

A biodisponibilidade não depende somente das variáveis físico-químicas, das fontes antrópicas e das vias de acesso do organismo (ar, água ou sedimento), mas também dependerá da maneira que o metal se encontra no ambiente, se o metal está associado a ligantes orgânicos ou inorgânicos. Outro fator muito importante relacionado a biodisponibilidade se refere ao tipo de organismo que será relacionado a concentração do metal no ambiente. Isso ocorre, pois a natureza do indivíduo é fundamental para estabelecer relações entre a biodisponibilidade e consequente contaminação/poluição da área (Worms et al, 2006).

Os organismos de regiões estuarinas estão sujeitos a assimilarem os metais traço de forma diferenciada. Mesmo animais vivendo numa mesma área e tendo mecanismos de alimentação comuns, a concentração de um determinado metal pode variar (Figure 1.2). Por isso, para tentar obter uma completa descrição da biodisponibilidade numa determinada área, pode ser necessário a utilização de um conjunto de biomonitores (Ruelas-Inzunza and Páez-Osuna 2000).

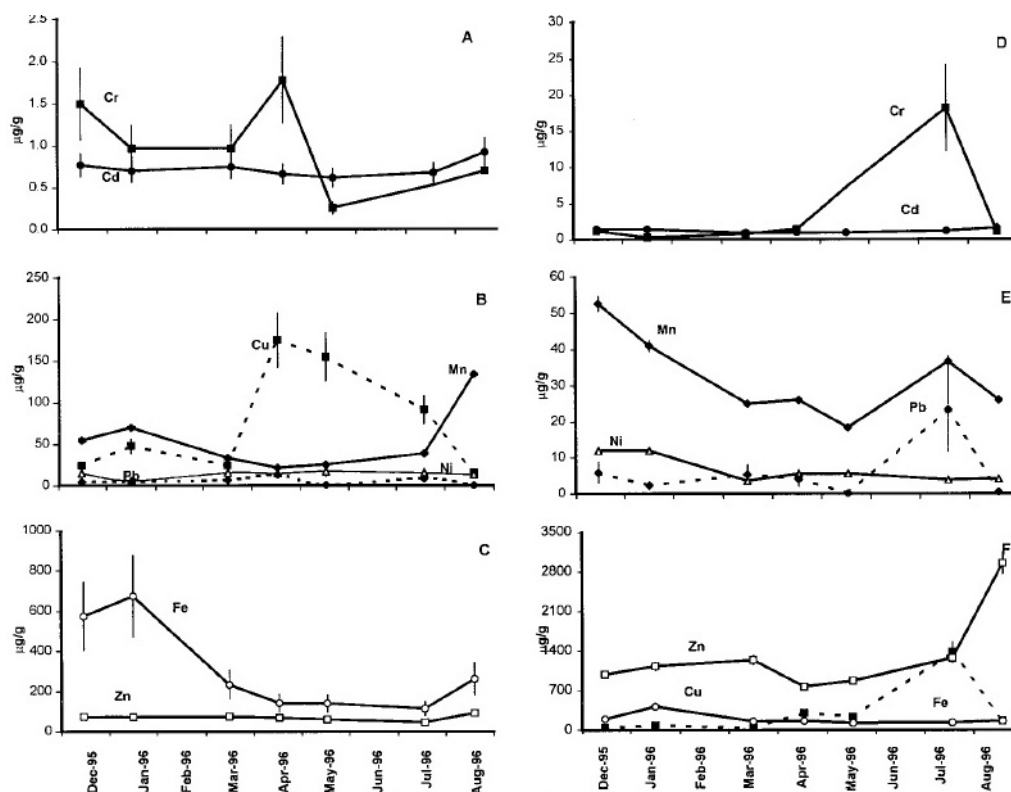


Figure 1.2 Flutuação sazonal de três concentrações de metais em tecidos de (A-C) *Mytella strigata* e (D-F) *Crassostrea corteziensis*. Fonte: (Ruelas-Inzunza and Páez-Osuna 2000).

A utilização de espécies biomonitoras para responder a possíveis casos de contaminação ambiental é de essencial relevância em áreas de estuário (Silva et al. 2006; Gonçalves et al. 2007). Os moluscos bivalves têm sido muito utilizados em diversos estudos ambientais no que se refere à qualificação e quantificação de contaminantes (Ruelas-Inzunza and Páez-Osuna 2000). Tais organismos são apontados como bons bioindicadores, o que tem contribuído significativamente para a interpretação de resultados em diversos trabalhos na área ambiental assim como a biodisponibilidade de elementos metálicos (Páez-Osuna et al. 1995; Silva et al. 2006). Esses organismos invertebrados, sésseis e filtradores, costumam acumular poluentes em seus tecidos, são de fácil coleta, de tamanho razoável, sedentarismo e possuem um longo tempo de vida, o que faz desses animais excelentes bioindicadores e/ou biomonitoras (Silva et al 2006).

Efeitos dos metais

Os metais que desenvolvem funções vitais em vários processos bioquímicos e biofísicos em organismos vivos são genericamente conhecidos como elementos essenciais a vida. Metais essenciais incluem por exemplo o cobre, manganês, níquel e zinco. Ótimas condições das atuações biológicas podem muitas vezes ser obtidas através de uma faixa bastante estreita de concentração, que pode ser chamada de "janela de essencialidade". Concentrações muito baixas de um metal essencial (abaixo da janela de essencialidade) pode levar a deficiência, enquanto que concentrações muito altas podem causar efeitos tóxicos (Hopkin, 1989). Elementos não essenciais são definidos como aqueles que não tem funções fisiológicas ou efeitos benéficos conhecidos para os organismos, como por exemplo cádmio, chumbo, mercúrio e prata (Peijnenburg and Vijver, 2007). Contudo, a não essencialidade é sempre difícil de provar e pode não ser assegurada para todos os organismos.

Organismos aquáticos e terrestres podem acumular os metais da água, solos e sedimentos através do contato direto ou indireto. Estes metais acumulados podem exercer efeitos adversos nos organismos através de seus comportamentos químicos e suas interações com biomoléculas nos sistemas biológicos, levando a efeitos tóxicos (Mudgal et al., 2010). Tem sido amplamente reconhecido que as concentrações de metais que excedem os limites fisiológicos podem resultar em toxicidade para plantas, animais e microorganismos. Uma alta concentração de metais podem também afetar o tamanho ou biomassa de comunidades microbianas, atividades enzimáticas, e processos microbianos como a mineralização e nitrificação de C e N (Giller et al., 1998). Além disso, a transferência de metais através da cadeia

alimentar é uma importante rota para a exposição humana, podendo causar diversos efeitos na saúde humana, como danos nos rins, disfunção endócrina, desordens imunológicas, e até a morte (Peralta-Videa et al., 2009).

A poluição de metais é um problema global que pode ter efeitos prejudiciais nos ecossistemas e também na saúde humana. Tal fato fortalece a necessidade de desenvolver criterios de qualidade precisos e padrões para avaliar qual a extensão dos riscos dos metais para os ecossistemas. Avaliação de risco requer avaliação de toxicidade dos efeitos dos contaminantes em plantas, invertebrados e micróbios. Os resultados de uma avaliação de risco pode promover a principal base para as legislações para reduzir os elevados riscos (Rooney et al., 2007). Um critério bem rigoroso pode resultar em aumento dos custos sociais para a redução da emissão e medidas de saneamento ambiental, enquanto que critérios muito vagos podem resultar em danos aos ecossistemas. Avaliações de risco não depende somente do conhecimento sobre a inerente toxicidade dos metais nos organismos. A exposição é também uma peça muito importante para determinar o real risco. Para os metais, somente uma (pequena) fração da concentração total presente no ambiente está disponível para ser captado e assimilado e consequentemente podendo causar efeitos nos organismos. Isto significa que a precisão da avaliação de riscos para metais nos força a habilidade de determinar a fração que realmente se encontra disponível para os organismos (Peijnenburg et al., 2007).

Interações entre química, física e biologia no processo de biodisponibilidade

As diversas interações, química, física e biológica dos metais traço no ambiente também podem ser decisivas para determinar a disponibilidade destes elementos. Essas variáveis são altamente interdependentes, onde, muitas vezes uma variável pode causar influencia em outra.

Muitas vezes fatores físico-químicos podem limitar a disponibilidade de metais para a biota, então, alguns organismos podem acabar se adaptando, de forma que modificam as velocidades dos fluxos, fazendo com que possam assimilar a quantidade necessária do elemento (Worms et al. 2006).

Os metais Zn e Fe são essenciais para o desenvolvimento de vários organismos. De fato, nas mesmas condições, a biodisponibilidade do metal está limitada pelo seu fluxo difuso ou pela cinética das trocas dos ligantes, de modo que, em adição ao íon livre, a instabilidade dos metais pode influenciar a biodisponibilidade (Ruelas-Inzunza and Páez-Osuna 2000).

Devido à baixa solubilidade dos oxihidróxidos, se prevê que o Fe^{+3} , por exemplo, se encontre em concentrações que não sejam suficientes para o crescimento ideal dos organismos. De fato, a maior parte do Fe biodisponível no ambiente natural esta fortemente associada a ligantes orgânicos, alguns dos quais estão relacionados especificamente ao Fe(III) (Worms et al. 2006).

Ainda de acordo com Worms et al. (2006) alguns complexos de Fe estão acessíveis ao fitoplâncton, e a disponibilidade dos metais pode também ser influenciada por processos fotoquímicos.

Alguns outros organismos (fitoplâncton e procariontes) possuem estratégias para aumentar a biodisponibilidade do Fe. Uma dessas estratégias é reconhecer o Fe(III) por um receptor da membrana específico (Figure 1.3).

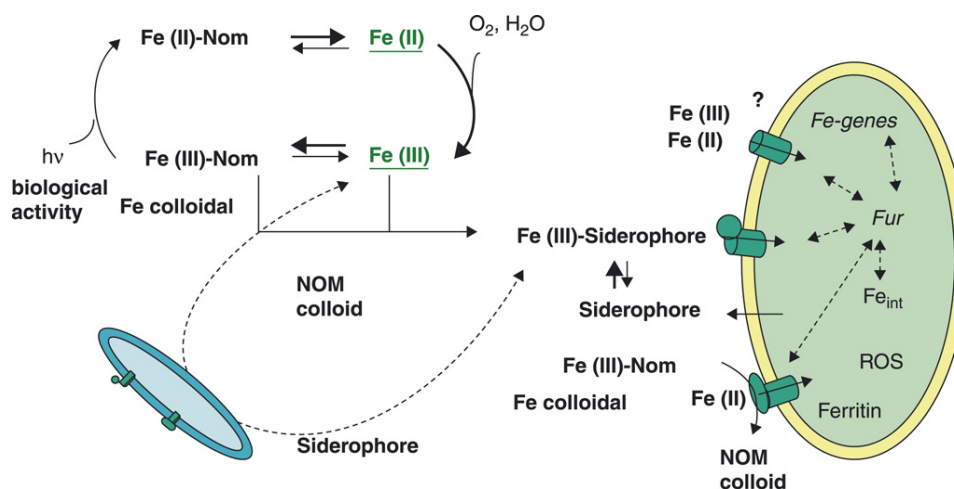


Figure 1.3 Representação esquemática da maioria dos processos que influenciam a biodisponibilidade do Fe em microorganismos. Neste diagrama simplificado, os ions Fe(II) e Fe(III) são considerados como as duas espécies químicas biodisponíveis. O ferro associado a matéria orgânica são potencialmente biodisponíveis, dependendo das concentrações, afinidade e estratégias de captação. Nesta figura, a

excreção, reconhecimento e transporte dos sideróforos leva a uma biodisponibilidade do ferro específica. A diminuição de complexos orgânicos de Fe(III) facilita sua dissociação de modo a permitir uma melhor assimilação. A largura das setas indica a instabilidade relativa dos complexos de Fe(III). Dentro do microorganismo, a regulação do ferro é mostrada com setas pontilhadas. Um segundo microorganismo capaz de competir pela biodisponibilidade do ferro usando sideróforos e/ou superfícies reduzidas também é ilustrada. Fonte: (Worms et al. 2006).

O Zn é outro exemplo de metal em que a interação entre os fluxos físico, químico e biológico presente no ambiente pode influenciar a concentração deste elemento no ambiente. Em condições naturais na água o Zn é encontrado como um íon livre ou em complexos. A absorção do Zn é estreitamente regulada. Em baixas concentrações, a internalização do Zn pode ser regulada ao ponto onde a difusão deste elemento se torna limitante e então complexos termodinamicamente fortes se tornam biodisponíveis para o organismo (Worms et al. 2006).

Tais fatos, atrelado a diversidade de características encontradas numa mesma região, fazem com que o estudo sobre as concentrações de metais e seus comportamento geoquímicos e interações entre o meio abiótico e biótico seja detalhadamente estudado, de forma que possa gerar o maior número de informações possíveis.

Baía de Todos os Santos

A Baía de Todos os Santos (BTS), na cidade de Salvador, Bahia-Brazil, é uma região que resguarda diversos ecossistemas onde podemos encontrar uma biodiversidade de fauna e flora associadas, mas também é uma região com inúmeras atividades industriais, como por exemplo, a indústria têxtil, atividades petrolíferas e petroquímicas. Essas atividades acarretam valores econômicos para a sociedade, contudo vem contribuindo para a deterioração do ambiente (Queiroz and Celino 2008). Essa degradação pode vir a causar prejuízos diretos para toda a biota dessa região e de regiões próximas, atingindo direta ou indiretamente os seres humanos.

Nessa baía encontram-se diversos estuários, onde abrigam um importantíssimo ecossistema que sofre com diversas atividades antrópicas, os manguezais. Ecossistemas localizados em regiões de zonas costeiras que servem de transição entre os ambientes terrestres e marinhos, no qual acontece o encontro das águas dos rios com o mar, estando sujeito ao regime das marés (Rodrigues and Farrapeira 2008), situação que favorece grandes variações de pH, Eh e condições permanentemente redutoras para os sedimentos (Masutti et al. 2000). Possui uma vegetação com poucas espécies, mas caracteriza-se por uma área de grande produtividade primária devido ao acúmulo de matéria orgânica, fazendo com que seja um respeitável segmento da cadeia alimentar (Rodrigues and Farrapeira 2008).

A BTS, que é uma reentrância costeira, integra geologicamente a bacia sedimentar do Recôncavo Baiano, de idade cretácea, sendo os sedimentos desta região predominantemente arenosos e argilosos, depositados num sistema delimitado por grandes falhas (BAHIA 1994). Esta Baía é considerada a maior e mais importante baía navegável da costa brasileira, tendo uma área total de 1.200 Km² e se estende por 462 Km de costa (Queiroz and Celino 2008).

Os rios e estuários ao longo da BTS tem uma grande importância para a população local pois também são utilizados como área de pesca artesanal pelos moradores que vivem nas regiões próximas, o que faz desses locais uma fonte de renda, assim como de subsistência para a região da localidade. Ao longo dos estuários desta Baía encontram-se naturalmente elementos químicos, os metais. Tais elementos são de relevância para a manutenção das condições favoráveis para os meios bióticos e abióticos (Buggy and Tobin 2008). Elementos metálicos são bons condutores de eletricidade, com alta densidade e que em concentrações ideais contribuem para a atividade de vários organismos (Pekey et al. 2004). Além de já se encontrarem naturalmente no ambiente esses elementos são introduzidos antropicamente, alterando as concentrações naturais, acarretando problemas ao ecossistema como, por exemplo, elevar as concentrações naturais de determinados metais nos organismos (Costa 2007).

Além das interferências antrópicas, situações naturais, como as diferentes características geoquímicas provocadas pelas condições da sazonalidade em relação ao volume de chuvas entre as estações do ano, acarretam na modificação do comportamento dos elementos metálicos nas regiões estuarinas (Milazzo et al. 2014). Tal situação interfere na biodisponibilidade e na bioconcentração dos metais para os compartimentos bióticos e abióticos da região.

O conhecimento do comportamento destes metais de acordo com suas características e a essencialidade para a matéria viva é de muita relevância. Sendo necessários estudos para estes elementos e suas implicações aos ecossistemas.

Estudar a biodisponibilidade nas águas superficiais e nos sedimentos, assim como estimar a bioconcentração de metais numa espécie de organismo de regiões estuarinas tem uma grande importância para que se possa realizar um estudo sistemático e assim coletar informações importantes para um estudo mais completo.

Ao longo do ano ocorrem diversas mudanças relacionadas ao clima, uma dessas mudanças diz respeito aos índices pluviométricos (sazonalidade) que pode variar nas mais diversas localidades. A cidade de Salvador e sua região metropolitana, mais especificamente a Baía de Todos os Santos, possui diferentes índices ao longo do ano, onde podemos identificar uma estação seca (dezembro a março) com pluviosidade em torno de 125 mm/mês e uma estação chuvosa (abril a julho) com médias de 300 mm/mês. Essa Baía e as diferentes características ao longo de sua variação temporal, bem como a espacial pode ter respostas diferentes em termos de concentração de elementos metálicos nas águas superficiais, nos sedimentos estuarinos, e conseqüentemente nos organismos. Estudos espaço-temporal tem-se tornado muito relevantes uma vez que interferem direta e indiretamente nas condições ambientais.

Devido a tais fatos, tem-se as hipóteses de que (i) os parâmetros físico-químicos (pH, Eh, salinidade, temperatura, oxigênio dissolvido, condutividade etc.) nas águas superficiais e sedimentos em regiões estuarinas sofrem influência direta da sazonalidade, bem como de características locais, (ii) as concentrações de metais traço nas águas superficiais e nos sedimentos estão conectadas aos parâmetros físico-químicos e (iii) a concentração interna de metais em organismos será dependente da biodisponibilidade que os metais traço se encontram na parte abiótica do ambiente.

De acordo com a literatura acima e com as hipóteses apresentadas, a presente tese tem os seguintes objetivos:

Objetivo Geral:

- Determinar a exposição temporal e espacial de metais traço em diferentes regiões estuarinas na Baía de Todos os Santos e entender como o comportamento geoquímico dos metais é afetado por essas exposições.

Objetivos Específicos:

- Realizar análises pontuais de parâmetros físico-químicos (pH, Eh, Salinidade, Temperatura, etc.) nas águas superficiais e sedimentos entre os períodos seco e chuvoso do ano em três diferentes regiões estuarinas.

- Análise da concentração de metais (Zn, Fe, Ni e Cu) nas águas superficiais e sedimentos;

- Medição da concentração interna em *Crassostrea rhizophorae* (ostra) para os metais (Zn, Fe, Ni e Cu);

- Realizar especiação química dos metais (Zn, Fe, Ni e Cu) e outros ions para checar possíveis flutuações na concentração de metais nas águas superficiais;

Para realizar tais objetivos, as seguintes perguntas sobre a pesquisa foram abordadas:

[1] Os parâmetros físico-químicos (pH, Eh, Salinidade, Temperatura, etc.) nas águas superficiais e sedimentos estuarinos estão sujeitos ao efeito sazonal bem como a variação espacial dentro de uma mesma baía como a de Todos os Santos? (Capítulo 2)

[2] As concentrações de metais (Zn, Fe, Ni e Cu) nas águas superficiais, nos sedimentos e também nos tecidos da ostra *Crassostrea rhizophorae* são afetadas de forma espaço-temporal de acordo com as variáveis físico-químicas? (Capítulo 3)

[3] A dinâmica dos estuários, bem como o curso dos rios afetam a concentração de metais no ambiente? A especiação química dos elementos é um fator decisivo para a concentração interna dos metais nos organismos? (Capítulo 4)

Para cumprir e responder a esses objetivos, três artigos foram produzidos e estão resumidamente apresentados nos capítulos a seguir:

No capítulo 2: A variação temporal e espacial dos diversos parâmetros físico-químicos (pH, Eh, Salinidade, Temperatura, Oxigênio Dissolvido e Condutividade) nas águas superficiais e em sedimentos (pH, Eh, Temperatura, Condutividade, Matéria Orgânica e Granulometria) foram investigadas. Foi assumido que as diferentes características das áreas estudadas junto com a sazonalidade alterariam os valores dos parâmetros analisados. Os resultados mostraram claramente que a diferença espacial e temporal tem uma influência significativa e determinante nas variáveis estuarinas e que tal achado deve influenciar nas concentrações de elementos metálicos.

No capítulo 3: De acordo com pesquisas já realizadas, as concentrações de metais no ambiente é dependente de diversas variáveis, que podem aumentar ou diminuir a concentração de acordo com a geoquímica. Para verificar e entender essa suposição, investigamos a exposição temporal e espacial de elementos metálicos (Zn, Fe, Ni e Cu) em diferentes regiões estuarinas na Baía de Todos os Santos e associamos com os resultados de diversos parâmetros físico-químicos. Nossos resultados mostraram uma variação espaço-temporal associada as características, bem como as condições meteorológicas de cada local de amostragem. Estudos sazonais são fundamentais para determinar os efeitos dos parâmetros físico-químicos sobre as concentrações de metais nas diversas matrizes (água, sedimento e biota) no ambiente e a especiação de metais é uma ferramenta fundamental para a melhor compreensão dos efeitos destes metais sobre os organismos.

No capítulo 4: Ambientes estuarinos são altamente dinâmicos e o formato e curso dos rios podem influenciar nas variáveis físico-químicas, conseqüentemente, as concentrações de metais no ambiente. Este fato foi analisado estudando-se como o formato dos rios e seu curso afetam os valores dos parâmetros físico-químicos de três diferentes rios pertencentes a Baía de Todos os Santos. Os resultados mostraram que a localização em relação ao oceano, bem como o formato e curso dos rios tem influência sobre as diversas variáveis ambientais. Tal estudo fornece conhecimento sobre a importância de se levar em consideração a dinâmica de cada lugar quando do estudo de metais em ambientes estuarinos.

A [figura 1.4](#) ilustra uma visão geral sistemática da pesquisa realizada nos capítulos 2-4.

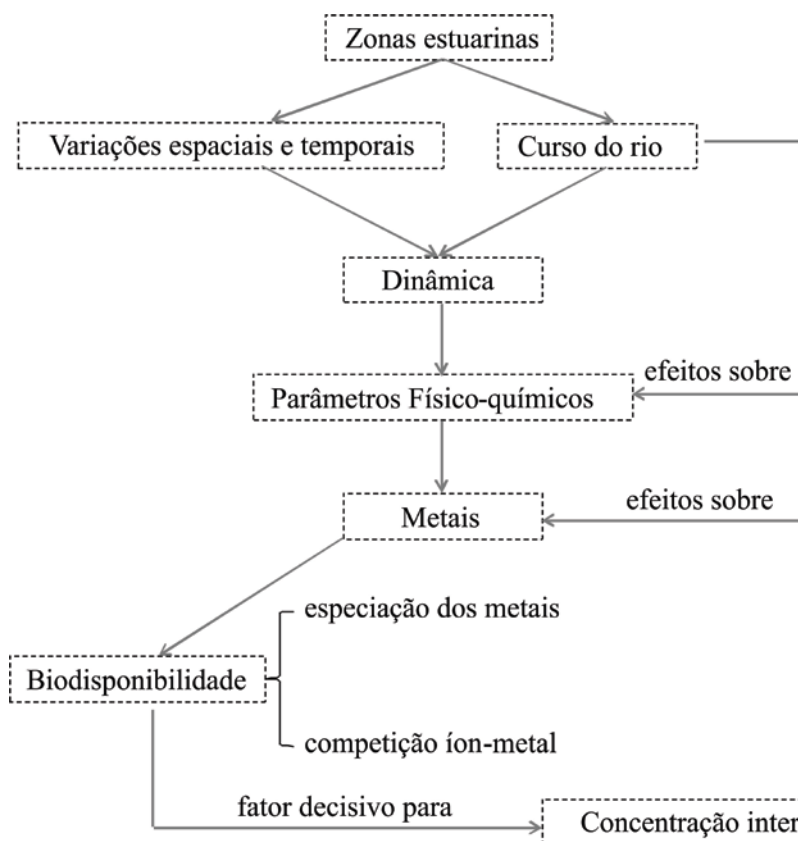


Figura 1.4 Visão sistemática geral da pesquisa realizada neste Tese de Doutorado.

CAPÍTULO 2 - PHYSICOCHEMICAL PARAMETERS IN ESTUARINE ZONES OF THE TODOS OS SANTOS BAY IN BAHIA, BRAZIL

Abstract

The physicochemical parameters in both surface waters and sediments are important to understand estuarine dynamics. Different input of natural processes along the year such as rainfall, wind, solar radiation and water influx as well as geomorphology will affect the physicochemical parameters. The present study was carried out to determine how the spatial-temporal difference play a role in the physicochemical parameters at three different locations from the Todos os Santos Bay. This involved analyzing pH, Eh (mV), temperature (°C), salinity (‰), dissolved oxygen (mg L^{-1}) and conductivity (ms cm^{-1}) in the water and pH, Eh (mV), Temp. (°C) and conductivity (ms cm^{-1}) in the sediments. Particle size and organic matter were also analyzed in the sediments. The results showed that the values of all parameters were different according to the sampling time as well as the location in the bay. The temperature and salinity of the surface water, for example, were higher during the dry season (1st and 3rd sampling time). The pH of the surface water was higher in the Maragogipe River (7.70) and for the sediment São Paulo River showed the highest pH (7.23). The organic matter in the sediment showed the lower percentage during the rainy season (2nd sampling time) and this parameter is strongly associated with the particle size. These results suggest that spatial variation along the bay together with the seasonality affect all the physicochemical parameters in the estuary.

Keywords: physicochemical parameters, spatial-temporal variation, seasonality

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2.1 Introduction

One of the most common and the most important resource on earth, which facilitates life on this planet as we know, is water (Anitha & Surgitha 2013). The marine environment is an essential part of the global life, mainly in the coastal and estuary areas (Dixit *et al.* 2013). As a transitional area between land and sea, estuarine zones are important for fishers in tropical regions, as economic activity or like places for feeding (Gadhia *et al.* 2012).

With its mangrove forests, which brings a significant ecological importance, estuarine areas are a complex and very dynamic kind of aquatic environment, mainly because of the mix between both sea and river waters, where many physicochemical processes take place and will affect the quality of water (Anitha & Surgitha 2013). The terrestrial and oceanic inputs in estuarine zones are modified by biogeochemical processes, which are modulated by many mechanisms, such as wind, water temperature, waves, tides or freshwater discharge (Regnier *et al.* 2013).

The Todos os Santos Bay, in Salvador, located in the Recôncavo Baiano region, North East of Brazil, is a unique area that has many ecosystems with a large fauna and flora biodiversity. The Bay is also used for industrial activities, which on one hand brings economic value for society, but on the other hand has led to possible exposure damage and deterioration of the environment. Lots of biological processes in aquatic ecosystems are influenced by many different factors, such as pH, redox conditions, organic matter, mineral particles and salinity (Du Laing *et al.* 2008; Reitermajer *et al.* 2011). These factors may vary during the year, mainly because of the difference in rainfall intensity between seasons, consequently, bringing important impacts on the environment (Nizoli & Luiz-Silva 2009). The Todos os Santos Bay is unique because it consists of a range of different habitats with different characteristics. This spatial variation in characteristics, together with the temporal variation, may however, lead to different values and results for many parameters (Queiroz & Celino 2008). The knowledge about how the physicochemical parameters are affected by the seasonality and river shapes can be a key to assess the quality of the mangrove areas in the bay.

The aim of this study is to identify how the variation in time and location affect the physicochemical characteristics of three different mangrove areas in the Todos os Santos Bay. This involved analyzing pH, Eh (mV), temperature (°C), salinity (‰), dissolved oxygen (mg L^{-1}) and conductivity (ms cm^{-1}) in the water and pH, Eh (mV), Temp. (°C) and conductivity (ms cm^{-1}) in the sediments. Particle size and organic matter were also analyzed in the sediments.

2.2 Materials and methods

This study was carried out in the Todos os Santos Bay ($32^{\circ} 02' 30'' - 38^{\circ} 37' 30''\text{W}$ and $13^{\circ} 07' 30'' - 12^{\circ} 37' 30''\text{S}$) in Brazil, in three different estuarine zones near the (A) Maragogipe, (B) Jaguaripe and (C) São Paulo Rivers (Figure 2.1). The Todos os Santos Bay is the biggest and most important navigable bay of the Brazilian coast, with a surface area of about 1.200 km^2 and a coast length of 462 km.

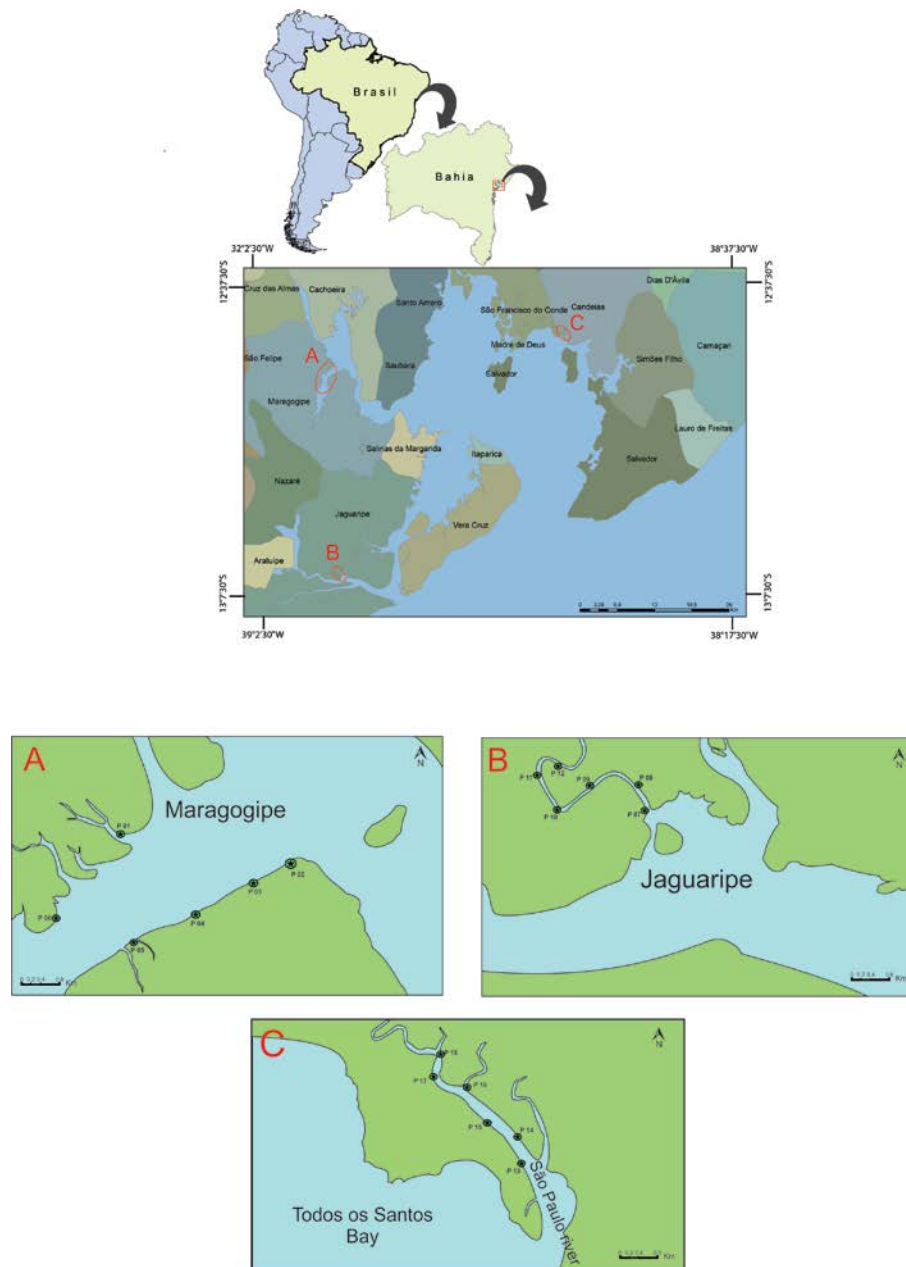


Figure 2.1 Location of the sampling sites used for this study. Insert shows a map of the Bahia region in Brazil with the Todos os Santos Bay. The detailed overview of the Todos os Santos Bay area shows the sampling sites near the Maragogipe (A), Jaguaripe (B) and São Paulo (C) Rivers.

These estuarine zones, near the Maragogipe, Jaguaripe and São Paulo Rivers, where a magnificent mangrove system develops, have a fundamental importance to the local food chain and also to the livelihood of many of the inhabitants of the region. Even though they belong to the same Bay, the three areas have different characteristics due to the spatial variation. These estuarine ecosystems have been affected by many human activities, such as contamination by chemical industries, which have contributed to their deterioration (De Carvalho 2007).

Geologically, the Todos os Santos Bay is included in the sedimentary basin of the Recôncavo Baiano. The climate is tropical-humid and presents a remarkable seasonal cycle (Figure 2.2). Rainfall in this region is around $300 \text{ mm month}^{-1}$ between April and June, characterizing the wettest period. Between January and March, the rain is less intense and well distributed with a precipitation of around $125 \text{ mm month}^{-1}$ and an average annual temperature of about $25 \text{ }^{\circ}\text{C}$ (Kirimurê 2013).

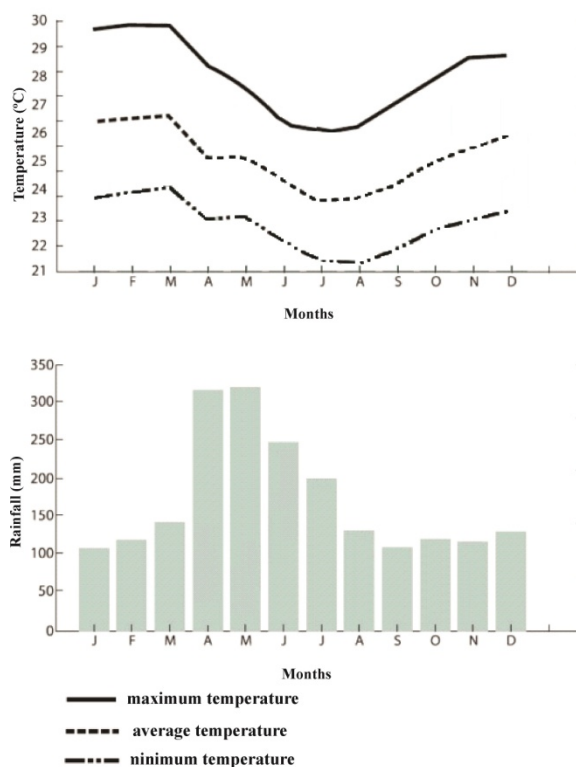


Figure 2.2 Average seasonal variation of temperature and rainfall in the study area registered by the Ondina Weather Station for the period of 1961-2009 (INMET 2015). This station, located in Salvador-Bahia, is the closest weather station of the Todos os Santos Bay.

The economic activities in this region are considered as industrial, and cases of oil spill has been reported, as well as emissions of industrial and domestic effluents from municipalities around the region (De Jesus 2011; Milazzo *et al.* 2014).

2.2.1 Sampling

The field work was carried out in three periods, March 2014, January 2015 (dry season) and August 2014 (rainy season). Sampling always was done during the low tide, taking into account the tidal period (Table 2.1).

Table 2.1 Location, dates, time and tide height (m) of the samplings of the three locations in the Todos os Santos Bay, Bahia, Brazil, using as reference Madre de Deus Port tide.

Location	Date			Hour			Tide height (m)		
	1 st (2014)	2 nd (2014)	3 rd (2015)	1 st (2014)	2 nd (2014)	3 rd (2015)	1 st (2014)	2 nd (2014)	3 rd (2015)
Maragogipe River	18/03	26/08	07/01	10:51 a.m.	10:02 a.m.	11:09 a.m.	0.2	0.2	0.4
Jaguaripe River	20/03	27/08	08/01	10:51 a.m.	10:54 a.m.	11:47 a.m.	0.3	0.3	0.5
São Paulo River	21/03	29/08	09/01	12:19 a.m.	11:49 a.m.	12:13 p.m.	0.4	0.4	0.6

Sediment and surface water samples were collected from 18 points (6 in each estuary), with a spatial distance of approximately 200 m between each sampling point. This distance is sufficient to

consider sampling points as true replicates. The sampling points were randomly chosen across each sampling location, in order to avoid any bias in the results.

2.2.2 Water collection and preparation for analysis

Surface water samples (500 mL) were taken at a depth of 0 - 20 cm using polyethylene bottles and the physicochemical parameters (pH, Eh (mV), temperature (°C), salinity (‰), conductivity (ms cm^{-1}) and dissolved oxygen (mg L^{-1})) were monitored at each sampling point. For all measurements, a HORIBA U-50 multiparameter water quality was used.

2.2.3 Sediment collection and preparation for analysis

For the sediments, approximately 300 g were sampled from the top 0 - 15 cm layer, and stored in polyethylene packages with a sufficient amount of water from the sampling site to preserve their characteristics. The samples were placed in coolers with ice to maintain a temperature of 4 °C, according to the methodology described by [Jesus et al \(2003\)](#). The cores were taken to the laboratory, where particle size distribution (classified as sand, silt and clay), and organic matter content were analyzed. To measure the physicochemical parameters (pH, Eh (mV), temperature (°C) and conductivity (ms cm^{-1})), a HORIBA U-50 multiparameter water quality was used.

2.2.4 Data analysis

The data were analyzed using STATISTICA 7 to observe summary statistics and trends and behaviors of the physicochemical parameters. Microsoft Office Excel 2007 as well as the STATISTICA 7 were used to correlate the physicochemical parameters.

2.3 Results

The physicochemical parameters measured in surface waters and sediments from the Maragogipe, Jaguaripe and São Paulo Rivers, sampled in three different seasons, are summarized in [Table 2.2](#). In the surface waters, the pH increased with time for all rivers, except for the São Paulo River which had the highest pH (7.29) during the second season. The pH of the sediments showed the same increasing trend with time, however, during the last sampling season, sediment pH in the Maragogipe River was lower than in the second season.

The Eh values showed a quite similar behavior for both surface waters and sediments. In the Maragogipe River, the Eh values were negative in all seasons. In the São Paulo River, Eh of surface water was negative at the first and second sampling. For the sediments, the values in general were negative during the first and last season and positive in the second season.

During the second sampling (rainy season), temperatures were lower than at the first and third sampling (dry season). In the sediments, the same trend was noticed for Jaguaripe and São Paulo Rivers while in the Maragogipe River temperature increased from the first to the third sampling.

Dissolved oxygen concentrations showed the same trends in the Maragogipe and São Paulo Rivers with the highest values recorded during the first (6.9 and 3.6 mg L^{-1}) and third (7.7 and 3.6 mg L^{-1}) seasons. In the Jaguaripe River the highest mean of the dissolved oxygen concentration was measured during the third season (9.3 mg L^{-1}), while the first and second seasons showed similar results (3.8 mg L^{-1}).

The conductivity of the surface water showed a different trend for the different Rivers. In the Maragogipe River, conductivity was highest during the second season (44.7 ms cm^{-1}), while in the São Paulo River it was lowest (49.9 ms cm^{-1}) during the second season. In the Jaguaripe River, the conductivity increased from the first to the third sampling. The conductivity of the sediments of the Jaguaripe and São Paulo Rivers was also lowest during the rainy season, while it was highest for the Maragogipe River sediments (49.5 ms cm^{-1}) during the rainy season.

Salinity of the São Paulo River was highest (34.6 and 33.1 ‰) during the first and third season, respectively, while in the Maragogipe River the highest value (28.6 ‰) was recorded during the second season. In the Jaguaripe River, salinity increased from the first to the third season, from 14.3 ‰ to 23 ‰.

Table 2.2 Physicochemical parameters of surface waters and sediments in the Maragogipe, Jaguaripe and São Paulo rivers, Brazil, sampled in three different seasons (1st: March 2014; 2nd: August 2014; 3rd: January 2015). The values shown are mean \pm standard deviation (n = 6).

Variables	River	Mean \pm St.dev.			
		Season	1 st	2 nd	3 rd
pH (water)	Maragogipe		6.75 \pm 0.29	7.59 \pm 0.13	7.70 \pm 0.43
	Jaguaripe		5.44 \pm 0.26	6.81 \pm 0.19	7.25 \pm 0.09
	São Paulo		5.91 \pm 0.25	7.29 \pm 0.16	7.05 \pm 0.42
Eh (mV) (Water)	Maragogipe		-7.8 \pm 17.9	-30.1 \pm 8.0	-25.1 \pm 27.3
	Jaguaripe		3.8 \pm 16.7	16.0 \pm 11.8	2.6 \pm 5.9
	São Paulo		-22.8 \pm 14.9	-12.3 \pm 9.9	16.0 \pm 25.4
Temp. (°C) (Water)	Maragogipe		29.2 \pm 0.5	26.1 \pm 1.1	30.7 \pm 1.3
	Jaguaripe		28.4 \pm 0.9	24.4 \pm 0.3	27.6 \pm 0.2
	São Paulo		29.7 \pm 0.6	25.5 \pm 0.6	27.3 \pm 0.4
Salinity (‰) (water)	Maragogipe		22.3 \pm 4.1	28.6 \pm 2.1	22.0 \pm 1.4
	Jaguaripe		14.3 \pm 2.8	16.0 \pm 3.5	23.0 \pm 2.0
	São Paulo		34.6 \pm 3.8	32.1 \pm 0.9	33.1 \pm 3.6
D.O. (mg L ⁻¹) (water)	Maragogipe		6.9 \pm 1.0	5.9 \pm 1.2	7.7 \pm 0.9
	Jaguaripe		3.8 \pm 0.4	3.8 \pm 0.3	9.3 \pm 1.1
	São Paulo		3.6 \pm 0.3	3.1 \pm 0.4	3.6 \pm 1.4
Cond. (ms cm ⁻¹) (water)	Maragogipe		35.8 \pm 6.0	44.7 \pm 2.3	35.4 \pm 1.9
	Jaguaripe		24.0 \pm 4.2	26.5 \pm 5.3	36.5 \pm 2.7
	São Paulo		52.7 \pm 4.6	49.9 \pm 1.4	50.6 \pm 4.7
pH (sed)	Maragogipe		6.81 \pm 0.13	7.10 \pm 0.36	6.80 \pm 0.18
	Jaguaripe		6.71 \pm 0.37	6.99 \pm 0.20	7.21 \pm 0.14
	São Paulo		6.85 \pm 0.21	7.06 \pm 0.23	7.23 \pm 0.18
Eh (mV) (sed)	Maragogipe		-5.6 \pm 7.1	-5.6 \pm 21.2	13.6 \pm 10.5
	Jaguaripe		-4.6 \pm 10.9	4.1 \pm 12.5	-1.5 \pm 7.4
	São Paulo		-5.0 \pm 14.0	0.0 \pm 13.3	-3.1 \pm 10.7
Temp. (°C) (sed)	Maragogipe		27.5 \pm 1.3	28.4 \pm 2.6	30.7 \pm 2.0
	Jaguaripe		27.6 \pm 1.3	25.5 \pm 0.7	29.5 \pm 2.4
	São Paulo		28.6 \pm 0.6	26.9 \pm 1.5	28.9 \pm 1.1
Cond. (ms cm ⁻¹) (sed)	Maragogipe		42.4 \pm 3.7	49.5 \pm 3.8	44.6 \pm 3.6
	Jaguaripe		40.1 \pm 3.4	31.3 \pm 3.7	41.1 \pm 3.9
	São Paulo		55.3 \pm 2.0	51.4 \pm 2.2	56.5 \pm 1.8

Table 2.3 shows the particle size distribution (sand, silt, clay) and organic matter content of the sediment for each river in the three different sampling seasons. Organic matter content showed the same trend for all three rivers, being much lower in the rainy season (2nd sampling) than in the dry seasons. Overall, the São Paulo River sediment had the lowest organic matter content.

Table 2.3 Particle size distribution (silt, clay and sand) and organic matter contents (O.M.) (in %) of sediments in the Maragogipe, Jaguaripe and São Paulo Rivers, sampled in three different seasons: March 2014 (1st), August 2014 (2nd) and January 2015 (3rd).

Variable	River		Sediments		
		Season	1 st	2 nd	3 rd
Silt	Maragogipe		24.8	35.5	36.2
	Jaguaripe		28.2	29.0	34.0
	São Paulo		29.9	27.2	28.3
Clay	Maragogipe		26.6	41.1	47.3
	Jaguaripe		23.0	18.4	24.5
	São Paulo		17.1	29.4	30.5
Sand	Maragogipe		48.4	23.2	16.3
	Jaguaripe		48.7	52.5	41.4
	São Paulo		52.8	43.3	41.0
O.M.	Maragogipe		10.3	6.1	13.2
	Jaguaripe		10.2	8.2	12.5
	São Paulo		9.7	5.6	9.6

Particle size distribution also showed some variation between seasons and rivers. Clay content, for instance, showed the same trend in the Maragogipe and São Paulo Rivers, increasing with time from 26.6 to 47.3% in the Maragogipe River and from 17.1 to 30.5% in the São Paulo River. In the Jaguaripe River, sediment clay content was highest (23.0 and 24.5%) during the first and third season and lowest (18.4%) during the second season.

2.4 Discussion

For both water and sediment samples, the physicochemical parameters analyzed at the three sampling locations showed different spatial and temporal trends during the sampling period of this study, similar results were found by Milazzo *et al.* (2014). Due to its characteristic and directly contact to the environment, the temperature of water and sediment is the first to react to the air temperature and water input. Once the rainy season starts, the temperature normally decreases, but all other parameters analyzed had also different behaviors during the different seasons. In some cases as the pH and salinity in the Maragogipe River, and the D.O. levels for all rivers studied, the results were not as expected, therefore, indicating that a combination of many factors can affect the physicochemical parameters of water and sediment according to the place of study.

In the present study, as expected, temperature of the surface water at all locations decreased during the rainy season. During June, July and August, the land breezes, the higher precipitation and fresh water influx together were essential for the lower temperatures compared with the dry season. The higher intensity of solar radiation and evaporation also affected surface water temperature, and as a consequence, during the dry season (1st and 3rd field works) this parameter was higher. This result was the same found by Dixit *et al.* (2013) and Anitha & Surgitha (2013).

The temperature of the sediments followed the same trends of the surface waters being higher during the dry season, except in the Maragogipe River which the temperature increased from the 1st to the 3rd sampling (Table 2.2). This situation might be connected with the same reasons (high intensity of solar radiation and evaporation) which affected the temperature of the surface waters.

The pH values from both surface waters and sediments varied between seasons and rivers, going from 5.44 to 7.70 in the surface waters and from 6.71 to 7.23 in the sediments (average values), ranging from acid to alkaline. In the surface waters the highest pH values were recorded in the Maragogipe River, which might be attributed to that region receiving more effluent discharge (mainly domestic ones) which may make the water more alkaline (Dublin-Green 1990), as reported by Otero *et al.* (2008), this region

suffer with cases of household sewage and industrial waste as well. Regarding the Jaguaripe and São Paulo Rivers, the latter one had the highest pH during the 1st and 2nd sampling (Table 2.3). This probably is explained from sea water penetration which may lead to an increase of the pH of estuarine waters (Anitha & Sugirtha 2013). With values ranging between 7.40 and 8.50 for sea waters, pH showed the influence of the ocean, which was different depending on the location and sampling time. The São Paulo River being closer to the ocean than the other two sampling areas may be one of the explanations for the highest pH values at this location.

Water pH will affect the solubility of metal ions in the environment and their binding to solid or dissolved phases like sediment or dissolved organic carbon (Niyogi & Wood 2004). This means that pH also controls the availability of metals for uptake by organisms (Dixit *et al.* 2013), in this way, bringing consequences to the environment. In the sediments, pH variation might be important to try to understand the behavior of the metals, since this parameter can explain ion binding process in soils and sediments (Niyogi & Wood 2004). For example, at pH decreasing, higher competition of protons may cause a reduced metal binding to sediments or the other way around.

The fact that the pH ranged not only between seasons but also between locations allows us to say that the different characteristics of each location will be important to explain the behavior of this parameter. Factors like dilution of seawater by freshwater influx leading to salinity reduction, organic matter decomposition and temperature are relevant for the oscillation of the pH (Gadhia *et al.* 2012). Once those factors can be completely different between places, it is expected that the pH will also be different between locations.

Eh values of the surface waters ranged from -30.1 to 16.7 mV in the different rivers and at different sampling times. Most of the time redox potential was negative, which is normal for estuarine environments and mangrove areas with their high organic matter content (Milazzo *et al.* 2014). In such environments, oxygen is rapidly consumed by microorganisms, giving this ecosystem a reductive feature (Queiroz & Celino 2008). The variation in Eh values might be related with the tide and sampling time among the rivers. Also in the sediments, the redox potential was mostly negative. The variation in Eh values can be associated with the location of sampling since for each location the microbial activity may be different.

The salinity of the surface waters did not show the same trend between rivers but showed different values according to each location. Salinity is a parameter associated and affected by many factors like evaporation rates, rainfall, dilution in the estuary and mainly by the flood and ebb tides (Dublin-Green 1990; Dixit *et al.* 2013) and this parameter acts as a factor of distribution for many living organisms (Gadhia *et al.*, 2012).

In this study, the salinity was higher in the São Paulo River during all seasons (32.1-34.6 ‰) which is easily explained from its location (closer to the sea compared to the other two rivers). Comparing both Maragogipe and Jaguaripe Rivers, the second one was expected to have shown higher salinity, but an opposite situation happened (Table 2.2). Due to practical problems, the second sampling in the Maragogipe River was carried out at the middle tide, in this way, there was a higher influence of the sea in the estuary. In the Jaguaripe River, a rainy day before and during the 1st season probably was the main reason for the lowest values (14.3 ‰).

Dissolved oxygen (D.O.) levels showed the same behavior for all rivers studied, being lower during the rainy season (Table 2.2). These results were not as expected since during lower temperatures the solubility of the gases increases, resulting in waters more oxygenated. As an important water quality indicator, D.O. has influence in many biological and chemical processes in the environment and is crucial for supporting life (Gadhia *et al.* 2012). In this research, the D.O. levels followed the same trend as temperature (Table 2.2). An opposite behavior was reported by Anita & Surgitha (2013).

According to Brazilian legislation (CONAMA 2005), the D.O. values shouldn't be below 5.0 mg L⁻¹. The D.O. values for the São Paulo River for all seasons and the Jaguaripe River for the 1st and 2nd samplings were below the latter limit. Low levels of D.O. in these rivers may cause reduction of some organisms like fishes; as well as an increase population of anaerobic microorganisms like bacteria can happen because of the deoxygenation of the waters. In this way, bringing a reproductive failure and death of fishes, causing changes in the local environment and modifying abundance and diversity of species (Abowei 2010). This situation might be triggered by the effects of nutrient pollution since there is no suitable sewage treatment in these locations.

The conductivity of the surface water showed opposite trends comparing the Maragogipe (with the highest value during the rainy season) and the São Paulo Rivers (lowest value in the rainy season), while in the Jaguaripe River it increased from the first to the third sampling period. The conductivity is directly related to the concentration of ions in the water and it can be a good indicator of the presence of some contaminants (Nazir *et al.* 2015).

As a result of being closer to the sea, the São Paulo River showed the highest values for conductivity in both surface waters and sediments comparing with the Maragogipe and Jaguaripe Rivers and this situation was already reported in the literature (Cox *et al.* 1967). In the surface waters, as expected, the conductivity showed the same patterns as the salinity (Figure 2.3). In the sediments, both Jaguaripe and São Paulo Rivers showed the same patterns with lower values in the rainy season. On the other hand, in the Maragogipe River, the highest values were during the rainy season. As it's known, the conductivity has an important relationship with metal concentration in the sediment (Nazir *et al.* 2015; Van Gestel & Koolhaas 2004), therefore, the metal behavior between these studied locations might show different values.

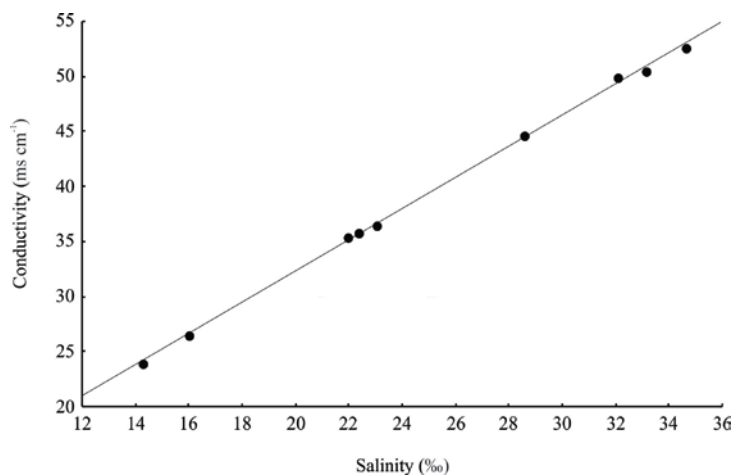


Figure 2.3 Relationship between average concentration of Conductivity (ms cm^{-1}) and average concentration of Salinity (‰) in the surface water of Maragogipe, Jaguaripe and São Paulo Rivers sampled in three different seasons (March 2014; August 2014; January 2015).

In the sediment, the organic matter also showed a variation between seasons, being lower during the rainy season for all rivers (Table 2.3). With lower temperatures, it is expected that the activities of the organisms decreases, which leads to a reduction of the degradation in the environment and consecutively of the organic matter. The organic matter content has a strong influence on cation exchange capacity, buffer capacity and on the retention of heavy metals in the sediments. During the dry season and with the highest percentage of organic matter together with the characteristic of high affinity for heavy metals (Marchand *et al.* 2001), the mangrove sediments might accumulate pollutants in the dry season, which can lead to disturbances in the environment.

The particle size distribution was different between seasons as well as between all the rivers in a general overview (Table 2.3). Once the water influx from the continent as well as the sea water intrusion are different along the year and locations, the sediments will be mobilized and moved by these powers, resulting in different patterns. It is expected a relationship between the particle size and the organic matter but this situation wasn't noticed in this study. Anyhow, a special attention should be given for the clay content, since it has properties which leads in favor to binding of cations (Finzgar *et al.* 2007), which will be important to explain possible correlations with the metal concentration for example.

2.5 Conclusion

The estuarine waters and sediments of Maragogipe, Jaguaripe and São Paulo Rivers showed a spatial and temporal variation for all parameters. These results might be related with the different mixing process of fresh water and sea water between locations and the variation of meteorological conditions. The different characteristics between each sampling location was decisive to lead to different parameters results. All these physicochemical parameters, which are governed by many factors, might affect metal concentration in the surface waters and sediments for example and, in this way, have an influence on organisms in the environment.

Spatial and temporal studies are important in determining the possible effects of physicochemical parameters on metal concentrations in water, sediment and biota, since metals are important for the maintenance of the environment. Further investigations were done to understand the real effects of the physicochemical parameters on the metal concentration in surface waters, sediments and biota, which will bring support to future statements about estuarine zones.

CAPÍTULO 3 - SPATIAL AND TEMPORAL VARIATION OF METAL CONCENTRATIONS IN ESTUARINE ZONES OF THE TODOS OS SANTOS BAY IN BAHIA, BRAZIL

Abstract

The knowledge of metal behavior in the aquatic environment is important for understanding its effects in estuarine zones and mangrove areas. These important and precious ecosystems are affected by many different factors that may vary temporally and spatially. The present study investigated the spatial and temporal variation of physicochemical parameters (pH, dissolved oxygen, temperature, salinity, etc.) and metal concentrations (Zn, Fe, Ni, Cu) at three different locations along the Todos os Santos Bay, North East Brazil, by analyzing surface water, sediment and mangrove oysters (*Cassostrea rhizophorae* (Guildin, 1828)). Metal concentrations in surface waters and sediments differed between the three sampling times (March and August 2014; January 2015) and locations and were affected by fluctuating physicochemical parameters, which in this way also affected the metal bioconcentration in the oysters. The pH of the surface waters, for example, increased from the 1st to the 3rd sampling time while the concentrations of Zn and Fe decreased during the same period. The sediment concentrations of Zn and Fe were strongly correlated with organic matter content. These results suggests that seasonality as well as the different water and sediment properties along the bay directly affect metal concentration and bioavailability in the environment.

Keywords: metal concentrations; physicochemical parameters; seasonality; variation.

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3.1 Introduction

Estuarine environments and its mangrove forests have large ecological importance by serving as habitat for many species (Campana et al. 2005; Onofre et al. 2007). Due their natural conditions, these ecosystems are very special, but also very sensitive to disturbances like pollution (Nizoli and Luiz-Silva 2009; Strady et al. 2011).

Because of human activities, the levels of metals in the environment have increased. This also concerns marine environments, so metals may also cause a potential threat to mangrove ecosystems (Nizoli and Luiz-Silva 2009; Strady et al. 2011). Metals may have direct effects on organisms living in mangrove areas, such as reducing their growth and reproduction and in this way potentially affecting population growth and eventually biodiversity. When metals accumulate in organisms, they may end up in the food chain and cause indirect effects. In this way, they may even pose a risk for human health.

Mollusks are sedentary animals that have the potential to accumulate high levels of metals in their tissues. They also are an important food source for humans. For these reasons, they have been considered important organisms for measuring and monitoring available metal concentrations, also in mangrove ecosystems (Silva et al. 2006; Strady et al. 2011; Ruelas-Inzunza and Paez-Osuna 2000; Harding 2007).

The Todos os Santos Bay, in Salvador, located in the Rencôncavo Baiano region, North East of Brazil, is a unique area that has many ecosystems with a high fauna and flora biodiversity. The Bay also is used for industrial activities, which on one hand brings economic value for society, but on the other hand has led to possible exposure with metals and deterioration of the environment. The dissolved or available levels of metals in aquatic ecosystems are influenced by many different factors, such as pH, redox conditions, organic matter, mineral particles and salinity (Du Laing et al. 2008; Reitermajer et al. 2011). These factors may vary during the year, mainly because of the difference in rainfall intensity between seasons. Therefore, seasonal patterns may have important impacts on metal availability due to their influence on the physicochemical parameters of the surface water (Nizoli and Luiz-Silva 2009). The Todos os Santos Bay is unique because it consists of a range of different habitats with different characteristics. This spatial variation in characteristics, together with the temporal variation, may however, also lead to large differences in metal availability and consequent metal risks (Queiroz and Celino 2008). It therefore is essential to evaluate metal concentrations in water, sediment and biota and combine this with knowledge about the geochemistry of the system to assess the quality of the mangrove areas in the bay (Cundy et al. 2005).

The aim of this study is determining the spatial and temporal exposure to metals of three different mangrove areas in the Todos os Santos Bay. This involved analyzing metal concentrations in surface water and sediment. Metal bioavailability was estimated by measuring concentrations in soft tissues of the oyster *Crassostrea rhizophorae* (Guildin 1828), popularly known as mangrove oyster. This species is widely distributed along the entire Todos os Santos Bay. It is a sessile filter-feeder of reasonable size and sedentary, which can easily be sampled. Water, sediment and oysters were sampled during three different seasons of the year. All samples were analyzed for Zn, Fe, Ni and Cu concentrations. By analyzing also physicochemical parameters in water and sediment, speciation calculations could be made to estimate possible fluctuations in available metal concentrations at different points in the bay.

3.2 Materials and methods

This study was carried out in the Todos os Santos Bay (32° 02' 30" - 38° 37' 30"W and 13° 07' 30" - 12° 37' 30"S) in Brazil, in three different estuarine zones near the (A) Maragogipe, (B) Jaguaripe and (C) São Paulo Rivers (Figure 3.1). The Todos os Santos Bay is the biggest and most important navigable bay of the Brazilian coast, with a surface area of about 1.200 km² and a coast length of 462 km.

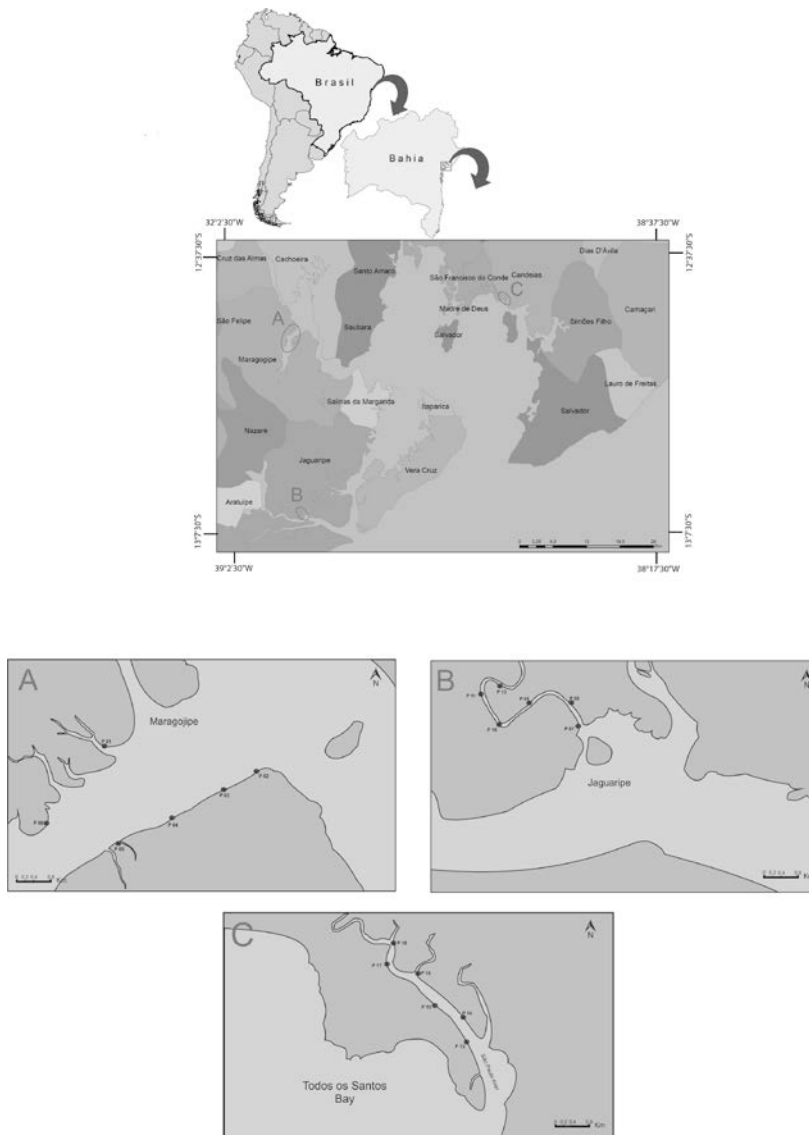


Figure 3.1 Location of the sampling sites used for this study. Insert shows a map of the Bahia region in Brazil with the Todos os Santos Bay. The detailed overview of the Todos os Santos Bay area shows the sampling sites near the Maragogipe (A), Jaguaripe (B) and São Paulo (C) Rivers.

These estuarine zones, near the Maragogipe, Jaguaripe and São Paulo Rivers, where a magnificent mangrove system develops, have a fundamental importance to the local food chain and also to the livelihood of many of the inhabitants of the region. Even though they belong to the same bay, the spatial variation makes these areas having different characteristics. These estuarine ecosystems have been affected by many human activities, such as contamination by chemical industries, which have contributed to their deterioration (De Carvalho 2007).

Geologically, the Todos os Santos Bay is included in the sedimentary basin of the Reconcavo Baiano. The climate is tropical-humid and presents a remarkable seasonal cycle (Figure 3.2). Rainfall in this region is around $300 \text{ mm month}^{-1}$ between April and June, characterizing the wettest period. Between January and March, the rain is less intense and well distributed with a precipitation of around $125 \text{ mm month}^{-1}$. Average annual temperature is about $25 \text{ }^{\circ}\text{C}$ (Kirimure 2013).

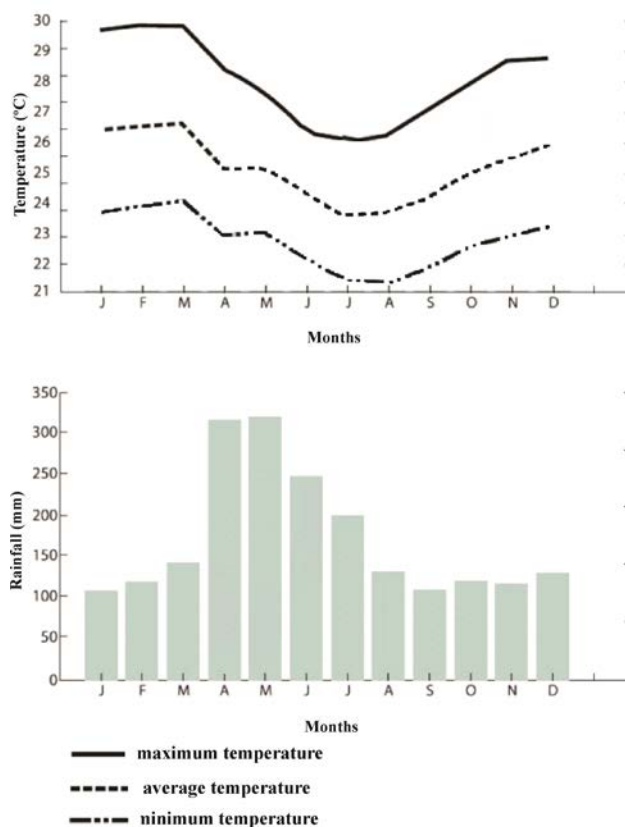


Figure 3.2 Average seasonal variation of temperature and rainfall in the study area registered by the Ondina Weather Station for the period of 1961-2009 (INMET 2015). This station, located in Salvador-Bahia, is the closest weather station of the Todos os Santos Bay.

The economic activities in this region are considered as industrial, and cases of oil spill have been reported, as well as emissions of industrial and domestic effluents from municipalities around the region (De Jesus 2011; Milazzo et al. 2014).

3.2.1 Sampling

The sampling was carried out in three periods, March 2014, January 2015 (dry season) and August 2014 (rainy season). Sampling always was done during the low tide, taking into account the tidal period, for more details see [Table S3.1 in the Supplementary Information](#).

Sediment, surface water and mollusk samples were collected from 18 points (6 in each estuary), with a spatial distance of approximately 200 m between each sampling point. This distance is sufficient to consider sampling points as true replicates, since the organisms collected for the study are sessile. The sampling points were randomly chosen across each sampling location, in order to avoid any bias in the results.

3.2.2 Water collection and preparation for analysis

Surface water samples (500 mL) were taken at a depth of 0 - 20 cm using polyethylene bottles, and kept in coolers at a temperature of approximately 4° C until arrival at the laboratory. In the laboratory, the water samples were acidified with 0.5 mL of HNO₃ (ACS ISO MERCK, 65%, for analysis), corresponding with a standard of 0.1% relative to the total volume of each sample (De Carvalho 2007). The water samples were analyzed for metals according to ASTM (1992). Physicochemical parameters (pH, Eh, temperature and salinity) were monitored at each sampling point. For pH, Eh and temperature measurements, a pH-meter/mV Handylab1 Schott Glaswerke Mainz was used. For salinity measurements, a portable refractometer Atogo S/Mill-E was used, and for dissolved oxygen determination a multiparameter water/Manta 2.

For metal analyses, the water samples were filtered over a 0.45 µm cellulose acetate membrane. After filtration, 100 mL were transferred to a beaker, and 10 mL of HNO₃ (ACS ISO MERCK, 65%, for

analysis) was added. The beakers were placed on a hot plate, until the volume was reduced to approximately 20 mL. After cooling, the fraction was diluted to 25 mL and stored in a volumetric flask for metal determination.

3.2.3 Sediment collection and preparation for analysis

For the sediments, approximately 300 g were sampled from the top 0 - 15 cm layer, and stored in polyethylene packages with a sufficient amount of water from the sampling site to preserve their characteristics. The samples were placed in coolers with ice to maintain a temperature of 4 °C, according to [Jesus et al \(2003\)](#). The cores were taken to the laboratory, and analyzed for metals, particle size distribution (classified as sand, silt and clay), and organic matter content.

To digest sediment samples, the microwave oven partial extraction technique was used, according to the D 5258-92 methodology from Standard Practice for Acid-Extraction of Elements from Sediments Using Closed Vessel Microwave Heating ([ASTM 1992](#)), adapted to the manual of the No. 11 equipment (Provecto DGT 100 plus Microwave Manual of the Institute of Geoscience of the Federal University of Bahia. The method consisted of weighing 1.0 g dry sediment samples in beakers and adding 10 mL of HNO₃ (ACS ISO MERCK, 65%, for analysis). After 30 minutes, 10 mL of H₂O ultrapure was added for digestion in a Microwave Oven. The digested samples were passed through a quantitative filter (0.80 µm), diluted to 50 mL with deionized water and stored in plastic 100 mL bottles for metal analysis.

3.2.4 Mollusk collection and preparation for analysis

The mollusks were sampled at the same sampling points as the sediment and water. A total of 16 specimen of *C. rhizophorae* were gathered at each sampling point, through active visual search. The specimens were maintained in polyethylene bags, transported and kept in coolers with ice. From each sampling point, twelve individuals were randomly selected for metal analysis. The body size of each individual was measured. Length and width were obtained based on the distance between posterior and anterior axle. The individual mollusks were weighted with the shell and the tissue. Subsequently, the tissue was removed and the shell was weighted again to obtain the weight of the tissue. Then the animal tissue was freeze-dried.

For the analysis of metals, 0.5 g of freeze-dried crushed tissue was digested in 5 mL of HNO₃ (ACS ISO MERCK, 65%, for analysis) and 3 mL of concentrated hydrogen peroxide (H₂O₂) according to the methodology adapted from the manual of equipment No. 24, Provecto DGT 100 plus Microwave Manual of the Institute of Geoscience institute of the Federal University of Bahia. The digested samples were diluted to 25 mL with deionized water and stored in 30 mL plastic flasks for metal analysis.

3.2.5 Metal analysis

Metal analysis in digests from different matrices was performed at the Laboratory of Petroleum Studies (LEPETRO), at the Center of Environment Studies (NEA) located at the Institute of Geoscience of the Federal University of Bahia (UFBA), at the Department of Ecological Science, Faculty of Earth and Life Sciences, of the Vrije Universiteit, Amsterdam and at the Chemical Biological Soil Laboratory of Wageningen University, The Netherlands. The concentrations of metals in sediment and mollusks were determined by flame atomic absorption spectrophotometry (AAS; Perkin Elmer Analyst 100) after digestion; metals in surface water were measured directly by inductively coupled plasma-mass spectrometry (ICP-MS NEXION 300D).

Quality control of the analysis was carried out using duplicates (20% of total samples) and triplicates (10% of total samples), while maintaining acceptable accuracy and precision in the analysis by the estimated experimental error, in addition to blank samples for each matrix. The certified reference materials SLEW-3 (Estuarine water; National Research Council of Canada), SEDIMENT ISE 989 (River clay Wageningen) and DOLT-4 (dogfish; LGC Standards) were used for quality control and the certified values for Zn, Fe, Ni and Cu, are shown in the [Table S3.2 in the Supplementary Information](#). One sample of reference material was measured for each batch of 9 samples for each matrix, and the metal concentrations were always within 83-122% of the certified values.

3.2.6 Data analysis

The data were analyzed using STATISTICA 7 to observe summary statistics and trends of metal behavior and physicochemical parameters. Microsoft Office Excel 2007 as well as STATISTICA 7 were used to correlate metal concentrations with physicochemical parameters. In addition, chemical speciation

of metals and some cations was estimated using Visual MINTEQ (Gustafsson 2016). Input parameters included pH, DOC (Dissolved Organic Carbon) and concentrations of Ca^{2+} , Cl^- , H^+ , K^+ , Mg^{2+} and SO_4^{2-} . Metal concentrations in the mollusks were related to metal concentrations and free metal ion activities in the water and metal concentrations in the sediment samples.

3.3 Results

The physicochemical parameters measured in surface waters and sediments from the Maragogipe, Jaguaripe and São Paulo Rivers, sampled in three different seasons, are summarized in Table 3.1.

In the surface waters, the pH increased with time for all rivers, except for the São Paulo River which had the highest pH (7.29) during the second season. The pH of the sediments showed the same increasing trend with time, however, during the last sampling season sediment pH in the Maragogipe River was lower than in the second season.

The Eh values showed a quite similar behavior for both surface waters and sediments. In the Maragogipe River, the Eh values were negative in all seasons. In the São Paulo River, Eh of surface water was negative at the first and second sampling. For the sediments the Eh values in general were negative during the first and last season and positive in the second season.

During the second sampling (rainy season), temperatures were lower than at the first and third sampling (dry season). In the sediments, the same trend was noticed for Jaguaripe and São Paulo Rivers while in the Maragogipe River temperature increased from the first to the third sampling.

Dissolved oxygen concentrations showed the same trends in Maragogipe and São Paulo rivers with the highest values recorded during the first (6.9 and 3.6 mg L^{-1}) and third (7.7 and 3.6 mg L^{-1}) season. In the Jaguaripe river the highest mean dissolved oxygen concentration was measured during the third season (9.3 mg L^{-1}), while it was similar during the first and second season (3.8 mg L^{-1}).

The conductivity of the surface water showed a different trend for the different Rivers. In the Maragogipe River conductivity was highest during the second season (44.7 ms cm^{-1}), while in the São Paulo River it was lowest (49.9 ms cm^{-1}) during the second season. In the Jaguaripe River conductivity increased from the first to the third sampling. The conductivity of the sediment of the Jaguaripe and São Paulo Rivers was also lowest during the rainy season, while it was highest for the Maragogipe River sediments (49.5 ms cm^{-1}) during the rainy season.

Salinity of the São Paulo River was highest (34.6 and 33.1 ‰) during the first and third season, respectively, while in the Maragogipe River the highest value (28.6 ‰) was recorded during the second season. In the Jaguaripe River, salinity increased from the first to the third season, from 14.3 ‰ to 23.0 ‰.

Table 3.1 Physicochemical parameters of surface waters and sediments in the Maragogipe, Jaguaripe and São Paulo rivers, Brazil, sampled in three different seasons (1st: March 2014; 2nd: August 2014; 3rd: January 2015. The values shown are mean \pm standard deviation (n = 6).

Variables	River	Mean \pm St.dev.			
		Season	1 st	2 nd	3 rd
pH (water)	Maragogipe		6.75 \pm 0.29	7.59 \pm 0.13	7.70 \pm 0.43
	Jaguaripe		5.44 \pm 0.26	6.81 \pm 0.19	7.25 \pm 0.09
	São Paulo		5.91 \pm 0.25	7.29 \pm 0.16	7.05 \pm 0.42
Eh (mV) (Water)	Maragogipe		-7.8 \pm 17.9	-30.1 \pm 8.0	-25.1 \pm 27.3
	Jaguaripe		3.8 \pm 16.7	16.0 \pm 11.8	2.6 \pm 5.9
	São Paulo		-22.8 \pm 14.9	-12.3 \pm 9.9	16.0 \pm 25.4
Temp. (°C) (Water)	Maragogipe		29.2 \pm 0.5	26.1 \pm 1.1	30.7 \pm 1.3
	Jaguaripe		28.4 \pm 0.9	24.4 \pm 0.3	27.6 \pm 0.2
	São Paulo		29.7 \pm 0.6	25.5 \pm 0.6	27.3 \pm 0.4
Salinity (water)	Maragogipe		22.3 \pm 4.1	28.6 \pm 2.1	22.0 \pm 1.4
	Jaguaripe		14.3 \pm 2.8	16.0 \pm 3.5	23.0 \pm 2.0
	São Paulo		34.6 \pm 3.8	32.1 \pm 0.9	33.1 \pm 3.6
D.O. (mg L ⁻¹) (water)	Maragogipe		6.9 \pm 1.0	5.9 \pm 1.2	7.7 \pm 0.9
	Jaguaripe		3.8 \pm 0.4	3.8 \pm 0.3	9.3 \pm 1.1
	São Paulo		3.6 \pm 0.3	3.1 \pm 0.4	3.6 \pm 1.4
Cond. (ms cm ⁻¹) (water)	Maragogipe		35.8 \pm 6.0	44.7 \pm 2.3	35.4 \pm 1.9
	Jaguaripe		24.0 \pm 4.2	26.5 \pm 5.3	36.5 \pm 2.7
	São Paulo		52.7 \pm 4.6	49.9 \pm 1.4	50.6 \pm 4.7

pH (sed)	Maragogipe	6.81 ± 0.13	7.10 ± 0.36	6.80 ± 0.18
	Jaguaripe	6.71 ± 0.37	6.99 ± 0.20	7.21 ± 0.14
	São Paulo	6.85 ± 0.21	7.06 ± 0.23	7.23 ± 0.18
Eh (mV) (sed)	Maragogipe	-5.6 ± 7.1	-5.6 ± 21.2	13.6 ± 10.5
	Jaguaripe	-4.6 ± 10.9	4.1 ± 12.5	-1.5 ± 7.4
	São Paulo	-5.0 ± 14.0	0.0 ± 13.3	-3.1 ± 10.7
Temp. (°C) (sed)	Maragogipe	27.5 ± 1.3	28.4 ± 2.6	30.7 ± 2.0
	Jaguaripe	27.6 ± 1.3	25.5 ± 0.7	29.5 ± 2.4
	São Paulo	28.6 ± 0.6	26.9 ± 1.5	28.9 ± 1.1
Cond. (ms cm ⁻¹) (sed)	Maragogipe	42.4 ± 3.7	49.5 ± 3.8	44.6 ± 3.6
	Jaguaripe	40.1 ± 3.4	31.3 ± 3.7	41.1 ± 3.9
	São Paulo	55.3 ± 2.0	51.4 ± 2.2	56.5 ± 1.8

Table 3.2 shows the particle size distribution (sand, silt, clay) and organic matter content of the sediment for each river in the three different sampling seasons. Organic matter content showed the same trend in all three rivers, being much lower in the rainy season (2nd sampling) than in the dry seasons. Overall, the Sao Paulo River sediment had the lowest organic matter content.

Table 3.2 Particle size distribution (silt, clay and sand) and organic matter contents (O.M.) (in %) of sediments in the Maragogipe, Jaguaripe and São Paulo Rivers, sampled in three different seasons: March 2014 (1st), August 2014 (2nd) and January 2015 (3rd).

Variable	River	Sediments		
	Season	1 st	2 nd	3 rd
Silt	Maragogipe	24.8	35.5	36.2
	Jaguaripe	28.2	29.0	34.0
	São Paulo	29.9	27.2	28.3
Clay	Maragogipe	26.6	41.1	47.3
	Jaguaripe	23.0	18.4	24.5
	São Paulo	17.1	29.4	30.5
Sand	Maragogipe	48.4	23.2	16.3
	Jaguaripe	48.7	52.5	41.4
	São Paulo	52.8	43.3	41.0
O.M.	Maragogipe	10.3	6.1	13.2
	Jaguaripe	10.2	8.2	12.5
	São Paulo	9.7	5.6	9.6

Particle size distribution also showed some variation between seasons and rivers. Clay content, for instance, showed the same trend in the Maragogipe and São Paulo Rivers, increasing with time from 26.6 to 47.3% in the Maragogipe River and from 17.1 to 30.5% in the São Paulo River. In the Jaguaripe River sediment clay content was highest (23.0 and 24.5%) during the first and third season and lowest (18.4%) during the second season.

Metal concentrations measured in surface water, sediment and oysters from the Maragogipe, Jaguaripe and São Paulo Rivers, sampled in three different seasons, are plotted in Figures 3.3, 3.4 and 3.5.

Cu levels showed almost the same trends in all matrices, with lower concentrations in the second season compared to the first and third one. Only exception was the Jaguaripe River, where copper concentration in the water was higher in the second season than in the first one.

The Zn levels in sediments and oysters of the Jaguaripe and São Paulo Rivers showed exactly the same trend, being higher in the first and third season. Ni concentrations showed quite different trends in time and between locations. In surface waters, the Ni concentration stayed below the detection limit for the first and second season and ranged from 0.16 to 0.27 µg L⁻¹ in the third season in the Jaguaripe and São Paulo Rivers (Figure 3.3).

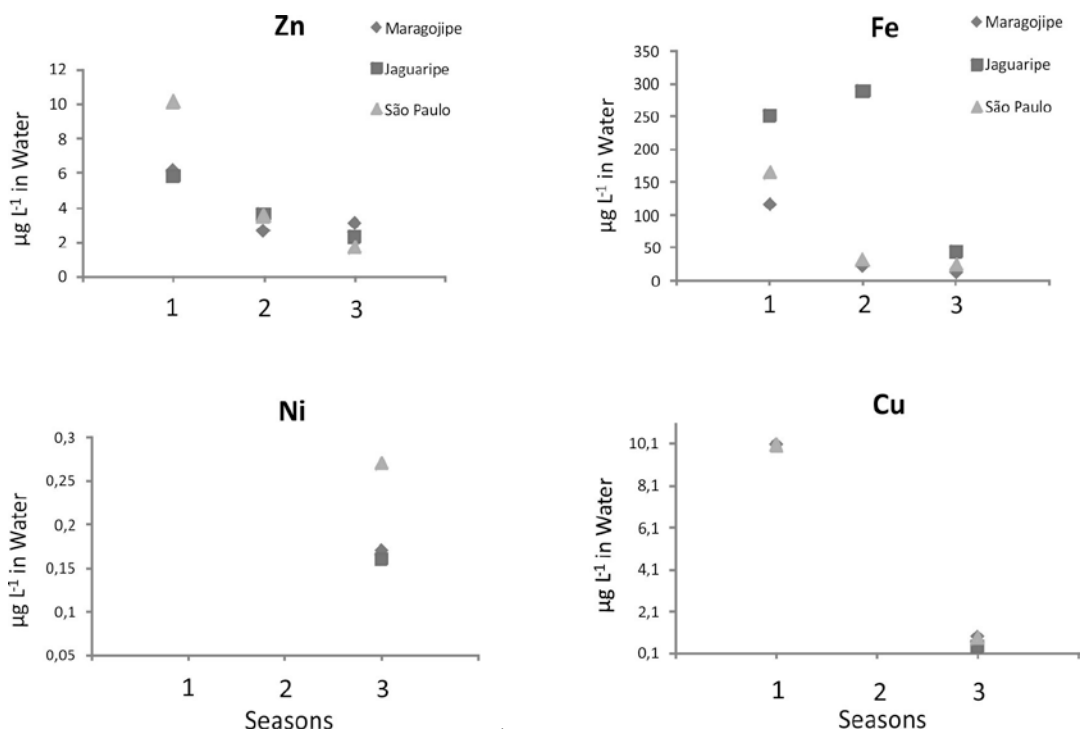


Figure 3.3 Average metal concentrations ($\mu\text{g L}^{-1}$) in surface water of the Maragojipe, Jaguaripe and São Paulo Rivers sampled in three different seasons: 1st: March 2014; 2nd: August 2014; 3rd: January 2015.

The Ni concentrations in sediments were highest in the third season with 12.1, 17.4 and 23.9 mg kg^{-1} in Jaguaripe, São Paulo and Maragojipe Rivers, respectively (Figure 3.4). In oysters, the concentrations of Ni showed quite some variation between seasons and rivers, but all ranged between 0.20 and 0.95 mg kg^{-1} dry weight (Figure 3.5).

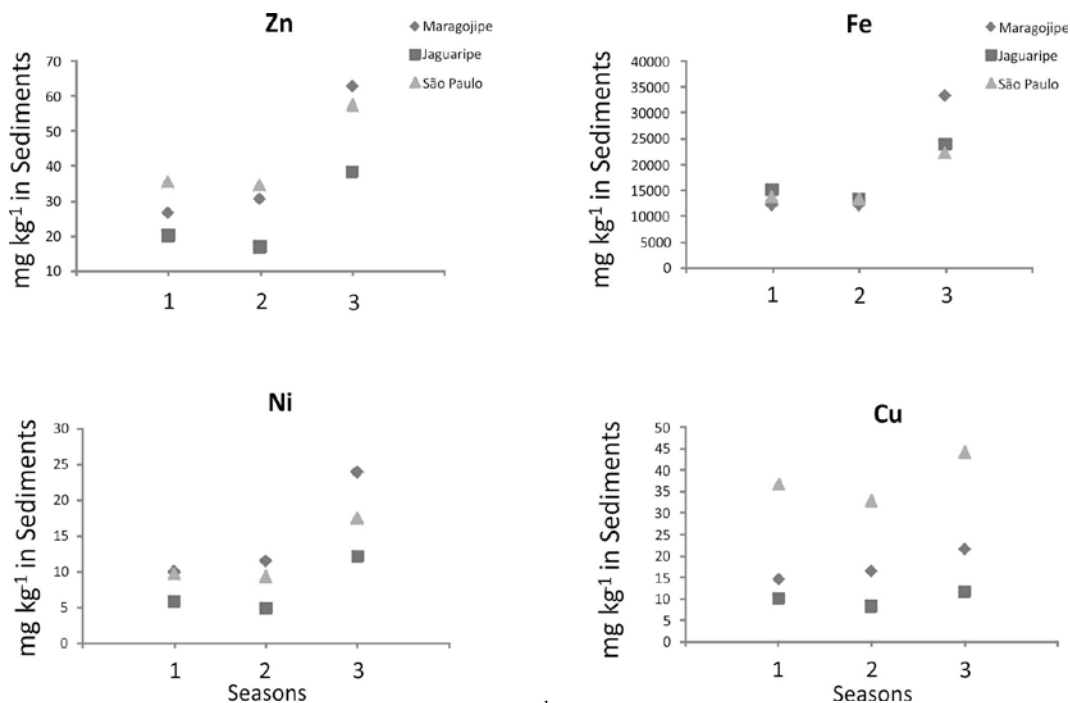


Figure 3.4 Average metal concentrations (mg kg^{-1} dry weight) in sediments from the Maragojipe, Jaguaripe and São Paulo Rivers, sampled in three different seasons: 1st: March 2014; 2nd: August 2014; 3rd: January 2015.

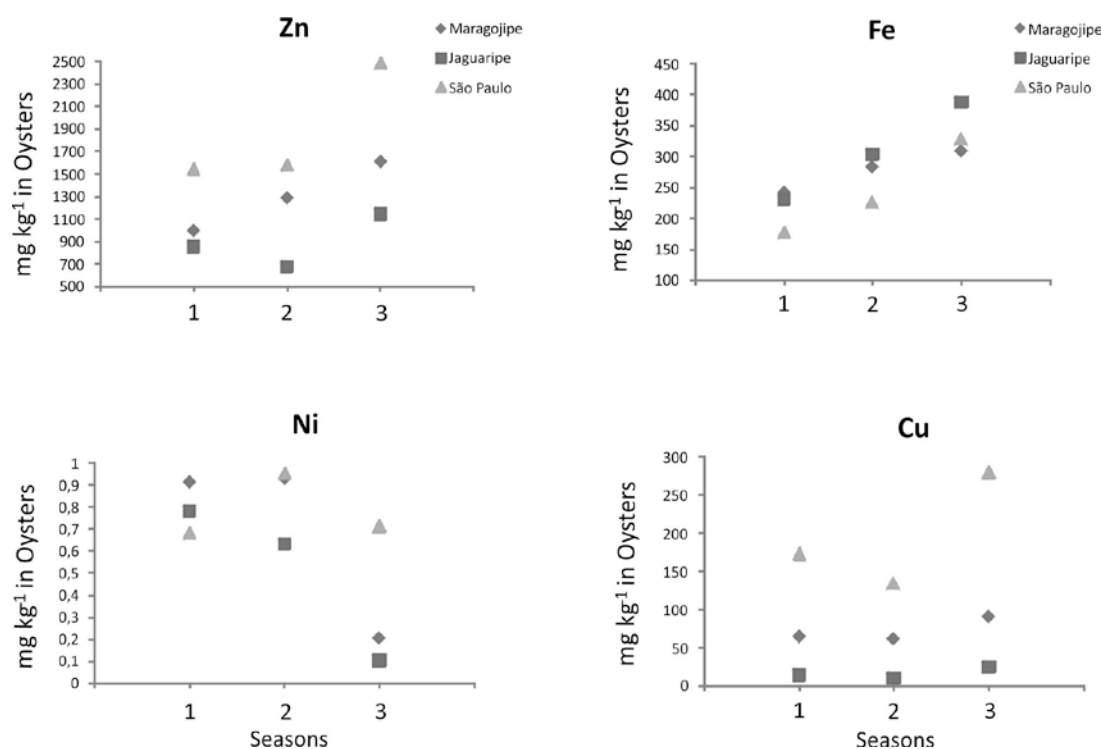


Figure 3.5 Average metal concentrations (mg kg⁻¹ dry weight) in oysters (*Crassostrea rhizophorae*) collected from the Maragogipe, Jaguaripe and São Paulo Rivers in three different seasons: 1st: March 2014; 2nd: August 2014; 3rd: January 2015.

Speciation calculations were made to check possible fluctuations in available metal concentrations in surface waters at different points in the bay. The results showed that the waters with the highest metal concentrations also had the highest free ion activities (1st season). The only exception was Zn in the São Paulo River where the highest free ion activity was found during the second season (Table S3.3 in the Supplementary Information). Metal speciation also showed some trends with the pH and ion activities of the water. The free metal ion activity generally decreased with increasing pH for all rivers studied.

3.4 Discussion

The physicochemical parameters and the metal concentrations in water, sediment and mollusks at the three sampling locations showed different spatial and temporal trends during the sampling period of this study. The temperature of water and sediment is the first to change in response to the input of water and to air temperature, which normally decreases when the rainy season starts. But many other parameters also showed different patterns during the different seasons. In some cases, these fluctuations were not expected, indicating that probably some other factors were affecting the physicochemical properties of the water and sediment of the sampling sites.

In the present study, temperature of the surface water at all locations decreased during the rainy season. In August, the land breezes, precipitation and fresh water influx together were responsible for the lower water temperatures compared with the dry season. The intensity of solar radiation and evaporation also influence surface water temperature, which, as a consequence, was higher during the dry season (1st and 3rd sampling).

The pH of the surface water varied from 5.44 to 7.70 between rivers, ranging from acid to alkaline. The highest pH values were recorded in the Maragogipe River, which might be attributed to that region receiving more effluent discharge (mainly domestic ones) which may make the water more alkaline (Dublin-Green 1990). Comparing the Jaguaripe and São Paulo Rivers, the latter one had the highest pH during the 1st and 2nd sampling (Table 3.1). This probably is explained from sea water penetration which may lead to an increase of the pH of estuarine waters (Anitha and Sugirtha 2013). With values ranging between 7.40 and 8.50 for sea waters, pH showed the influence of the ocean, which was different depending on the location and sampling time. São Paulo River is closer to the ocean which can explain the highest pH values.

The pH fluctuation of surface water generally is attributed to factors like dilution of seawater by freshwater influx leading to salinity reduction, temperature and decomposition of organic matter (Gadhia et al. 2012). The variation in water pH between seasons and locations can easily be explained by the different characteristics of each location. The studied rivers are at a different distance from the ocean and differ in the input of effluent discharge.

Metal concentrations in the surface waters can be affected by pH. Water pH will affect the solubility of metal ions in the environment and their binding to solid or dissolved phases like sediment or dissolved organic carbon (Niyogi and Wood 2004). This means that pH also may control the availability of these metals for uptake by organisms (Dixit et al. 2013).

The zinc and iron concentrations in the surface waters generally decreased with increasing pH (Figure 3.6). The concentrations of these elements decreased when the pH values increased from the 1st to the 3rd sampling. Only exceptions were Zn concentrations in the Maragogipe River at the 3rd sampling and Fe concentrations in the Jaguaripe River at the 2nd sampling.

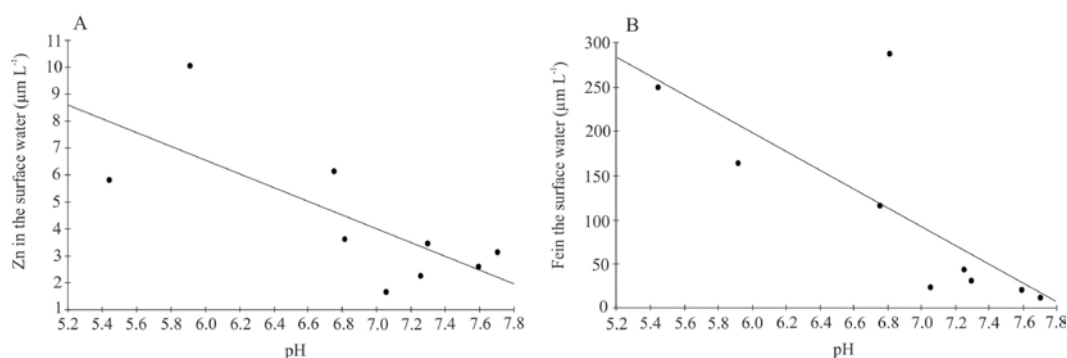


Figure 3.6 Relationship between average concentrations of Zn (A) and Fe (B) in the surface water ($\mu\text{g L}^{-1}$) and average pH of Maragogipe, Jaguaripe and São Paulo Rivers sampled in three different seasons (March 2014; August 2014; January 2015).

Eh values of the surface waters ranged from -30.1 to 16.7 mV in the different rivers and at different sampling times. Most of the time redox potential was negative, which is normal for estuarine environments and mangrove areas with their high organic matter content. In such environments, oxygen is rapidly consumed by microorganisms giving this ecosystem a reductive feature (Queiroz and Celino 2008). The variation in Eh values might be related with the tide and sampling time among the rivers. Also in the sediments redox potential mostly was negative. The variation in Eh values can be associated with the location of sampling since for each location the microbial activity may be different.

Dissolved oxygen (D.O.) levels showed the same pattern for all locations studied, being lower during the rainy season (Table 3.1). Theoretically, the D.O. level is mostly affected by the temperature and salinity of the water (Palpandi 2011). In this study, the D.O. level followed the same trend as temperature: when the temperature decreased, the D.O. level also decreased. The opposite was shown by Anita and Surgitha (2013). The salinity also affects the water's capacity to dissolve oxygen, but in an opposite manner: with increasing salinity, D.O. level will decrease (Abowei 2010). In this study, this trend was only seen in the Maragogipe River (Table 3.1).

D.O. is an important indicator of water quality as it influences many biological and chemical processes. In general, a D.O. level of 4-5 mg L^{-1} is indicative of good quality, while a D.O. lower than 2 mg L^{-1} is the lowest level for life and defined as hypoxic conditions (NOAA 2012; Sato et al. 2016). In this study, for all locations the D.O. values ranged between 3.1 and 9.3 mg L^{-1} , so it may be qualified as good according to the international guidelines. However, according to Brazilian legislation (CONAMA 2005), the D.O. values shouldn't be below 5.0 mg L^{-1} . The D.O. values for São Paulo River for all seasons and Jaguaripe River for the 1st and 2nd samplings were below the latter limit. The low D.O. levels in these locations may cause reduction of some organisms like fishes and the deoxygenation can increase the population of anaerobic microorganisms, specially bacteria. This can induce reproductive failure and death of fishes, in this way causing changes in the local environment, changing abundance and diversity of species (Abowei 2010). This situation might be triggered by the effects of nutrient pollution since there is no suitable sewage treatment in these locations.

The salinity of the surface waters showed no clear trend. This parameter is always associated with the flood and ebb tides, evaporation rates, rainfall, river discharge and dilution in the estuary (Dublin-Green 1990; Dixit et al. 2013). Theoretically, salinity should have been lower during the rainy season (2nd sampling period), when the rainfall was higher leading to a higher dilution by the higher input

of river discharge. Only in the São Paulo River salinity level followed this trend. The São Paulo River had the highest salinity (32.1-34.6 ‰) which is easily explained from its location closer to the sea compared to the other two rivers. Similar results were reported by [Milazzo et al \(2014\)](#). However, in the Jaguaripe River salinity increased from the first to the third sampling and for the Maragogipe River the opposite trend was seen, with highest salinity during the rainy season.

Because no tide information was available for the sampling sites, the present study used the Madre de Deus port tide as a reference. This is a harbor about 30, 45 and 10 km away from the sampling locations in the Maragogipe, Jaguaripe and São Paulo Rivers, respectively. It was used to estimate the time of the low tide, so to determine the appropriate time to sample the field. The use of a reference so far away from the sampling points may have caused small errors in assessing the correct time of the low and high tide of the sea. In the Maragogipe River during the second sampling period (rainy season), due to practical problems, the sampling was carried out at the middle tide, which means that there was a higher influence of the sea water. In the Jaguaripe River the sampling during the 1st season was carried out after and during a rainy day. Also events like rain (before sampling) in the dry season and/or the influence of sea water with flood and ebb tide effects during the sampling may have contributed to the different patterns of the salinity in the Maragogipe and Jaguaripe Rivers. These factors may have contributed to the deviating patterns in salinity of the water.

The conductivity of the surface water showed opposite trends in the Maragogipe (with the highest value during the rainy season) and São Paulo Rivers (lowest value in the rainy season), while in the Jaguaripe River it increased from the first to the third sampling period. The conductivity is directly related to the concentration of ions in the water and it can be a good indicator of the presence of some contaminants ([Nazir et al. 2015](#)). However, the metal concentrations showed quite different patterns compared with the conductivity, which confirms that many others parameters influenced the metal concentrations in the surface waters.

The highest conductivity in the São Paulo River compared with the other rivers confirms its location closer to the sea ([Cox et al. 1967](#); [Mantyla 1980](#)). As expected, the conductivity showed the same patterns as the salinity ([Table 3.1](#)).

The metal concentrations in the surface waters did not show a clear pattern. For Zn, for example, there were two trends. The Maragogipe River had the highest concentrations (6.1 and 3.1 $\mu\text{g L}^{-1}$) during 1st and 3rd season, respectively, while in the Jaguaripe and São Paulo Rivers, Zn concentrations decreased from the 1st (5.8 and 10.1 $\mu\text{g L}^{-1}$) to the 3rd (2.3 and 1.6 $\mu\text{g L}^{-1}$) season. Related to the Brazilian legislation ([CONAMA 2005](#)), these concentrations are well below the maximum limit of 90 $\mu\text{g L}^{-1}$ for brackish (Maragogipe and Jaguaripe Rivers) and saline (São Paulo River) waters ([Table S3.4 in the Supplementary Information](#)).

Also for the iron concentrations in the water two different trends were observed. In the Jaguaripe River, Fe concentration increased from 250 $\mu\text{g L}^{-1}$ to 288 $\mu\text{g L}^{-1}$ in the 1st and 2nd season, respectively and decreased to 44 $\mu\text{g L}^{-1}$ in the 3rd season. In the Maragogipe and São Paulo Rivers the concentrations of iron decreased from 116 and 165 $\mu\text{g L}^{-1}$ in the 1st season to 12 and 23 $\mu\text{g L}^{-1}$ in the 3rd season, respectively. For all rivers, Fe concentrations were below the maximum limit (300 $\mu\text{g L}^{-1}$) established by [CONAMA \(2005\)](#) for both brackish and saline waters ([Table S3.4 in the Supplementary Information](#)). For the other metals analyzed, Ni and Cu, no real pattern was observed because most concentrations were below the detection limits.

Even though metal concentrations were below the levels established by the Brazilian legislation, it is known from the literature that the total metal content is not a reliable indicator of risk. A better indicator of the bioavailability and possible environmental risk of metals is the free ion activity ([Temminghoff et al. 2000](#)). In this study, the free ion activities were higher when the metal concentrations were also higher, except for Zn in the São Paulo River ([Table S3](#)). The metal free ion activities showed a negative relation with pH for all rivers studied ([Table S3.3](#)). An increase in pH may increase the sorption of the metals, reducing free ion activity in the water column ([Lee and Saunders 2003](#)), and in this way also reducing metal availability for uptake by organisms. Along the seasons studied, the availability of Zn and Fe generally decreased when the pH increased. But metal uptake by biota also depends on the nature of the organism and its metabolism, size, mass, etc. In addition, organisms like mollusks may not only interact with metals in the water but may also be exposed to metals in the sediment.

For all metals studied in the sediment (Zn, Fe, Ni and Cu) the trend was the same for Jaguaripe and São Paulo Rivers with the lowest values being recorded during the 2nd sampling period (rainy season). The same pattern was noticed for organic matter content, which also showed the lowest values during the rainy season. These results might be connected since organic matter has a high affinity for binding metals ([Lin and Chen 1998](#); [Marchand et al. 2011](#)).

The metal concentrations in the sediment also strongly correlated with clay content ([Figure 3.7](#)), which can be explained from the surface chemical properties that favour binding of cations ([Finzgar et al.](#)

2007). This was obvious for the Maragogipe River, where metal concentrations and clay contents increased from the 1st to the 3rd sampling, the only exception was the iron concentration, which was slightly lower in the 2nd sampling compared with the 1st one and increased in the 3rd season.

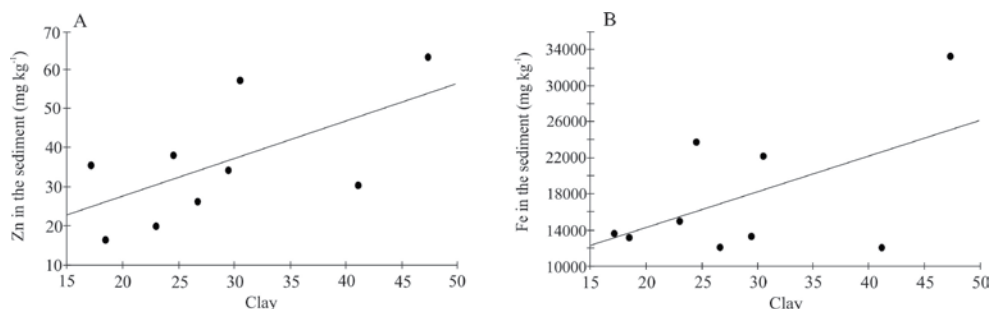


Figure 3.7 Relationship between Zn (A) and Fe (B) concentrations in the sediment (mg kg^{-1}) and clay content of the Maragogipe, Jaguaripe and São Paulo Rivers sampled in three different seasons (March 2014; August 2014; January 2015).

The metal concentrations in the studied sediments were negatively correlated with pH (for more details see Figure S3.1 in the Supplementary Information). In all cases the metal concentrations in the sediment decreased when pH increased from 6.71 to 7.06, which represent two of the three sampling times. Metal concentrations in the sediment, however, increased when pH increased from 7.10 to 7.23, except for Fe in the Maragogipe River. In general, pH is an important parameter to explain ion binding processes in soils and sediments (Niyogi and Wood 2004). At decreasing pH, the higher competition of protons may cause a reduced metal binding to sediments. This explains the first finding. The second finding, however, indicates that one parameter (pH) by itself cannot fully explain the total metal concentrations in sediments. Rather a set of parameters will be involved.

The sediment metal concentrations were compared with the limit values established by CONAMA (2009) (Table S3.4 in the Supplementary Information). This legislation doesn't bring limits for iron, as it is an element which by nature is highly abundant in soils and sediments. For the other metals studied (Zn, Ni and Cu), the values found were below the limits established as prevention values, 300 mg kg^{-1} for Zn, 30 mg kg^{-1} for Ni and 60 mg kg^{-1} for Cu. The total concentration however, is not the best indicator of the risk of metals to the environment (Shivakumar et al. 2012). Even though the total metal concentrations were below the limits established by Brazilian legislation, a study on their bioavailability should be done to check the actual exposure risk.

Internal metal concentrations, which reflect the actual exposure of organisms in a specific area, allow for a more trustful assessment of the actual risks to the environment than do reference values or effect levels reported in the literature. In this study, metal concentrations in oysters (*C. rhizophorae*) fluctuated in time, with a seasonal pattern being observed for Cu, while for Fe tissue concentrations increased with time. The variation in metal concentrations in the oysters was larger than the fluctuations observed in sediment and surface water concentrations at the same sampling sites.

Iron concentrations in *C. rhizophorae* were higher during the 3rd season for all rivers and quite high in comparison with other studies in the São Paulo River, which reported a concentration of 272 mg kg^{-1} (Milazzo et al. 2014). The copper concentrations showed the same pattern for all rivers, with the highest values (63.9 and 89.6 mg kg^{-1} in the Maragogipe River, 14.0 and 23.8 mg kg^{-1} in the Jaguaripe River and 172 and 279 mg kg^{-1} in the São Paulo River) during the 1st and 3rd season, respectively. For the Ni and Zn no defined pattern was observed, but in some cases we could identify some trends. Nickel concentrations in oysters from the Maragogipe and São Paulo Rivers were higher during the 2nd season (0.98 and 1.0 mg kg^{-1} , respectively), whereas in the Jaguaripe River the concentrations decreased from the 1st (0.8 mg kg^{-1}) to the 3rd (0.09 mg kg^{-1}) season. Zinc concentrations in *C. rhizophorae* didn't show a clear pattern. In the Maragogipe River the levels increased from the 1st to the 3rd season (ranging from 996 to 1603 mg kg^{-1}), in the Jaguaripe River the values were higher during the 1st and 3rd season (849 and 1140 mg kg^{-1} , respectively), and in the São Paulo River the highest value was found in the 3rd season (2478 mg kg^{-1}) (Figure 3.5). Zinc, being an essential element, can be regulated to fairly constant concentrations by organisms as long as sediment concentrations are below the toxic limit (Chu et al. 1990; Van Gestel et al. 2009).

In Brazil, there is no legislation with guidelines or maximum limits for metal concentration in mollusks. For this reason, a comparison was made with the Certified Reference Materials developed by the National Institute of Standards and Technology (NIST), USA (Table S3.4 in the Supplementary Information). The Ni concentrations in oysters were below the limits, in all rivers during all seasons. For

copper the levels were above the limits in the São Paulo River during all seasons and in the 3rd season in the Maragogipe River. Zn concentration was below the limits in the Jaguaripe (all seasons) and Maragogipe (1st and 2nd seasons) Rivers, and for Fe only the concentrations in the São Paulo River during the 1st season were below the limit.

Although in some cases the metal concentrations in oysters were above the limits, it is important to note that these elements are essential for organisms, with important functions in metabolism. This means that the levels found not necessarily are dangerous.

Speciation calculation can help to understand the possible risks of metals to organisms in the environment. In the present study, a competition effect of H⁺ in surface waters and the Zn and Fe uptake in *C. rhizophorae* was found. The metal concentrations in the oysters significantly decreased when the free ion activity in the water increased (Figure S3.2 in the Supplementary Information). This indicated that H⁺ activity in the surface waters inhibited the uptake of Zn and Fe by *C. rhizophorae*. This is in agreement with the hypothesis that metal ions and other cations compete for binding on the biotic ligands on biological surfaces (He et al. 2014).

Probably other cations should have different effects on metal uptake by the oysters since different metal ions generally have different paths to enter organisms by, for example, employing ion channels or carriers involved in the uptake of different cations (Bridges and Zalups 2005). In this way, effects of cations like Ca²⁺, Mg²⁺, and K⁺ may also affect metal uptake. In addition, there also may have been uptake of metals from sediment by the oysters, further complicating the situation. The mechanisms of the interaction of different cations and the contribution of water and sediment to metal bioaccumulation in oysters should be studied further.

3.5 Conclusion

The physicochemical parameters and the metal concentrations of surface waters, sediments and the internal metal concentrations in the oyster *C. rhizophorae* along the Todos os Santos bay exhibited spatial and temporal variations. These variations were related with the different characteristics of each sampling location as well as the meteorological conditions, which change the input of rain and the penetration of seawater into the rivers. In the Maragogipe River domestic sewage may have contributed to the high water pH, indicating that not only natural but also anthropogenic factors are responsible for the conditions of the estuarine zones.

Metal concentrations in the sediment and water of the sampling sites along the Todos os Santos bay generally were below limits established by the Brazilian regulations. Concentrations in the oysters however, did exceed the limits in a few cases but this does not mean that levels found are dangerous as some elements are essential to the organisms. Further research is needed to obtain more detailed information on metal speciation in these estuarine environments and to investigate their actual risk to organisms. This may support a proper risk assessment of metal pollution in the Todos os Santos Bay.

Supplementary Information

Table S3.1. Location, dates, time and tide height (m) of the samplings of the three locations in the Todos os Santos Bay, Bahia, Brazil, using Madre de Deus Port tide as a reference.

Location	Date			Hour			Tide height (m)		
	1 st (2014)	2 nd (2014)	3 rd (2015)	1 st (2014)	2 nd (2014)	3 rd (2015)	1 st (2014)	2 nd (2014)	3 rd (2015)
Maragogipe River	18/03	26/08	07/01	10:51 a.m.	10:02 a.m.	11:09 a.m.	0.2	0.2	0.4
Jaguaripe River	20/03	27/08	08/01	10:51 a.m.	10:54 a.m.	11:47 a.m.	0.3	0.3	0.5
São Paulo River	21/03	29/08	09/01	12:19 a.m.	11:49 a.m.	12:13 p.m.	0.4	0.4	0.6

Table S3.2. Metal concentrations reported for certified reference materials (average (\pm SD)) and values found upon quality control (min., max., average (\pm SD); n=2)) in this study for Water (SLEW-3), Sediment (ISE 989) and biota (DOLT-4).

	SLEW-3* ($\mu\text{g L}^{-1}$)	Sediment ISE 989** (mg kg^{-1})	DOLT-4*** (mg kg^{-1})	Water	Sediment	Oysters	Recovery (%) of elements from reference material		
				values found ($\mu\text{g L}^{-1}$)	values found (mg kg^{-1})	values found (mg kg^{-1})	Water	Sediment	DOLT
Zn	0.20 (± 0.03)	1060 (± 43)	116 (± 6)	0.21 0.23 0.22 (± 0.01)	1052 1072 1062 (± 13.6)	138 147 142,5 (± 7)	110	100	122
Fe	0.56 (± 0.05)	40100 (± 1180)	1833 (± 75)	0.55 0.59 0.57 (± 0.02)	33498 35345 34421,5 (± 1305)	1505 1522 1513,5 (± 12.6)	109	83	83
Ni	1.23 (± 0.07)	62.2 (± 3.2)	0.97 (± 0.11)	1.19 1.20 1.19 (± 0.01)	56.3 59.2 57.7 (± 2.08)	0.99 0.99 0.99 (± 0.00)	97	92	83
Cu	1.55 (± 0.12)	157 (± 5.2)	31.2 (± 1.1)	1.57 1.60 1.58 (± 0.02)	144 145 144,5 (± 0.32)	37.6 39.0 38.3 (± 0.97)	101	92	122

* Estuarine Water; National Research Council of Canada

** River Clay Wageningen

*** Dogfish liver; LGC Standards

Table S3.3. Results of the metal speciation analysis in the surface waters. Data shows the pH values and free ion activities of Cu^{2+} , Fe^{2+} and Zn^{2+} (mol L^{-1}) in the Maragogipe, Jaguaripe and São Paulo Rivers in three different seasons (1st: March 2014; 2nd: August 2014; 3rd: January 2015).

Rivers	Season	pH	Ions		
			Cu^{2+}	Fe^{2+}	Zn^{2+}
Maragogipe	1 st	6.75 ± 0.29	$2,83 \times 10^{-10}$	$4,63 \times 10^{-7}$	$2,00 \times 10^{-8}$
	2 nd	7.59 ± 0.13	$3,67 \times 10^{-11}$	$2,30 \times 10^{-8}$	$7,75 \times 10^{-9}$
	3 rd	7.70 ± 0.43	$1,91 \times 10^{-12}$	$1,89 \times 10^{-9}$	$9,15 \times 10^{-9}$
Jaguaripe	1 st	5.44 ± 0.26	$4,91 \times 10^{-11}$	$1,38 \times 10^{-6}$	$2,46 \times 10^{-8}$
	2 nd	6.81 ± 0.19	$7,90 \times 10^{-12}$	$1,87 \times 10^{-6}$	$1,97 \times 10^{-8}$
	3 rd	7.25 ± 0.09	$2,67 \times 10^{-12}$	$1,13 \times 10^{-7}$	$7,32 \times 10^{-9}$
São Paulo	1 st	5.91 ± 0.25	$1,16 \times 10^{-9}$	$6,56 \times 10^{-7}$	$2,48 \times 10^{-8}$
	2 nd	7.29 ± 0.16	$1,13 \times 10^{-12}$	$6,97 \times 10^{-8}$	$3,98 \times 10^{-8}$
	3 rd	7.05 ± 0.42	$1,94 \times 10^{-11}$	$3,34 \times 10^{-8}$	$4,31 \times 10^{-9}$

Table S3.4. Maximum acceptable metal concentrations in surface water ($\mu\text{g L}^{-1}$), sediment (mg kg^{-1}) and mollusks (mg kg^{-1}) established by national and international institutions.

Institutions		Metals/Values			
		Zn	Fe	Ni	Cu
CONAMA (2005)	Water	90	300	25	5
CONAMA (2009)	Sediment	300	**	30	60
NIST	mollusks	1424 ± 46	205 ± 6.8	1.04 ± 0.09	71.6 ± 1.6

CONAMA: Brazilian National Environment Council.

NIST: National Institute of Standards and Technology, USA.

** No value available.

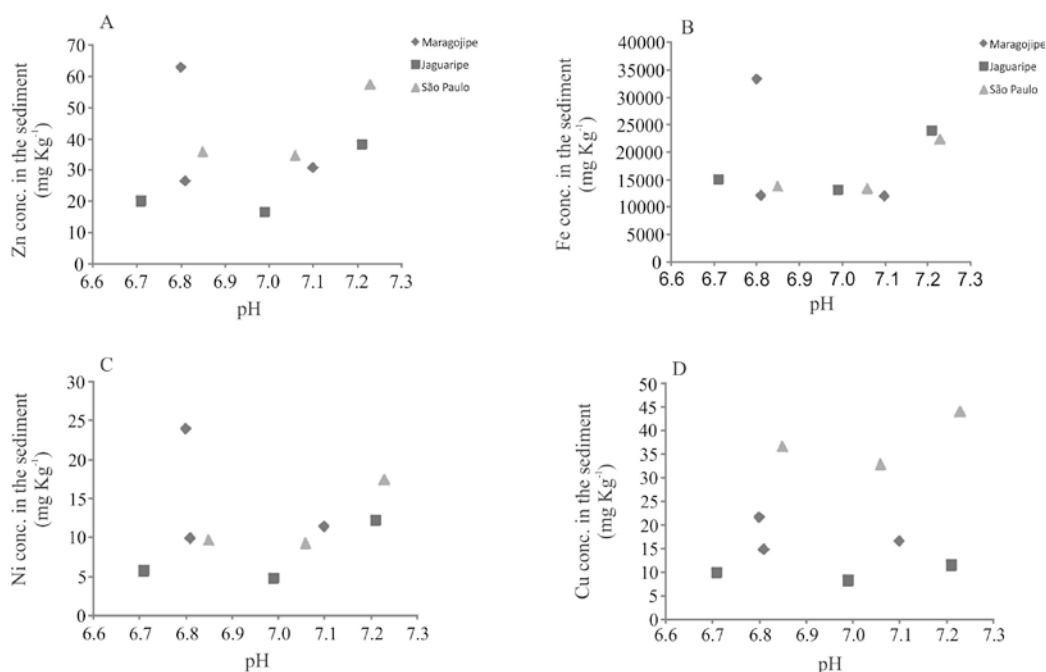


Figure S3.1: Relationship between average concentrations of Zn (A), Fe (B), Ni (C) and Cu (D) in the sediment (mg kg^{-1}) and average pH of Maragogipe, Jaguaripe and São Paulo Rivers sampled in three different seasons (March 2014; August 2014; January 2015).

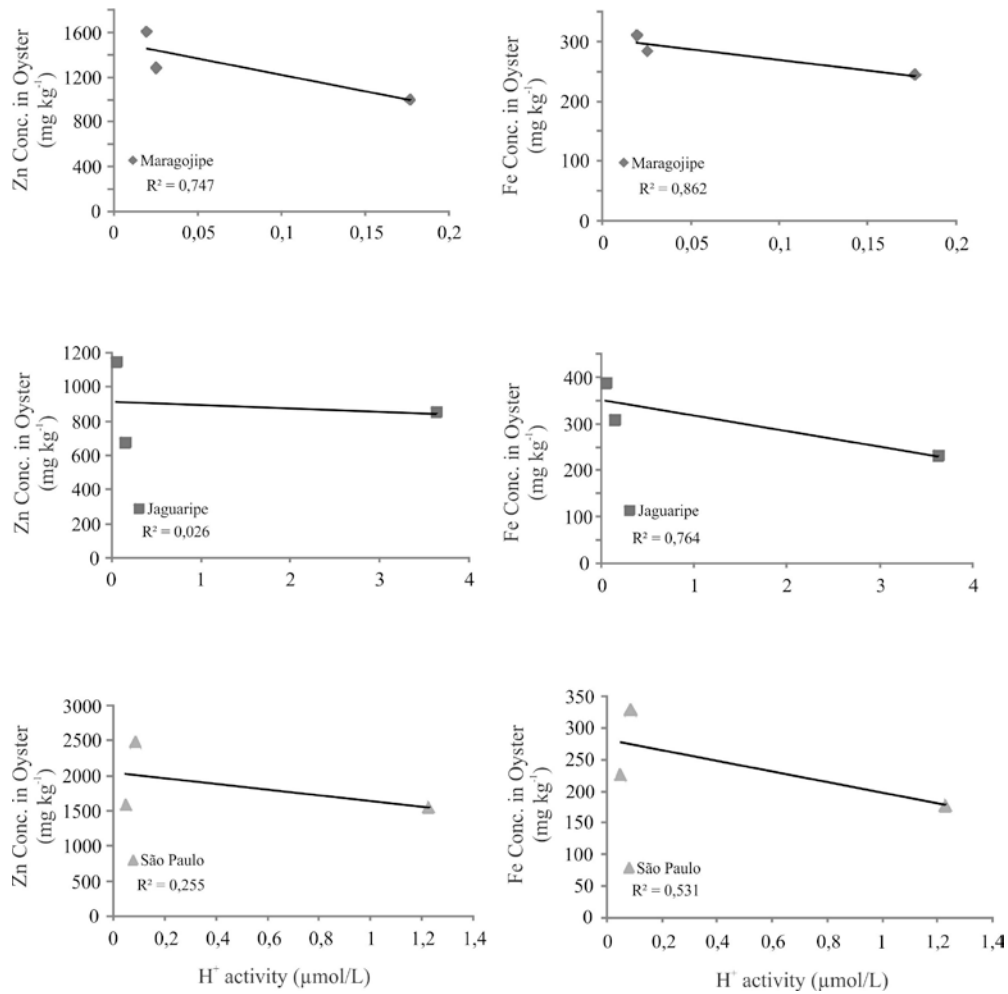


Figure S3.2. The relationship between average Zn and Fe body concentrations in *Crassostrea rhizophorae* (mg kg⁻¹) and the free H⁺ ion activity (μmol L⁻¹) in surface waters from the Maragojipe, Jaguaripe and São Paulo Rivers in three different seasons (March 2014; August 2014; January 2015).

CAPÍTULO 4 - SPATIAL VARIATION AND RIVER'S COURSE EFFECTS ON THE METAL CONCENTRATIONS IN THE SURFACE WATERS AND OYSTER IN ESTUARINE ZONES

Abstract

Estuarine spatial dynamics and its effect on the metal concentration in the surface waters and oysters can bring important results to try to understand the geochemical behavior in this kind of environment. The spatial dynamic and river's course plays an important, and not so well described, role for the physicochemical parameters which has influence over the metal concentration in different matrices. Samples of different points into the same river were taken from three completely different locations along the Todos os Santos Bay, North East Brazil, to investigate how the spatial variation affect the results of metal concentration in the surface waters and mangrove oysters (*Cassostrea rhizophorae* (Guildin, 1828)). All physicochemical parameters analyzed had different behavior between the three sampling rivers and different values along the same river as well. The pH was one of the parameters which showed gradient patterns from the sampling point closest to the sea to the one farther. The metal concentrations in the surface water were negatively related to the pH results. The internal metal concentration in oysters were related in different ways to the free ion activities for all rivers studied. The results suggest that the spatial variation and the river's course affect metal concentration in different ways between places along the same bay.

Keywords: spatial variation; river's course; physicochemical parameters; metal concentrations.

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4.1. Introduction

Metals as a result of both natural and anthropogenic process are present in the terrestrial and aquatic environments. Its concentration and dynamics in the aquatic environments has becoming as an important tool for development of bioavailability predictions and reliable risk assessment strategies (Van Leeuwen et al., 2005). As a transition between marine and freshwater environments, estuarine zones and its mangrove ecosystems are important components of the ocean-land aquatic continuum (Regnier et al., 2013), which make them very special, once due their natural conditions but also because the large diversity of characteristics, which can bring totally different geochemistry between close zones (Nizoli and Luiz-Silva, 2009; Strady et al., 2011).

The terrestrial and oceanic inputs in estuarine zones are modified by biogeochemical processes which are modulated by many mechanisms, such as wind, water temperature, waves, tides or freshwater discharge (Regnier et al., 2013). Many different factors like pH, redox conditions, salinity, organic matter are played by those mechanisms and may influence water quality (Anitha and Sugirtha, 2013) which can brings important impacts on metal concentration and availability (Nizoli and Luiz-Silva, 2009).

The Todos os Santos Bay, in Salvador, located in the Rencôncavo Baiano region, North East of Brazil, is a unique area that has many ecosystems with a large fauna and flora biodiversity. The Bay also is used for industrial activities, which on one hand brings economic value for society, but on the other hand has led to possible exposure with metals and deterioration of the environment. This Bay is unique because it consists of a range of different habitats with different characteristics. This spatial variation in characteristics, may however, also lead to large differences in metal availability and consequent metal risks (Queiroz and Celino, 2008). It therefore is essential to evaluate metal concentrations in water and biota and combine this with knowledge about the geochemistry of the system to assess the quality of the mangrove areas in the bay (Cundy et al., 2005).

The aim of this study is determining the spatial exposure to metals of three different mangrove areas in the Todos os Santos Bay. This involved analyzing metal concentrations in surface water. Metal bioavailability was estimated by measuring concentrations in soft tissues of the oyster *Crassostrea rhizophorae* (Guildin, 1828), popularly known as mangrove oyster. This species is widely distributed along the entire Todos os Santos Bay. It is a sessile filter-feeder of reasonable size and sedentary, which can easily be sampled. Water and oysters were sampled during a dry season of the year. All samples were analyzed for Zn, Fe, Ni and Cu concentrations. By analyzing also physicochemical parameters in water, speciation calculations could be made to estimate possible fluctuations in available metal concentrations at different points in the bay.

4.2. Materials and methods

This study was carried out in the Todos os Santos Bay (32° 02' 30" - 38° 37' 30"W and 13° 07' 30" - 12° 37' 30"S) in Brazil, in three different estuarine zones near the (A) Maragogipe, (B) Jaguaripe and (C) São Paulo Rivers (Figure 4.1). The Todos os Santos Bay is the biggest and most important navigable bay of the Brazilian coast, with a surface area of about 1.200 km² and a coast length of 462 km.

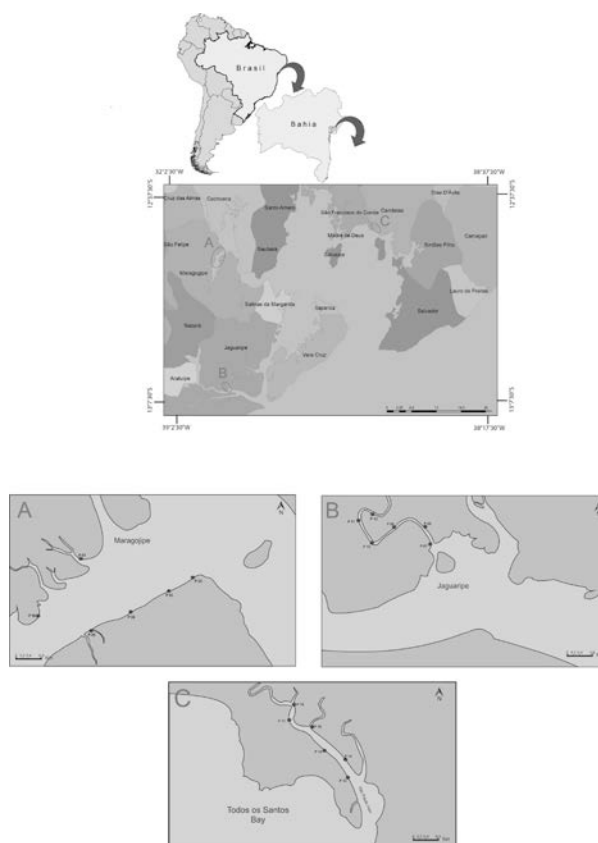


Figure 4.1 Location of the sampling sites used for this study. Insert shows a map of the Bahia region in Brazil with the Todos os Santos Bay. The detailed overview of the Todos os Santos Bay area shows the sampling sites near the Maragogipe (A), Jaguaripe (B) and São Paulo (C) Rivers.

These estuarine zones, near the Maragogipe, Jaguaripe and São Paulo Rivers, where a magnificent mangrove system develops, have a fundamental importance to the local food chain and also to the livelihood of many of the inhabitants of the region. Even though they belong to the same Bay, the spatial variation makes with these areas having different characteristics. These estuarine ecosystems have been affected by many human activities, such as contamination by chemical industries, which have contributed to their deterioration (De Carvalho, 2007).

Geologically, the Todos os Santos Bay is included in the sedimentary basin of the Reconcavo Baiano. The economic activities in this region are considered as industrial, and cases of oil spill has been reported, as well as emissions of industrial and domestic effluents from municipalities around the region (De Jesus, 2011; Milazzo et al., 2014).

4.2.1. Sampling

The field work was carried out in three different estuarine zones of the Todos os Santos Bay during January 2015 (dry season). Sampling always was done during the low tide, taking into account the tidal period (Table 4.1).

Table 4.1 Location, date, time and tide height (m) of the samplings of the three locations in the Todos os Santos Bay, Bahia, Brazil, using as reference Madre de Deus Port tide.

Location	Date	Hour	Tide height (m)
	January (2015)	January (2015)	January (2015)
Maragogipe River	07/01	11:09 a.m.	0.4
Jaguaripe River	08/01	11:47 a.m.	0.5
São Paulo River	09/01	12:13 p.m.	0.6

Surface water and mollusk samples were collected from 18 points (6 in each estuary), with a spatial distance of approximately 200 m between each sampling point. This distance is sufficient to consider sampling points as true replicates, since the organisms collected for the study are sessile. The sampling points were randomly chosen across each sampling location, in order to avoid any bias in the results.

4.2.2. Water collection and preparation for analysis

Surface water samples (500 mL) were taken at a depth of 0 - 20 cm using polyethylene bottles, and kept in coolers at a temperature of approximately 4° C until arrival at the laboratory. Physicochemical parameters (pH, Eh, temperature and salinity) were monitored *in situ* at each sampling point. For pH, Eh and temperature measurements, a pH-meter/mV Handylab1 Schott Glaswerke Mainz was used. For salinity measurements, a portable refractometer Atogo S/Mill-E was used, and for dissolved oxygen determination a multiparameter water/Manta 2. In the laboratory, 100 mL of the water samples for the metals analyses were filtered through 0.45 µm cellulose acetate membrane and acidified with 0.5 mL of HNO₃ (ACS ISO MERCK, 65%, for analysis).

4.2.3. Mollusks collection and preparation for analysis

The mollusks were sampled at the same sampling points as the sediment and water. A total of 16 specimens of *C. rhizophorae* were gathered at each sampling point, through active visual search. The specimens were maintained in polyethylene bags, transported and kept in coolers with ice. Twelve individuals of each sampling point were randomly selected for metal analysis. The body size of each individual was measured and weighed. Length and width were obtained based on the distance between posterior and anterior axle. The individual mollusks were weighted with the shell and the tissue. Subsequently, the tissue was removed and the shell was weighted again to obtain the weight of the tissue. Then the animal tissue was freeze-dried.

For the analysis of metals, 100 mg of dried sample was digested in a 4:1 destruction mixture of concentrated HNO₃ (Mallbaker Ultrex Ultra Pure, 65%) and HCl (Mallbaker Ultrex Ultra Pure, 37%). The mixed solution was placed in the destruction oven (Binder) at 140 °C for 7 hrs of destruction time.

4.2.4. Metal analysis

Metal analysis in digests from different matrices was performed at the Department of Ecological Science, Faculty of Earth and Life Sciences, of the Vrije Universiteit, Amsterdam and at the Chemical Biological Laboratory Soil, of the Wageningen University, Netherlands. The concentrations of metals in mollusk were determined by flame atomic absorption spectrophotometry (AAS; Perkin Elmer Analyst 100) after digestion procedures and metals on surface water were measured directly by inductively coupled plasma-mass spectrometry (ICP-MS NEXION 300D).

Quality control of the analysis was carried out using duplicates (20% of total samples) and triplicates (10% of total samples), while maintaining acceptable accuracy and precision in the analysis by the estimated experimental error, in addition to blank samples for each matrix. The certified reference materials SLEW-3 (Estuarine water; National Research Council of Canada) and DOLT-4 (dogfish; LGC Standards) were used for quality control and the certified values for Zn, Fe, Ni and Cu, are shown in the Table 4.2. One sample of reference material was measured for each batch of 9 samples for each matrix, and the metal concentrations were always within 83-122% of the certified values.

Table 4.2 Certified reference materials reported (average (\pm SD)) and values found as quality control (min.. max.. average (\pm SD)) in this study for Water (SLEW-3) and biota (DOLT-4).

	SLEW-3* ($\mu\text{g L}^{-1}$)	DOLT-4** (mg kg^{-1})	Water values found ($\mu\text{g L}^{-1}$)	Oysters values found (mg kg^{-1})	Recovery (%) of elements from reference material	
					Water	DOLT
Zn	0.20 (± 0.03)	116 (± 6)	0.21 0.23 0.22 (± 0.01)	138 147 142 (± 7)	110	122
Fe	0.56 (± 0.05)	1833 (± 75)	0.55 0.59 0.57 (± 0.02)	1505 1522 1513 (± 12.6)	109	83
Ni	1.23 (± 0.07)	0.97 (± 0.11)	1.19 1.20 1.19 (± 0.01)	0.99 0.99 0.99 (± 0.00)	97	83
Cu	1.55 (± 0.12)	31.2 (± 1.1)	1.57 1.60 1.58 (± 0.02)	37.6 39.0 38.0 (± 0.97)	101	122

* Estuarine Water; National Research Council of Canada

** Dogfish liver; LGC Standards

4.2.5. Data analysis

The data were analyzed using STATISTICA 7 to observe summary statistics and trends of metal behavior and physicochemical parameters. Microsoft Office Excel 2007 as well as the STATISTICA 7 were used to correlate metal concentrations with physicochemical parameters. In addition, chemical speciation of metals and some ions and cations was estimated using Visual MINTEQ. The measured pH values, DOC (Dissolved Organic Carbon) and concentrations of Ca^{2+} , Cl^- , H^+ , K^+ and Mg^{2+} were used as a input parameters. Metal concentrations in the mollusks were related to metal concentrations and free metal ion activities in the water samples.

4.3. Results

The physicochemical parameters measured in surface waters from the Maragogipe, Jaguaripe and São Paulo Rivers are summarized in Table 4.3. Taking a general overview, it's possible notice that the values ranged between rivers.

If we have a look in the river's course and compare the results, we can see that the values had a different behavior. For Jaguaripe and São Paulo rivers, where the sampling following a path going into the river from one place closer to the sea to another one farther, some parameters followed a significant patterns, decreasing or increasing, from the sampling point closer the ocean to the point more far. In the Maragogipe river, where there isn't a path and the sampling points are spread along the river, without any kind of direction, was observed a fluctuation for the values found.

In the surface waters, the pH had different pattern between Maragogipe and São Paulo rivers. While in the São Paulo river the values decreased from the first (7.61) to the last (6.80) sampled point, in the Maragogipe river the values decreased and increased more than one time from the first to the last sampled point. This result shows a fluctuation behavior for the pH values in the Maragogipe river.

This situation happened for many parameters analyzed as well. The salinity for example, the same behavior was found comparing the Maragogipe to Jaguaripe and São Paulo Rivers. In the Jaguaripe and São Paulo Rivers, the values decreased from the first (26 and 36 ‰) to the last (20 and 34 ‰) sampled points respectively, from closer to the sea to more faraway, whereas the values in the Maragogipe river increased from the 1st (20 ‰) to the 4th (24 ‰) sampling point and decreased to the 6th (22‰) sampling points, showing a fluctuation behavior.

Dissolved oxygen concentrations showed the same trends comparing Maragogipe to Jaguaripe rivers. In the Maragogipe river the values showed an oscillation from the first to the last sampled point,

increasing and decreasing more than one time. Whereas in the Jaguaripe river even though have happened one simple oscillation, the values decreased from the 1st (11.14 mg L⁻¹) to last (8.84 mg L⁻¹) sampling.

The conductivity showed different trends, but there were oscillation for all rivers. In the Maragogipe river conductivity increased from the first to the fourth sampling and decreased from the fourth to the last sampling. In the São Paulo river the values decreased from the first to the fourth sampling and back to increase till the last sampling, but with the last value (51.6 ms cm⁻¹) lower than the first (54.3 ms cm⁻¹). Whereas for the Jaguaripe river a different pattern on the oscillation was noticed, decreasing from the 1st (40.6 ms cm⁻¹) to the 3rd (27.9 ms cm⁻¹) sampling, increasing in the 4th (36.0 ms cm⁻¹) and returning to decrease till the 6th (32.4 ms cm⁻¹) sampling, but the concentration in the 6th was lower than in the 1st sampling.

Table 4.3 Physicochemical parameters of surface waters in the Maragogipe, Jaguaripe and São Paulo rivers, Brazil, sampled in January of 2015. The values shown are mean \pm standard deviation (n = 6).

Variables	River	Sampling points						Mean \pm St.dev.
		1	2	3	4	5	6	
pH (water)	Maragogipe	7.23	7.12	8.00	7.90	7.80	8.20	7.70 \pm 0.43
	Jaguaripe	7.34	7.15	7.16	7.28	7.38	7.34	7.27 \pm 0.09
	São Paulo	7.61	7.33	7.14	6.39	7.06	6.80	7.05 \pm 0.42
Temp. (°C) (Water)	Maragogipe	30.1	29.8	30.0	30.9	30.3	33.5	30.7 \pm 1.3
	Jaguaripe	27.6	27.3	27.6	27.7	27.9	27.5	27.6 \pm 0.2
	São Paulo	28	27.5	27.2	26.8	27.2	27.1	27.3 \pm 0.4
Salinity (‰) (water)	Maragogipe	20	21	23	24	22	22	22 \pm 1.4
	Jaguaripe	26	23	24	23	22	20	23.0 \pm 2.0
	São Paulo	36	35	35	26	33	34	33.1 \pm 3.65
D.O. (mg L ⁻¹) (water)	Maragogipe	9.12	6.76	8.01	7.76	8.32	6.67	7.77 \pm 0.93
	Jaguaripe	11.14	10.15	9.20	8.36	8.25	8.84	9.32 \pm 1.12
	São Paulo	2.86	2.60	2.06	3.55	5.11	5.69	3.64 \pm 1.45
Cond. (ms cm ⁻¹) (water)	Maragogipe	32.9	34	36.8	38.5	35.1	35.6	35.4 \pm 1.99
	Jaguaripe	40.6	36.5	27.9	36	34.7	32.4	36.3 \pm 2.79
	São Paulo	54.3	53.3	52.7	41.2	51.0	51.6	50.6 \pm 4.79

Table 4.4 shows the results of the ions concentration (Cl⁻, K⁺, Ca²⁺, Mg²⁺) as well as the DOC (Dissolved Organic Carbon) levels for each river studied. Overall, the behavior for the ions concentration were the same in the Jaguaripe and São Paulo rivers, lower in the last sampled point comparing with the first, except for Mg²⁺. Whereas in the Maragojope river the concentrations had an oscillation behavior, without a real pattern.

Table 4.4 Ions concentration (Cl⁻, K⁺, Ca²⁺, Mg²⁺) and DOC (Dissolved Organic Carbon) (mg L⁻¹) of the surface waters in the Maragogipe, Jaguaripe and São Paulo Rivers, sampled in January 2015.

Variables	River	Sampling points						Mean \pm St.dev.
		1	2	3	4	5	6	
Chloride (Cl ⁻)	Maragogipe	13000	13533	13800	18625	12850	14166	14329 \pm 2160
	Jaguaripe	13883	14925	14483	13283	12533	10816	13320 \pm 1492
	São Paulo	19250	18725	20900	18266	17933	18083	18859 \pm 1108
Potassium (K ⁺)	Maragogipe	2.22	2.29	2.45	2.69	2.44	2.45	2.42 \pm 0.16
	Jaguaripe	2.83	2.74	2.63	2.43	2.35	2.2	2.53 \pm 0.24
	São Paulo	3.83	3.81	3.64	3.42	3.68	3.68	3.68 \pm 0.14
Calcium (Ca ²⁺)	Maragogipe	3.66	3.74	4.08	4.29	3.92	3.99	3.95 \pm 0.22
	Jaguaripe	4.60	4.29	4.20	3.64	3.83	3.62	4.03 \pm 0.39
	São Paulo	6.47	6.45	6.29	5.76	6.19	6.32	6.25 \pm 0.26
Magnesium (Mg ²⁺)	Maragogipe	0.49	0.52	0.54	0.54	0.52	0.52	0.52 \pm 0.01
	Jaguaripe	0.30	0.53	0.52	0.26	0.53	0.49	0.44 \pm 0.12
	São Paulo	0.40	0.40	0.42	0.39	0.41	0.40	0.40 \pm 0.01
DOC	Maragogipe	5.974	5.041	4.817	4.420	4.708	4.942	4.98 \pm 0.53
	Jaguaripe	4.713	5.386	5.927	6.836	7.263	8.075	6.37 \pm 1.25
	São Paulo	3.541	3.795	4.111	4.095	4.839	4.338	4.12 \pm 0.44

The ion concentrations of potassium in the Jaguaripe River was the most outstanding result, going from 2.20 to 3.83 mg L⁻¹.

Dissolved organic carbon showed an opposite behavior than the ions. The concentration were higher in the last (8.075 and 4.338 mg L⁻¹) sampled point than the first (4.713 and 3,541 mg L⁻¹) in the Jaguaripe and São Paulo rivers respectively, while in the Maragogipe the oscillation was clear, decreasing from the 1st (5.974 mg L⁻¹) to the 4th (4.420 mg L⁻¹) sampling and increasing to the 6th (4.942 mg L⁻¹).

Metal concentration measured in surface water and oysters from the Maragogipe, Jaguaripe and São Paulo Rivers are plotted in Figures 4.2 and 4.3 respectively.

Zn levels showed quite similar trends in both water and mollusks matrices, with a little oscillation between the sampling points but without a big difference in the concentration, except for the 1st sampled point in the water for Maragogipe River (Figure 4.2). These results also showed a little difference between the concentrations in the oysters comparing the São Paulo River to the Maragogipe and Jaguaripe Rivers.

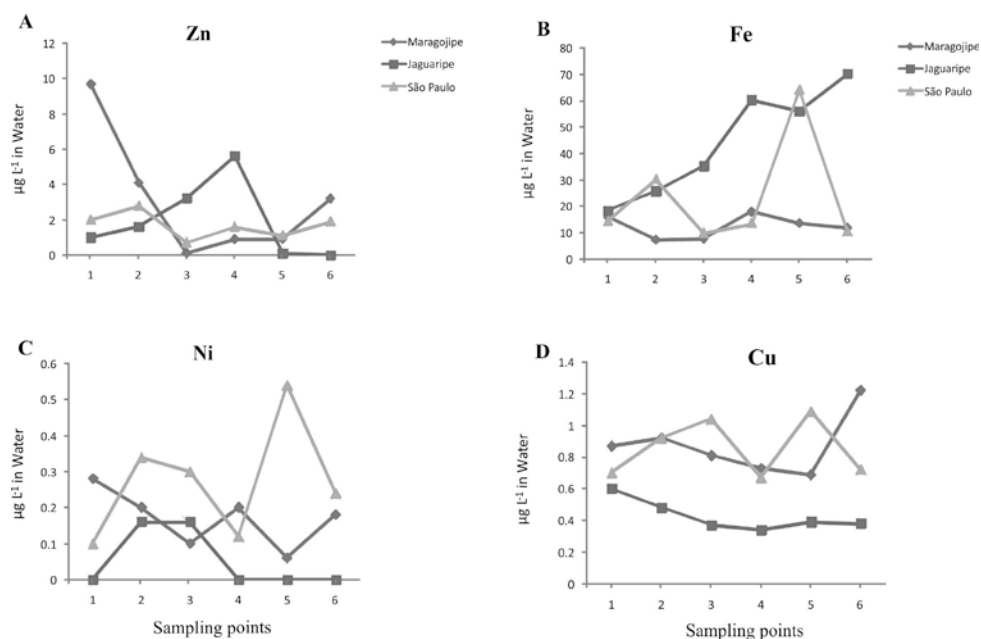


Figure 4.2 Metal concentrations (µg L⁻¹) of Zn (A), Fe (B), Ni (C) and Cu (D) in surface water of the Maragogipe, Jaguaripe and São Paulo Rivers sampled in January 2015.

The Fe concentrations in the surface waters were quite different with values ranging from 7.4 µg L⁻¹ in the 2nd sampling point at the Maragogipe River to 70 µg L⁻¹ in the 6th sampling point at the Jaguaripe River (Figure 4.2). In oysters, the concentration of Fe showed similar values for all rivers, except in the 1st and 6th sampling point in the Jaguaripe River (711 and 546 mg kg⁻¹ respectively) and in the 6th sampling point in the São Paulo River (540 mg kg⁻¹) (Figure 4.3).

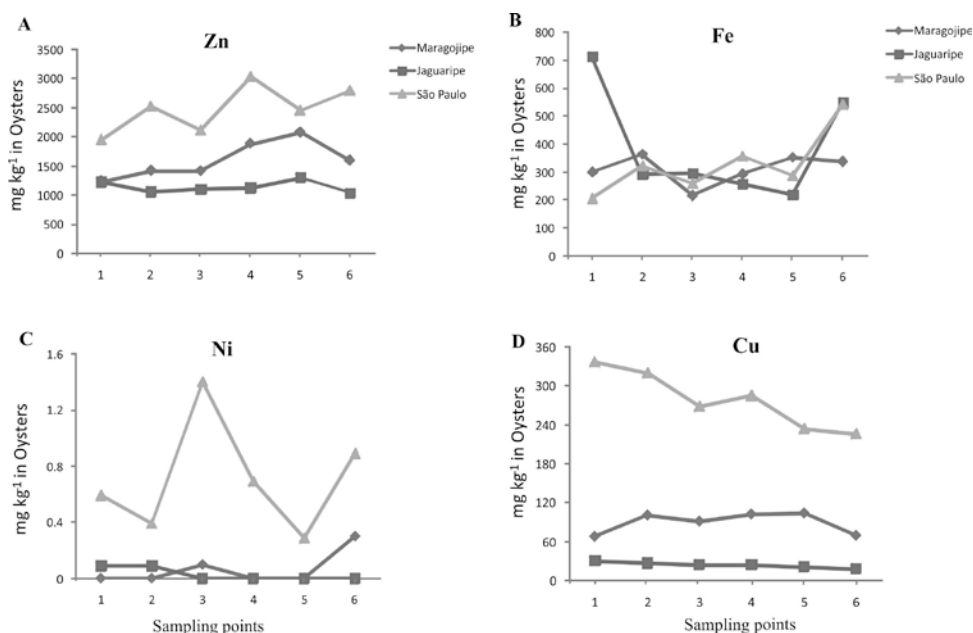


Figure 4.3 Metal concentrations (mg kg^{-1} dry weight) of Zn (A), Fe, (B), Ni (C) and Cu (D) in oysters collected from the Maragogipe, Jaguaripe and São Paulo Rivers sampled in January 2015.

Ni levels were really low in both oysters and surface waters, with many sampling points being below of the detection limit for this metal. Comparing all rivers, only for São Paulo River was noticed results above the detection limits for both matrices.

For Cu levels, Jaguaripe River showed the lowest values in oyster and surface water. São Paulo River was the one with highest values in oysters (278 mg kg^{-1} of average) whereas Maragogipe and Jaguaripe Rivers the average were 89 and 23 mg kg^{-1} respectively. Also in the São Paulo River we noticed a decrease behavior in the Cu concentrations from the 1st sampling to the last one in oyster (Fig. 4.3).

Speciation calculations were made to check possible fluctuations in available metal concentrations in surface waters of one same river and to compare the results between different places into the same bay. The results showed that the river's course affect the free ion activity along the sampling points (Table S4.1 in the Supplementary Information). Metal speciation also showed some different trends with the internal metal concentration in the oysters and the ion activities of the surface water. The oyster metal concentration had both decrease and increase results when related to different metal ion activities from the different rivers studied.

4. Discussion

The physicochemical parameters and the metal concentration in water and mollusks at the three sampling locations showed different spatial trends in this study. Estuarine environments generally shows gradient behaviors for the parameters (Regnier et al., 2013) and it could be easily noticed in the results (Tables 4.3 and 4.4). The salinity and pH of the water are the mostly affected by the gradient, varying from the place more close to the sea to the place more faraway, mainly due the input of the sea water.

Not only the physicochemical parameters showed gradient patterns. Some ions also had different concentrations from the 1st to the last sampling point at each river studied. This situation shows how the characteristics into the same river can change along its course. Changing ions concentrations like K^+ , Ca^{2+} and Mg^{2+} per example together with different physicochemical parameters values in the surface waters, the metal concentration will be affected, in this way, affecting and selecting organisms according its ecological niches (Kearney, 2006; Kearney and Porter, 2009).

In the present study, the salinity showed the same pattern in both Jaguaripe and São Paulo Rivers, which the values decreased from the 1st sampling point to the last one. Taking a look at the maps, it's possible to see that in both cases there is a path from the 1st sampling point going into the rivers, getting far away from the sea influence. This situation makes the input of sea water less strong, in this way, the salinity decreases. On the other way around, taking a look into the Maragogipe River we can see an opposite situation, where the sampling points are scattered and there is no path for the sampling sites and in this case, the decreasing pattern was not observed, instead of that, a fluctuation behavior happened (Table 4.3).

Mainly associated to the flood and ebb tides, but also affected by rainfall, river discharge, evaporation rates and dilution in the estuary (Dublin-Green, 1990; Dixit et al., 2013), salinity was higher in the São Paulo River, place closer to the ocean, and lower in the Maragogipe River, the place more far away to the sea. Once the presence of salts in the water affects chemical conditions like dissolved oxygen, it will have an effect on the organisms who lives in estuarine zones as well. This can happen in many different ways and in some cases it will have influence in their lives, changing growth and reproduction per example, in this way, their survival (NOAA, 2017; Savenije, 2012; Telesh and Khlebovich, 2010). Some animals from that environments zones can tolerate some variation in salinity, like crabs and oysters, but since the salinity will change along the river, it is expected to see some kind of variation for the organisms as well.

Connected to the salinity, dissolved oxygen (D.O.) levels and behavior between the three rivers studied were quite different (Table 4.3). The highest values were recorded in the Jaguaripe River and the lowest ones in the São Paulo River. In the Maragogipe River a fluctuation behavior was very clear, whereas in the Jaguaripe River there was a decrease behavior in the concentrations and in the São Paulo River the D.O. decrease from the 1st to the 3rd sampling and increase till the last sampling point. According with different studies (Abowei, 2009), the levels of D.O. should decrease when the salinity increases, or the other way around, but this situation was noticed clearly only in the São Paulo River.

D.O. is taken in account as a good factor of water quality once it has influence in many biological and chemical process. A place to be indicated of good quality needs to have the levels of D.O. ranging between 4 and 5 mg L⁻¹, if the levels are lower than 2.0 mg L⁻¹, the place is defined as hypoxic conditions (NOAA, 2017; Pereira et al., 2012) and is the lowest level for life. According the Brazilian laws CONAMA 357 (2005), the values shouldn't be below the 5.0 mg L⁻¹. In this study, the values ranged between 2.06 to 11.14 mg L⁻¹ in the São Paulo and Jaguaripe Rivers respectively, being above the limits established as a good level by the international guidelines, but three sampling points in the São Paulo River the levels were below the Brazilian limits. All rivers studied are important for the local communities once they can use the rivers as a local to fish, in this way, important to the human health. Low levels of D.O. may cause reduction of some aquatic organisms and increase the population of anaerobic organisms, which can result death of fishes, changing the local environment and abundance and diversity of species (Abowei, 2009).

Dissolved organic carbon is also an important parameter in biogeochemical studies once the marine biogeochemical cycle of carbon is played in a significant way for this factor (Guo et al., 1995). In this study, was observed gradient patterns for DOC in the Jaguaripe and São Paulo Rivers (Table 4.3) and a correlation to the salinity for all rivers studied (Fig. S4.1). The DOC values increased when the salinity decreased, this situation can be easily notice in the Jaguaripe and São Paulo Rivers once there is a gradient going into the rivers. In the Maragogipe River even without a gradient is possible note that the DOC had a correlation with the salinity, decreasing from the 1st to the 4th sampling (5.974 to 4.420 mg L⁻¹ respectively) and backing to increase till the 6th sampling (4.942 mg L⁻¹), these results follows the study in Guo et al (1995), when the salinity and DOC were correlated. As places strongly connected to the ocean, estuarine zones and the DOC concentrations might have decisive role in the biogeochemical process and together with others physicochemical parameters, like pH per example, those results are very important to try understand this environment.

The pH of the surface water varied from 6.39 to 8.20 between rivers, being more alkaline than acid for most of the sampling sites (Table 4.3). Due the dilution of seawater by freshwater influx, which leads to a salinity reduction (Gadhia et al., 2012), would be expected that the sampling sites more far away from the sea, in the Maragogipe River, the values of pH would be lower than in the Jaguaripe and São Paulo River. But the highest value (8.00) and the highest average (7.70) were recorded in the Maragogipe River. Between the three rivers, Maragogipe River is the one which receives more effluent discharge (specially domestic ones) and this situation might be responsible for the different pH values.

The pH values in the São Paulo River showed a decrease behavior going from 7.61 in the 1st sampling point to 6.80 in the last one. In the Jaguaripe River a fluctuation was observed, the values decreased from 7.34 to 7.15 from the 1st to the 2nd sampling point, increased till 7.38 in the 5th sampling and returned to decrease (7.34) in the last sampling point.

Water pH affects the solubility of metal ions in the environment and their binding to solid or dissolved phases like sediment or dissolved organic carbon, which leads to a pH influence on the metal concentrations in the surface waters (Niyogi and Wood, 2004). In this way, the pH also controls the availability of these metals for uptake by organisms (Dixit et al., 2013).

Regarding to the metal concentrations of Zn, Fe, Ni and Cu in the surface waters, in a general overview, it had different patterns comparing the three rivers studied. This situation was expected since the characteristics between places was different and the river's course as well. The normal situation would be that the metal concentration in the surface waters would increase when the pH decrease, which

happened in some cases. In the São Paulo River per example, the concentration for Ni and Cu was higher in the last sampling point (Fig. 4.2), where the pH was lower (Table 4.2). In this same river, the Fe concentration was much higher in the 5th sampling point comparing to the 1st sampling point, in this case, the pH was lower in the 5th sampling point than in the first one.

In the Jaguaripe River, the same situation was observed for Zn, Fe and Ni. The metal concentration increased when the pH decreased. In the Maragogipe River, an oscillation was observed and in many cases following the opposite behavior to the pH values. Since those results wasn't exactly the same for all rivers and metals, others physicochemical parameters should interfere in the metal concentration in the surface waters.

The zinc concentration showed normal trends when compared to the pH values in the Jaguaripe and Maragogipe Rivers. In a general overview, the metal concentration had the opposite behavior than the pH values. In the Maragogipe River, even with the pH oscillation between the sampling points, was observed that the Zn concentration was lower ($3.2 \mu\text{g L}^{-1}$) (Fig. 4.2) when the pH was higher (8.2) (Table 4.3). In the Jaguaripe River, the metal concentration for Zn increased (Fig. 4.2) when the pH values started to decrease (Table 4.3) and back to decrease when the pH values increases.

This situation shows how the river's course will interfere in the metal concentration in the surface waters. The gradient which goes into the river will change the physicochemical characteristics, in this way, each river according its course will present distinct results and values for the many parameters studied.

Many organisms who lives in a specific area are exposed to several risks in the environment and the internal metal concentration allow for a more trustful evaluation than reference values or effect levels reported in the literature. In this study, metal concentrations in oysters (*C. rhizophorae*) oscillated between rivers and into the same river as well for one same metal, however, in some cases a pattern was observed.

In the Jaguaripe River, all metals studied had concentrations lower in the sampling point farther from the ocean. The other way around was observed in the São Paulo River, where the concentration for Zn, Fe and Ni was higher in the sampling point farther from the ocean (Fig. 4.3). In the Maragogipe River no pattern was observed and the metal concentration fluctuate between sampling points for all metals studied. This indicate that the spatial variation together with the river's course and the gradient which is formed along the rivers will affect the metal concentration. This effect will of course be different for each metal once the characteristics of each element and its geochemistry can be totally different.

The variation in metal concentrations in the oysters was larger than the fluctuations observed in surface water at the same sampling sites. Many different metals develops essential functions in the organisms but in many different way as well. Therefore, is understandable that the internal metal concentrations in oysters had more variation than on surface waters. The nature of the organism (metabolism, size or mass and habitat) is also important since the absorption and eliminate rates will depend of the necessity or not for the animal (Worms et al., 2006; Jansen et al., 2002).

Some ion activities will interfere in the internal metal concentration once the uptake by the oysters will depend of these parameters. Speciation calculations were made to understand better this situation and the real effect of some ions on metal uptake by this organism.

Following the results of Cl^- , K^+ , Ca^{2+} , Mg^{2+} and DOC measurements (Table 4.4), in a general overview, the free ion activity of these elements and DOC activity had the same pattern in both Jaguaripe and São Paulo River. The free ion activity was higher in the 1st sampling point (closest to the sea) and lower in the last sampling point (farther from the sea). On the other way around, DOC activities increased from the first to the last sampling point (Table S4.1 in the Supplementary Information).

Making an association to the metal concentration in the oysters, was observed different patterns between the internal concentration to both free ion and DOC activities. Decreasing $\{\text{Ca}^{2+}\}$, $\{\text{Cl}^-\}$ and $\{\text{K}^+\}$ resulted in a decrease for Cu (Fig. 4.4), but in a significant increase for Zn internal metal concentration in the São Paulo River (Fig. 4.5). This indicated that Ca^{2+} , Cl^- and K^+ had opposite responses for different metals to the metal uptake by the *C. rhizophorae*, inhibiting the uptake for Cu but promoting the uptake for Zn in the same organism.

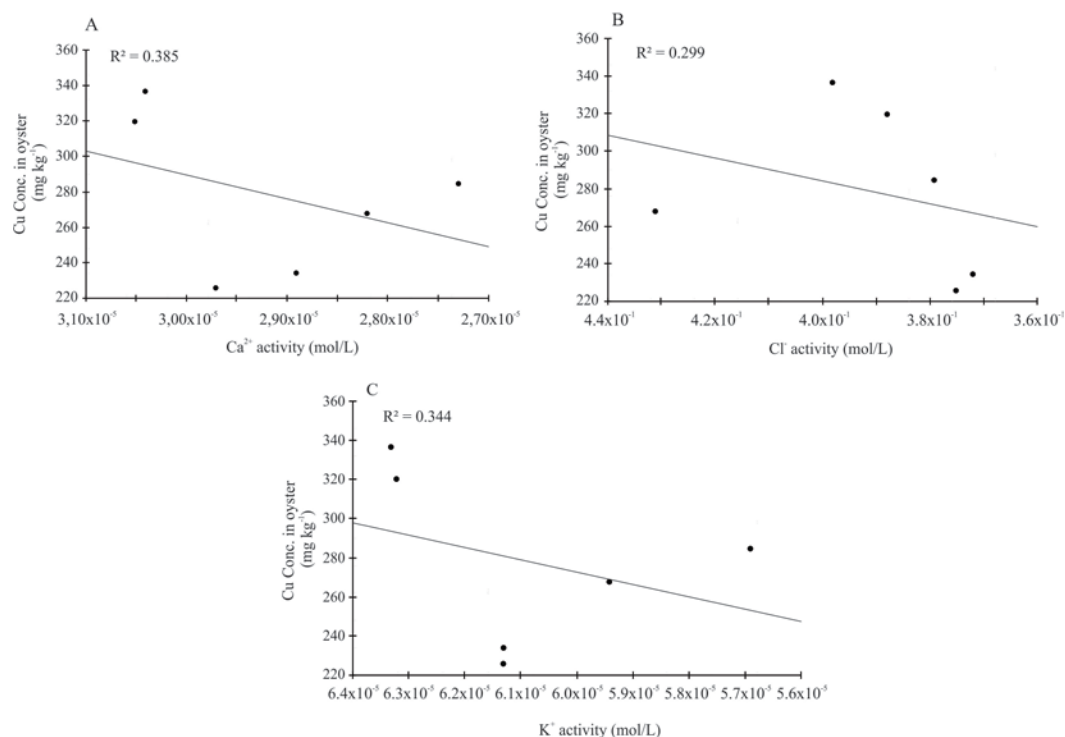


Figure 4.4 The relationship between Cu internal concentration in *C. rhizophorae* (mg kg⁻¹) and the free Ca²⁺ (A), Cl⁻ (B) and K⁺ (C) ion activity (mol L⁻¹) in the surface waters from the São Paulo River.

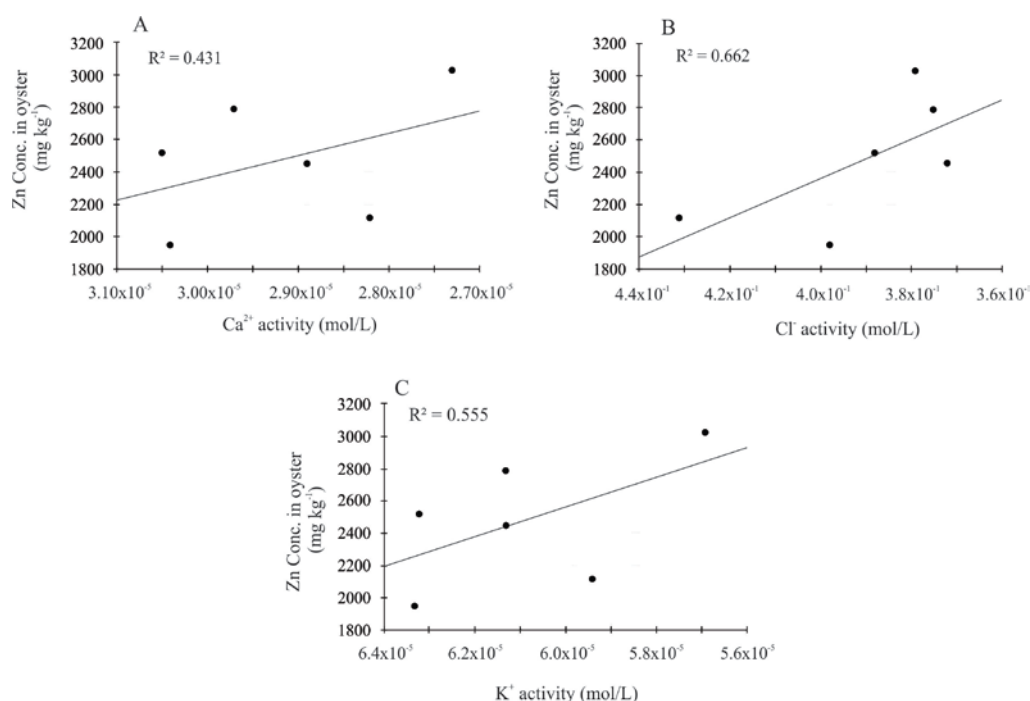


Figure 4.5 The relationship between Zn internal concentration in *C. rhizophorae* (mg kg⁻¹) and the free Ca²⁺ (A), Cl⁻ (B) and K⁺ (C) ion activity (mol L⁻¹) in the surface waters from the São Paulo River.

However, in the Jaguaripe River the internal metal concentration for all metals studied decreased when the {Ca²⁺} and {K⁺} activities also decreased, mainly for Ni and Cu (Fig. 4.6 and 4.7 respectively). Others free ion activities and its effect on the internal metal concentration can be checked in more details in the Figures S4.1 and S4.2 in the Supplementary Information.

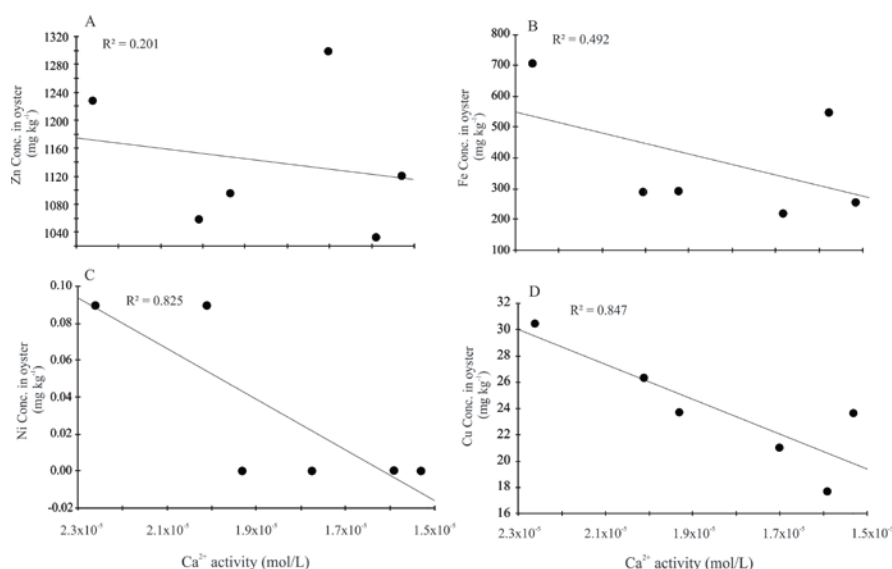


Figure 4.6 The relationship between internal metal concentrations of Zn (A), Fe (B), Ni (C) and Cu (D) in *C. rhizophorae* (mg kg^{-1}) and the free Ca^{2+} ion activity (mol L^{-1}) in the surface waters from the Jaguaripe River.

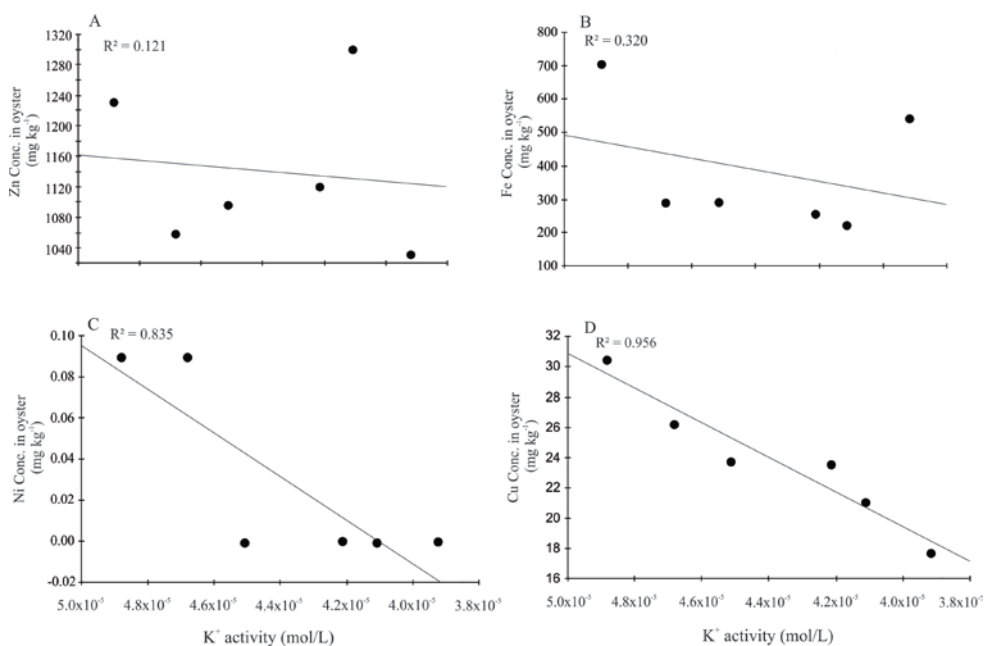


Figure 4.7 The relationship between internal metal concentrations of Zn (A), Fe (B), Ni (C) and Cu (D) in *C. rhizophorae* (mg kg^{-1}) and the free K^{2+} ion activity (mol L^{-1}) in the surface waters from the Jaguaripe River.

The metal uptake by the oysters seems also have been affected in different ways by the DOC results. In both Jaguaripe and São Paulo Rivers this parameters increased once the sampling points were getting farther from the sea, but the all studied metals instead of that had different behaviors (Fig. 4.3).

In the Maragogipe River no pattern was noticed for both internal concentration in the organism and the other parameters. This indicated that the river's course affect the behavior of the parameters and the effect of anions and cations on the uptake for metals by *C. rhizophorae* will be different according to the river's characteristics.

5. Conclusion

All the parameters analyzed in this study varied between rivers. The spatial variation together with the river's course were decisive to determine the different results between different rivers into the same Todos os Santos Bay. The gradient which happens inside estuarine zones was the mainly reason for

the different values to the physicochemical parameters, in this way, affecting the metal concentration in the surface waters and internal metal concentration in the oysters.

Metal concentration in the surface waters and the metal uptake by the *C. rhizophorae* was influenced in different ways by parameters analyzed. This situation shows that not only one, but a range of factors needs to be taken in account to make judgments about metal concentrations and its behaviors in estuarine zones.

Supplementary Information

Table S4.1. Results of the speciation analysis in the surface waters. Data shows the Ca^{2+} , Cl^- , H^+ , K^+ , Mg^{2+} free ion (mol L^{-1}) and Dissolved Organic Carbon (DOC) (mol L^{-1}) activities in the Maragogipe, Jaguaripe and São Paulo Rivers.

Variables	Rivers	Sampling Points					
		1	2	3	4	5	6
Ca^{2+}	Maragogipe	1,67E-05	1,78E-05	1,96E-05	1,87E-05	1,93E-05	1,85E-05
	Jaguaripe	2,26E-05	2,01E-05	1,93E-05	1,53E-05	1,70E-05	1,59E-05
	São Paulo	3,04E-05	3,05E-05	2,82E-05	2,73E-05	2,89E-05	2,97E-05
Cl^-	Maragogipe	2,74E-01	2,84E-01	2,91E-01	3,85E-01	2,71E-01	2,96E-01
	Jaguaripe	2,92E-01	3,12E-01	3,04E-01	2,80E-01	2,65E-01	2,31E-01
	São Paulo	3,98E-01	3,88E-01	4,31E-01	3,79E-01	3,72E-01	3,75E-01
H^+	Maragogipe	5,88E-08	7,58E-08	1,00E-08	1,25E-08	1,58E-08	6,31E-09
	Jaguaripe	4,57E-08	7,07E-08	6,91E-08	5,34E-08	4,16E-08	4,57E-08
	São Paulo	2,45E-08	4,67E-08	7,24E-08	4,07E-07	8,71E-08	2,08E-08
K^+	Maragogipe	3,86E-05	3,97E-05	4,23E-05	4,46E-05	4,26E-05	4,22E-05
	Jaguaripe	4,88E-05	4,68E-05	4,51E-05	4,21E-05	4,11E-05	3,92E-05
	São Paulo	6,33E-05	6,32E-05	5,94E-05	5,69E-05	6,13E-05	6,13E-05
Mg^{2+}	Maragogipe	3,21E-06	3,54E-06	3,69E-06	3,29E-06	3,67E-06	3,42E-06
	Jaguaripe	2,08E-06	3,52E-06	3,40E-06	1,54E-06	3,37E-06	3,11E-06
	São Paulo	2,61E-06	2,64E-06	2,61E-06	2,60E-06	2,69E-06	2,62E-06
DOC	Maragogipe	4,98E-04	4,21E-04	4,01E-04	3,68E-04	3,92E-04	4,11E-04
	Jaguaripe	3,92E-04	4,48E-04	4,93E-04	5,69E-04	6,05E-04	6,72E-04
	São Paulo	2,95E-04	3,16E-04	3,42E-04	3,41E-04	4,03E-04	3,61E-04

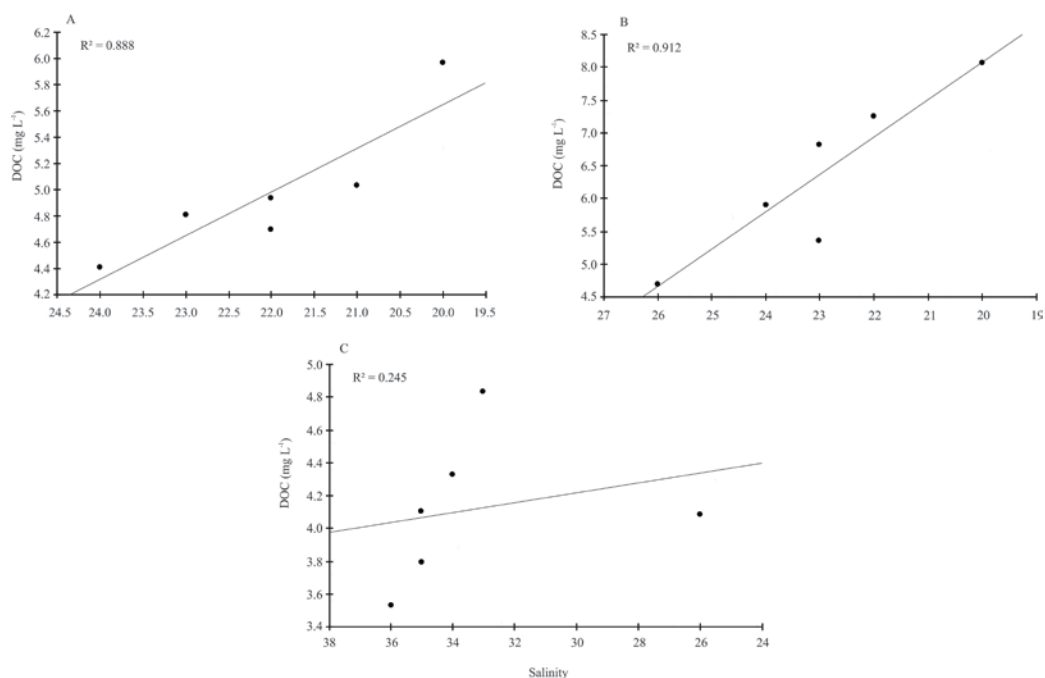


Figure S4.1. The relationship between Dissolved Organic Carbon (DOC) (mg L^{-1}) and the salinity in the Maragogipe (A), Jaguaripe (B) and São Paulo (C) Rivers in the surface waters.

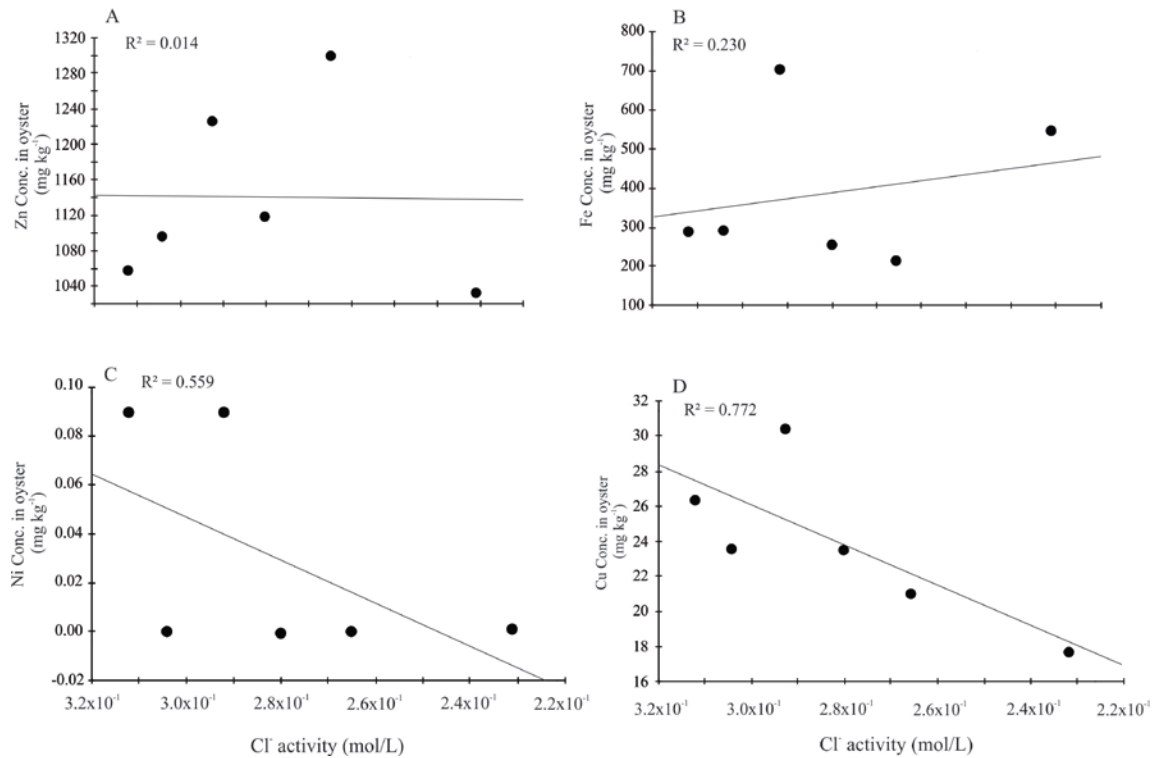


Figure S4.2. The relationship between the internal metal concentrations of Zn (A), Fe (B), Ni (C) and Cu (D) in *Crassostrea rhizophorae* (mg kg⁻¹) and the free Cl⁻ ion activity (mol L⁻¹) in the surface waters from Jaguaripe River.

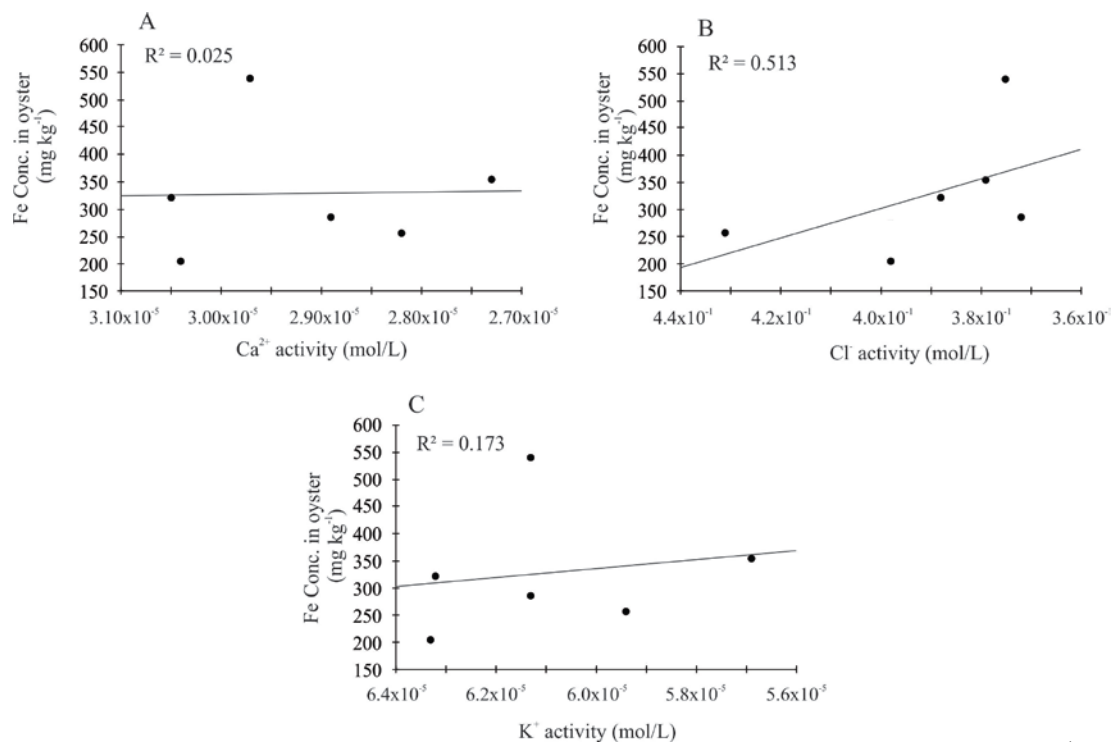


Figure S4.3. The relationship between Fe internal concentration in *Crassostrea rhizophorae* (mg kg⁻¹) and the free Ca²⁺ (A), Cl⁻ (B) and K⁺ (C) ion activity (mol L⁻¹) in the surface waters from the São Paulo River.

CAPÍTULO 5 - CONCLUSÃO

Esta presente Tese teve como principal proposta adquirir resultados e conhecimentos necessários para futuras pesquisas na área de estuário e principalmente na região da Baía de Todos os Santos. A avaliação exata de possíveis riscos ambientais dos metais em regiões estuarinas e os organismos ali presentes é dificultada pela falta de conhecimento sobre os mecanismos subjacentes à sua biodisponibilidade e possível toxicidade.

Fazendo referência as questões da pesquisa levantadas ao final da introdução, a discussão abaixo tem como foco integrar os resultados apresentados nos três artigos (capítulos 2-4) e objetiva prover respostas para aquelas questões de pesquisa.

Questão de pesquisa 1: Os parâmetros físico-químicos (pH, Eh, Salinidade, Temperatura, etc.) nas águas superficiais e sedimentos estuarinos são variáveis altamente dependentes da variação espaço-temporal. Os processos de mistura entre as águas do oceano e das águas doce nos diferentes locais de estudo e a variação das condições meteorológicas entre os períodos analisados são fundamentais para os diferentes resultados das variáveis analisadas. Desta forma, os estudos espaço-temporal em regiões estuarinas são fundamentais para entender a dinâmica deste ambiente.

Questão de pesquisa 2: As concentrações de metais nas águas superficiais, nos sedimentos e na ostra *Crassostrea rhizophorae* em ambientes estuarinos são altamente dependentes dos parâmetros físico-químicos bem como dos efeitos espaço-temporal. As diferentes características de cada local (rio estudado) de amostragem bem como a sazonalidade, que acabar por mudar o volume de chuva e a influência das águas do oceano para dentro das regiões estuarinas contribuíram para os diferentes resultados. Sendo assim, verificou-se que os parâmetros físico-químicos são governados pela entrada de água do oceano, pelo fluxo de água dos rios e também por ações antrópicas (esgotos), afetando assim as concentrações de metais nas matrizes biótica e abiótica do ambiente.

Questão de pesquisa 3: As concentrações de metais nas águas superficiais e na ostra *Crassostrea rhizophorae* exibiram diferentes valores de acordo com a dinâmica estuarina e o curso de cada rio estudado. Os gradientes que são formados devido a configuração dos rios foi fundamental para os diferentes resultados dos parâmetros físico-químicos estudados e desta forma, afetando as concentrações de metais nas matrizes estudadas. A especiação química dos metais é fator decisivo para a absorção destes elementos pelos organismos uma vez que ânions e cátions irão competir de forma diferente por sítios de ligação nas superfícies biológicas de acordo com a necessidade do animal. As atividades de íons livres poderão aumentar ou diminuir a captação dos metais pela biota.

Em resumo, os achados desta tese de doutorado abrem uma perspectiva diferente sob a forma de estudar as concentrações de metais em ambientes estuarinos e sua dependência espaço-temporal no ambiente.

Desta forma, o estudo da biodisponibilidade e da concentração de metais em organismos é muito mais complexo do que parece ser. A biodisponibilidade de metais traço sofre influência de diversas variáveis, inclusive em relação à contaminação por ação antrópica, o que pode dificultar nos resultados neste tipo de estudo. Assim sendo, o mais importante em trabalhos sobre biodisponibilidade e bioconcentração de metais traço e tentar entender como as diversas variáveis associadas a este tipo de pesquisa poderá influenciar nos resultados finais.

Como a biodisponibilidade de metais traço sofre influência de parâmetros físico-químicos e essas variáveis estão sujeitas a variações sazonais significativas, para trabalhos sobre concentração de elementos metálicos no ambiente, é interessante que se faça pesquisas em diferentes estações do ano. Pois os resultados das concentrações nas matrizes analisadas muito provavelmente serão diferentes. Então, a depender do foco do trabalho, o estudo deverá ser realizado numa determinada estação do ano (seca ou chuvosa) ou então em ambas.

Além do fator sazonalidade, a variação espacial de características de regiões estuarinas, juntamente com o curso dos rios, afetará as diversas variáveis fundamentais para o equilíbrio do ambiente. Tais variáveis por sua vez são governadas pela influência da água do mar, do input das águas dos rios bem como de fatores antrópicos como esgotos e essas situações causam influência na concentração de metais nas águas superficiais, nos sedimentos e organismos presentes nos estuários.

Sabendo dessas características, bons trabalhos sobre biodisponibilidade podem gerar uma possível modelagem sobre os metais traço. Prevendo níveis de concentração de um determinado metal, bem como sua distribuição ao longo de regiões estuarinas.

Porém, possíveis estimativas não devem ser totalmente confiáveis, pois cada região possui características peculiares, contudo, com as informações necessárias e sabendo de possíveis comportamentos e das concentrações de metais, o trabalho a ser realizado pode vir a ser facilitado com as informações preliminares.

Enquanto fatores físico-químicos podem limitar ou dificultar a captação dos metais, alguns organismos podem se adaptar, resultando em modificações no fluxo e na velocidade de assimilação e conseqüentemente alterando a disponibilidade dos complexos metálicos. Neste sentido, cálculos de especiação podem ajudar a entender possíveis riscos dos metais nos organismos. Os ions presentes no ambiente tem papel fundamental na absorção dos metais pelos organismos, inibindo ou aumentando a captação de determinado elemento, uma vez que anions e/ou cations competem por sítios de ligação nas superfícies biológicas e os metais geralmente tem diferentes caminhos de entrada nos organismos.

Em resumo, a biodisponibilidade de metais traço é dependente de fatores físicos, químicos e biológicos que são altamente complexos e interdependentes.

Através dos resultados sobre o estudo da biodisponibilidade e bioconcentração de metais numa determinada região, governos locais podem gerar uma relação de possíveis elementos contaminantes e tentar minimizar seus impactos ambientais.

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APÊNDICE A – RESULTADOS BRUTOS OBTIDOS DURANTE TODO O TRABALHO REALIZADO

Table 1 Physicochemical parameters on surface waters and sediments in the Maragogipe, Jaguaripe and São Paulo rivers, Brazil, sampled in March of 2014. The values shown are mean \pm standard deviation (n = 6).

Variables	River	Sampling points						Mean \pm St.dev.
		1	2	3	4	5	6	
pH (water)	Maragogipe	6.18	6.78	6.86	6.83	6.85	7.04	6.75 \pm 0.29
	Jaguaripe	4.98	5.65	5.62	5.57	5.26	5.6	5.44 \pm 0.26
	São Paulo	5.91	6.01	6.1	6.06	5.98	5.41	5.91 \pm 0.25
Eh (mV) (water)	Maragogipe	27	-10	-14	-12	-13	-25	-7.8 \pm 17.8
	Jaguaripe	33	-8	-7	-4	15	-6	3.8 \pm 16.6
	São Paulo	-24	-23	-35	-33	-28	6	-22.8 \pm 14.9
Temp. (°C) (Water)	Maragogipe	28.3	29.1	28.9	29.5	29.3	29.7	29.2 \pm 0.5
	Jaguaripe	30.3	28.3	28.2	28.1	27.9	27.7	28.4 \pm 0.9
	São Paulo	29.3	30.9	29.7	29.0	29.5	29.6	29.7 \pm 0.6
Salinity (‰) (water)	Maragogipe	16	29	22	23	21	23	22.3 \pm 4.1
	Jaguaripe	17	18	14	14	13	10	14.3 \pm 2.8
	São Paulo	35	37	37	37	27	35	34.6 \pm 3.8
D.O. (mg L ⁻¹) (water)	Maragogipe	7.98	5.7	7.91	6.86	7.78	5.68	6.98 \pm 1.08
	Jaguaripe	4.5	4.02	4.15	3.77	3.53	3.27	3.87 \pm 0.44
	São Paulo	3.85	3.92	3.81	2.98	3.58	3.55	3.61 \pm 0.34
Cond. (ms cm ⁻¹) (water)	Maragogipe	26.7	45.5	35.9	36.2	33.9	36.9	35.8 \pm 6
	Jaguaripe	28	29.5	23.3	23.8	21.5	17.9	24 \pm 4.2
	São Paulo	53.3	55.6	55.1	55.3	43.4	53.5	52.7 \pm 4.6
pH (sed)	Maragogipe	6.66	6.82	6.89	6.82	7.03	6.67	6.81 \pm 0.13
	Jaguaripe	7.02	6.97	6	6.71	6.93	6.64	6.71 \pm 0.37
	São Paulo	7.16	7.01	6.7	6.87	6.84	6.57	6.85 \pm 0.21
Eh (mV) (sed)	Maragogipe	0.9	-12	-12	-4	-11	4.3	-5.6 \pm 7.12
	Jaguaripe	-16	-12	15.4	-5	-7	-3	-4.6 \pm 10.9
	São Paulo	-25	-17	4.1	-5	-1	13.4	-5.1 \pm 14
Temp. (°C) (sed)	Maragogipe	25	28.5	28.95	28	27.2	27.7	27.5 \pm 1.4
	Jaguaripe	26	26	28.6	28.5	28.8	27.9	27.6 \pm 1.3
	São Paulo	28.9	29.4	29	27.8	28.6	27.9	28.6 \pm 0.6
Cond. (ms cm ⁻¹) (sed)	Maragogipe	41.4	42.4	43.8	40.1	49	38	42.4 \pm 3.7
	Jaguaripe	38	40	44.1	44	39.3	35.2	40.1 \pm 3.4
	São Paulo	57.4	55	57.7	55.9	53	53.2	55.3 \pm 2.1

Table 2 Physicochemical parameters on surface waters and sediments in the Maragogipe, Jaguaripe and São Paulo rivers, Brazil, sampled in August of 2014. The values shown are mean \pm standard deviation (n = 6).

Variables	River	Sampling points						Mean \pm St.dev.
		1	2	3	4	5	6	
pH (water)	Maragogipe	7.51	7.84	7.49	7.6	7.49	7.61	7.59 \pm 0.13
	Jaguaripe	7.18	6.78	6.59	6.76	6.83	6.72	6.81 \pm 0.19
	São Paulo	7.6	7.35	7.23	7.21	7.16	7.19	7.29 \pm 0.16
Eh (mV) (water)	Maragogipe	-25	-45	-24	-31	-24	-32	-30.1 \pm 8.1
	Jaguaripe	-6	18	29	19	15	21	16 \pm 11.7
	São Paulo	-31	-16	-9	-7	-5	-6	-12.3 \pm 9.9
Temp. (°C) (Water)	Maragogipe	24.6	25.1	25.8	27.1	26.5	27.5	26.1 \pm 1.1
	Jaguaripe	25.1	24.3	24.5	24.3	24.1	24.0	24.4 \pm 0.3
	São Paulo	26.3	26.1	25.3	24.6	25.6	25.1	25.5 \pm 0.6
Salinity (‰) (water)	Maragogipe	30	31	26	26	29	30	28.6 \pm 2.1
	Jaguaripe	20	19	18	15	13	11	16 \pm 3.5
	São Paulo	31	33	33	32	31	33	32.1 \pm 0.9
D.O. (mg L ⁻¹) (water)	Maragogipe	4.83	4.48	4.26	5.44	5.01	7.72	5.29 \pm 1.25
	Jaguaripe	4.13	4.07	4.11	3.63	3.63	3.27	3.81 \pm 0.35
	São Paulo	3.77	3.72	3.21	2.85	2.62	2.79	3.16 \pm 0.49
Cond. (ms cm ⁻¹) (water)	Maragogipe	46.2	47.7	42.1	41.9	44.3	46.3	44.7 \pm 2.3
	Jaguaripe	33.1	30.7	29	25	22.4	19.1	26.5 \pm 5.3
	São Paulo	49	51.4	51.1	50.1	47.6	50.5	49.9 \pm 1.4
pH (sed)	Maragogipe	6.98	7.44	7.07	7.16	6.61	7.64	7.15 \pm 0.36
	Jaguaripe	7.37	7.08	6.88	6.89	6.89	6.84	6.99 \pm 0.20
	São Paulo	7.19	7.21	6.97	7.08	7.28	6.64	7.06 \pm 0.23
Eh (mV) (sed)	Maragogipe	4	-22	-1	-8	27	-34	-5.6 \pm 21.2
	Jaguaripe	-18	-3	10	11	9	16	4.1 \pm 12.5
	São Paulo	-6	-9	5	-1	-13	24	0 \pm 13.3
Temp. (°C) (sed)	Maragogipe	25.8	26.1	27.4	28.5	29.8	33	28.4 \pm 2.6
	Jaguaripe	25.9	24.6	24.9	25.6	25.6	26.8	25.5 \pm 0.7
	São Paulo	29.7	26.2	26.3	25.7	28	25.7	26.9 \pm 1.5
Cond. (ms cm ⁻¹) (sed)	Maragogipe	45.8	46.6	47.2	49.5	52.6	55.5	49.5 \pm 3.8
	Jaguaripe	36.6	33.3	29.5	33	29.7	25.9	31.3 \pm 3.7
	São Paulo	55.6	49.1	51	51	51.8	50.3	51.4 \pm 2.2

Table 3 Physicochemical parameters on surface waters and sediments in the Maragogipe, Jaguaripe and São Paulo rivers, Brazil, sampled in January of 2015. The values shown are mean \pm standard deviation (n = 6).

Variables	River	Sampling points						Mean \pm St.dev.
		1	2	3	4	5	6	
pH (water)	Maragogipe	7.23	7.12	8.00	7.90	7.80	8.20	7.70 \pm 0.43
	Jaguaripe	7.34	7.15	7.16	7.28	7.38	7.34	7.27 \pm 0.09
	São Paulo	7.61	7.33	7.14	6.39	7.06	6.80	7.05 \pm 0.42
Eh (mV) (water)	Maragogipe	5	12	-43	-35	-34	-56	-25.1 \pm 27.3
	Jaguaripe	-1	10	10	2	-4	-1	2.6 \pm 5.9
	São Paulo	-17	-1	11	56	16	31	16 \pm 25.4
Temp. (°C) (Water)	Maragogipe	30.1	29.8	30.0	30.9	30.3	33.5	30.7 \pm 1.3
	Jaguaripe	27.6	27.3	27.6	27.7	27.9	27.5	27.6 \pm 0.2
	São Paulo	28	27.5	27.2	26.8	27.2	27.1	27.3 \pm 0.4
Salinity (‰) (water)	Maragogipe	20	21	23	24	22	22	22 \pm 1.4
	Jaguaripe	26	23	24	23	22	20	23.0 \pm 2.0
	São Paulo	36	35	35	26	33	34	33.1 \pm 3.65
D.O. (mg L ⁻¹) (water)	Maragogipe	9.12	6.76	8.01	7.76	8.32	6.67	7.77 \pm 0.93
	Jaguaripe	11.14	10.15	9.20	8.36	8.25	8.84	9.32 \pm 1.12
	São Paulo	2.86	2.60	2.06	3.55	5.11	5.69	3.64 \pm 1.45
Cond. (ms cm ⁻¹) (water)	Maragogipe	32.9	34	36.8	38.5	35.1	35.6	35.4 \pm 1.99
	Jaguaripe	40.6	36.5	27.9	36	34.7	32.4	36.3 \pm 2.79
	São Paulo	54.3	53.3	52.7	41.2	51.0	51.6	50.6 \pm 4.79
pH (sed)	Maragogipe	6.63	6.72	7.03	7.06	6.82	7.06	6.88 \pm 0.18
	Jaguaripe	7.06	7.32	7.12	7.44	7.17	7.16	7.21 \pm 0.14
	São Paulo	7.45	7.43	7.04	7.19	7.28	7.02	7.23 \pm 0.18
Eh (mV) (sed)	Maragogipe	26	28	10	4	7	7	13.6 \pm 10.5
	Jaguaripe	7	-8	3	-13	1	1	-1.5 \pm 7.4
	São Paulo	-16	-15	8	-1	-4	9	-3.1 \pm 10.7
Temp. (°C) (sed)	Maragogipe	29	28.8	30.5	33	29.7	33.5	30.7 \pm 2
	Jaguaripe	26.9	28.1	28.5	32.6	32.8	28.5	29.5 \pm 2.4
	São Paulo	30.2	30.6	28.3	28.2	28.2	28	28.9 \pm 1.1
Cond. (ms cm ⁻¹) (sed)	Maragogipe	40.4	44.2	46.8	44	50.7	42	44.6 \pm 3.6
	Jaguaripe	37.4	38.2	45.5	45.2	43.4	37.1	41.1 \pm 3.9
	São Paulo	58.5	57.4	56.4	58.3	54.4	54.4	56.5 \pm 1.83

Table 4 Metal concentration ($\mu\text{g l}^{-1}$) on surface waters in the Maragogipe, Jaguaripe and São Paulo rivers, Brazil, sampled in March of 2014. The values shown are mean \pm standard deviation ($n = 6$).

Metals	Rivers	Sampling points						
		01	02	03	04	05	06	Mean \pm St.dev.
Al	Maragogipe	30	20	110	80	10	10	43.3 \pm 41.8
	Jaguaripe	< D. L.	< D. L.	< D. L.	30	10	10	*
	São Paulo	30	10	60	10	< D. L.	800	*
Cu	Maragogipe	< D. L.	10	< D. L.	< D. L.	< D. L.	< D. L.	*
	Jaguaripe	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	*
	São Paulo	< D. L.	10	< D. L.	< D. L.	< D. L.	10	*
Fe	Maragogipe	100	90	210	160	60	80	116.6 \pm 56.8
	Jaguaripe	70	470	120	210	300	330	250 \pm 147.1
	São Paulo	40	50	30	340	60	470	165 \pm 190.6
Mn	Maragogipe	70	10	10	20	10	110	38.3 \pm 42.1
	Jaguaripe	50	70	90	130	150	180	111.6 \pm 49.9
	São Paulo	40	40	60	100	90	90	70 \pm 26.8
Ni	Maragogipe	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	*
	Jaguaripe	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	*
	São Paulo	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	*
Zn	Maragogipe	6	7	6	7	4	7	6.2 \pm 1.1
	Jaguaripe	7	9	4	5	5	5	5.8 \pm 1.8
	São Paulo	7	23	6	12	5	8	10.2 \pm 6.7

Table 5 Metal concentration ($\mu\text{g l}^{-1}$) on surface waters in the Maragogipe, Jaguaripe and São Paulo rivers, Brazil, sampled in August of 2014. The values shown are mean \pm standard deviation ($n = 6$).

Metals	Rivers	Sampling points						Mean \pm St.dev.
		01	02	03	04	05	06	
Al	Maragogipe	60	50	30	40	60	40	46.7 \pm 12.1
	Jaguaripe	30	100	70	110	170	210	115 \pm 65.6
	São Paulo	40	20	90	90	30	100	61.7 \pm 35.4
Cu	Maragogipe	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	*
	Jaguaripe	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	*
	São Paulo	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	*
Fe	Maragogipe	40	20	30	20	10	10	21.6 \pm 11.7
	Jaguaripe	130	190	260	340	410	400	288.3 \pm 114.4
	São Paulo	30	30	20	40	30	40	31.7 \pm 7.5
Mn	Maragogipe	50	10	30	20	30	30	28.3 \pm 13.3
	Jaguaripe	100	130	130	120	110	100	115 \pm 13.8
	São Paulo	110	140	100	110	70	90	103.3 \pm 23.4
Ni	Maragogipe	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	*
	Jaguaripe	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	*
	São Paulo	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	*
Zn	Maragogipe	1	6	< D. L.	1	< D. L.	< D. L.	*
	Jaguaripe	< D. L.	< D. L.	5	1	< D. L.	5	*
	São Paulo	4	3	1	3	2	8	3.5 \pm 2.4

Table 6 Metal concentration ($\mu\text{g l}^{-1}$) on surface waters in the Maragogipe, Jaguaripe and São Paulo rivers, Brazil, sampled in January of 2015. The values shown are mean \pm standard deviation ($n = 6$).

Metals	Rivers	Sampling points						
		01	02	03	04	05	06	Mean \pm St.dev.
Al	Maragogipe	41.7	7.9	15.8	17.2	20.0	28.5	21.8 \pm 11.8
	Jaguaripe	31.2	11.3	16.0	12.4	31.5	26.0	21.4 \pm 9.3
	São Paulo	18.0	34.9	16.6	27.0	43.5	7.3	24.5 \pm 13.2
Cu	Maragogipe	0.87	0.92	0.81	0.73	0.69	1.22	0.9 \pm 0.2
	Jaguaripe	0.60	0.48	0.37	0.34	0.39	0.38	0.4 \pm 0.1
	São Paulo	0.70	0.92	1.04	0.67	1.09	0.72	0.8 \pm 0.2
Fe	Maragogipe	15.8	7.4	7.9	18.0	13.7	11.9	12.4 \pm 4.2
	Jaguaripe	18.4	25.8	35.2	60.2	55.9	70.0	44.2 \pm 20.7
	São Paulo	14.4	30.2	9.9	13.5	64.1	10.3	23.7 \pm 21.1
Mn	Maragogipe	42.3	3.48	5.60	11.6	31.3	11.1	17.5 \pm 15.6
	Jaguaripe	49.0	64.5	84.7	92.2	101	113	84.1 \pm 23.6
	São Paulo	49.6	33.2	44.9	61.7	49.3	51.5	48.4 \pm 9.3
Ni	Maragogipe	0.28	0.20	0.10	0.20	0.06	0.18	0.2 \pm 0.1
	Jaguaripe	< D.L.	0.16	0.16	< D.L.	< D.L.	< D.L.	*
	São Paulo	0.10	0.34	0.30	0.12	0.54	0.24	0.3 \pm 0.2
Zn	Maragogipe	9.7	4.1	0.1	0.9	0.9	3.2	3.1 \pm 3.5
	Jaguaripe	1.0	1.6	3.2	5.6	0.1	-0.5	1.8 \pm 2.2
	São Paulo	2.0	2.8	0.7	1.6	1.1	1.9	1.6 \pm 0.7

Table 7 Organic Matter (%) on the mangrove sediments in the Maragogipe, Jaguaripe and São Paulo rivers, Brazil, sampled in March of 2014, August of 2014 and January of 2015 (1st, 2nd and 3rd season respectively). The values shown are mean \pm standard deviation ($n = 6$).

Season	Rivers	Sampling points						
		01	02	03	04	05	06	Mean \pm St.dev.
1st	Maragogipe	9.29	11.87	12.03	8.97	9.7	10.1	10.32 \pm 1.31
	Jaguaripe	10.1	14.52	7.68	5.51	10.14	15.57	10.18 \pm 3.87
	São Paulo	6.48	6.72	10.74	8.81	12.99	11.22	9.69 \pm 2.61
2nd	Maragogipe	8.52	1.3	6.82	7.42	7.12	5.52	6.11 \pm 2.55
	Jaguaripe	8.32	6.62	6.77	5.52	9.07	13.64	8.22 \pm 2.89
	São Paulo	2.41	2.11	7.82	7.32	7.22	6.92	5.63 \pm 2.63
3rd	Maragogipe	16.01	16.12	14.51	14.81	14.74	4.12	13.18 \pm 4.59
	Jaguaripe	14.22	12.3	6.4	6.78	15.81	20.32	12.53 \pm 5.38
	São Paulo	6.97	2.64	12.08	11.91	13.39	10.96	9.65 \pm 4.07

Table 8 Particle size (%) on the mangrove sediments in the Maragogipe, Jaguaripe and São Paulo rivers, Brazil, sampled in March of 2014 (1st season). The values shown are mean \pm standard deviation (n = 6).

Rivers	Particle size		
	Silt	Clay	Sand
Maragogipe	23.6	25.2	51.2
	23.2	32.2	44.6
	33.4	25.5	41.1
	26.3	26.5	47.2
	22.4	24.7	52.9
	20.4	26	53.6
Jaguaripe	30.4	23.1	46.5
	37.1	33.3	29.6
	17.8	20.1	62.1
	15.7	18.1	66.2
	34.5	18.6	46.9
	33.7	25	41.3
São Paulo	9.7	12	78.3
	24.5	15.9	59.6
	32	16.1	51.9
	38.1	22.2	39.7
	36.3	16.3	47.4
	39.3	20.5	40.2
Mean \pm St.dev.	27.7 \pm 8.5	22.3 \pm 5.6	50.1 \pm 11.3

Table 9 Particle size (%) on the mangrove sediments in the Maragogipe, Jaguaripe and São Paulo rivers, Brazil, sampled in August of 2014 (2nd season). The values shown are mean \pm standard deviation (n = 6).

Rivers	Particle size		
	Silt	Clay	Sand
Maragogipe	45.6	49.4	5
	2.1	3	94.9
	50.2	48.8	0.9
	40.2	57.5	2.2
	39.9	57.8	2.2
	35.2	30.6	34.2
Jaguaripe	36.5	16.4	47.1
	25.9	15.6	58.5
	21.9	17.9	60.2
	17.9	12.9	69.6
	24.8	14.4	60.8
	47.5	33.4	19.1
São Paulo	10.6	7.5	81.9
	12.2	6.7	81.1
	35.9	48.5	15.6
	37.3	42.5	20.2
	28.4	25.8	45.8
	38.9	45.9	15.2
Mean \pm St.dev.	30.6 \pm 13.5	29.7 \pm 18.6	39.5 \pm 30.9

Table 10 Particle size (%) on the mangrove sediments in the Maragogipe, Jaguaripe and São Paulo rivers, Brazil, sampled in January of 2015 (3rd season). The values shown are mean \pm standard deviation (n = 6).

Rivers	Particle size		
	Silt	Clay	Sand
Maragogipe	47.3	43.9	8.8
	37.6	59.8	2.6
	38.2	59.9	1.9
	43.3	53.3	3.3
	39.9	57.8	2.3
	11.3	9.2	79.3
Jaguaripe	45.9	32.2	21.8
	34.6	24.9	40.5
	15.1	10.2	74.7
	15.1	10.6	74.4
	42.4	34.4	23.2
	51.2	34.9	13.9
São Paulo	13.4	11.7	74.9
	11.4	5.2	82.8
	34	40.7	25.3
	37.2	45.8	17
	35.9	41.5	22.6
	38.3	38.2	23.4
Mean \pm St.dev.	32.9 \pm 13.3	34.1 \pm 18.4	32.9 \pm 29.9

Table 11 DOC (Dissolved Organic Carbon) concentration (mg l^{-1}) on surface waters in the Maragogipe, Jaguaripe and São Paulo rivers, Brazil, sampled in January of 2015 (3rd season). The values shown are mean \pm standard deviation ($n = 6$).

Rivers	Sampling points						
	01	02	03	04	05	06	Mean \pm St.dev.
Maragogipe	5,974	5,041	4,817	4,42	4,708	4,942	4,983 \pm 0,53
Jaguaripe	4,713	5,386	5,927	6,836	7,263	8,075	6,366 \pm 1,25
São Paulo	3,541	3,795	4,111	4,095	4,839	4,338	4,119 \pm 0,44

Table 12 Physicochemical parameters (Cloreto, Fósforo, Nitrato and Amônia (mg/L)) on surface waters and Cloreto Solúvel ($\mu\text{g/g}$) and Carbonatos (CO_3 cmolc/kg) in the sediments in the Maragogipe, Jaguaripe and São Paulo rivers, Brazil, sampled in March of 2014. The values shown are mean \pm standard deviation (n = 6).

Variables	River	Sampling points						Mean \pm St.dev.
		1	2	3	4	5	6	
Cloreto (water)	Maragogipe	7915	15500	15100	12700	12700	12700	12769,1 \pm 2700,6
	Jaguaripe	10200	9140	8440	7210	6510	5630	7855 \pm 1712,7
	São Paulo	19700	19500	19900	19900	18800	18300	19350 \pm 656,5
Fósforo (water)	Maragogipe	<LDM**	<LDM**	<LDM**	0,58	0,155	0,036	* \pm *
	Jaguaripe	0,026	0,041	0,037	0,052	0,049	0,055	0,043 \pm 0,011
	São Paulo	0,022	0,026	0,127	0,017	0,027	0,029	0,041 \pm 0,0421
Nitrato (Water)	Maragogipe	<LDM***	<LDM***	<LDM***	<LDM***	<LDM***	<LDM***	* \pm *
	Jaguaripe	<LDM***	0,04	<LDM***	<LDM***	<LDM***	<LDM***	* \pm *
	São Paulo	0,46	<LDM***	<LDM***	<LDM***	<LDM***	<LDM***	* \pm *
Amônia (water)	Maragogipe	<LDM****	<LDM****	<LDM****	<LDM****	<LDM****	<LDM****	* \pm *
	Jaguaripe	<LDM****	<LDM****	<LDM****	<LDM****	<LDM****	<LDM****	* \pm *
	São Paulo	<LDM****	<LDM****	<LDM****	<LDM****	<LDM****	<LDM****	* \pm *
Cloreto Solúvel (Sed)	Maragogipe	64250	74900	115000	121000	97000	51000	87191 \pm 23808
	Jaguaripe	57600	57200	22900	30200	47500	37100	42083 \pm 12016
	São Paulo	18900	23200	32600	44800	55500	46500	36916 \pm 12016
Carbonatos (Sed)	Maragogipe	173	162	174	170	169	161	168,1 \pm 4,4
	Jaguaripe	163	184	165	165	180	182	173,1 \pm 8,8
	São Paulo	157	171	169	169	175	176	169,5 \pm 4,5

* Do not applicable

**<0.013

***<0.035

****<0.04

Table 13 Physicochemical parameters (Cloreto, Fósforo, Nitrato and Amônia (mg/L)) on surface waters and Cloreto Solúvel ($\mu\text{g/g}$) and Carbonatos (CO_3 cmolc/kg) in the sediments in the Maragogipe, Jaguaripe and São Paulo rivers, Brazil, sampled in August of 2014. The values shown are mean \pm standard deviation (n = 6).

Variables	River	Sampling points						Mean \pm St.dev.
		1	2	3	4	5	6	
Cloreto (water)	Maragogipe	14900	15600	15600	15600	15800	15600	15516 \pm 205,5
	Jaguaripe	6860	5100	5100	3690	3340	2640	4455 \pm 1231,6
	São Paulo	6860	8620	10400	7910	10400	10400	9098 \pm 1301,6
Nitrato (Water)	Maragogipe	<LDM**	0,492	<LDM**	<LDM**	<LDM**	<LDM**	* \pm *
	Jaguaripe	<LDM**	<LDM**	<LDM**	<LDM**	<LDM**	<LDM**	* \pm *
	São Paulo	1,74	2,17	0,432	0,307	0,743	0,752	1,024 \pm 0,621
Amônia (water)	Maragogipe	1,65	<LDM***	0,44	<LDM***	<LDM***	0,37	* \pm *
	Jaguaripe	0,13	0,34	0,44	0,41	0,31	0,22	0,31 \pm 0,08
	São Paulo	0,71	0,41	0,32	0,38	0,38	0,35	0,42 \pm 0,09
Cloreto Solúvel (Sed)	Maragogipe	26600	22100	26700	33600	26500	13800	24883 \pm 4622,2
	Jaguaripe	6560	9660	6510	6920	10800	12000	8741 \pm 2078,3
	São Paulo	17000	10400	14900	12100	4960	14900	12376 \pm 3223,3
Carbonatos (Sed)	Maragogipe	<LDM****	<LDM****	<LDM****	<LDM****	<LDM****	<LDM****	* \pm *
	Jaguaripe	<LDM****	<LDM****	<LDM****	<LDM****	<LDM****	<LDM****	* \pm *
	São Paulo	<LDM****	<LDM****	<LDM****	<LDM****	<LDM****	<LDM****	* \pm *

* Do not applicable

**<0.035

***<0.04

****<0.01

Table 14 Chemical speciation of metals and some cations and ions estimated using Visual MINTEQ 3.1 in the sampled point P01 of the Maragogipe River in January of 2015. The measured pH values, DOC (Dissolved Organic Carbon) and concentrations of Ca^{2+} , Cl^- , H^+ , K^+ , Mg^{2+} and SO_4^{2-} were used as a input parameters.

Especies Químicas	Concentration (mol / L)	Activity (mol / L)	Log activity (mol / L)
(6)Ca+2D(aq)	0,000017011	0,000017011	-4,769
(6)Cl-1D(aq)	1,943E-08	1,943E-08	-7,712
(6)Cu+2D(aq)	2,4158E-14	2,4158E-14	-13,617
(6)Fe+2D(aq)	1,1126E-12	1,1126E-12	-11,954
(6)H+1D(aq)	1,3769E-10	1,3769E-10	-9,861
(6)K+1D(aq)	9,0455E-08	9,0455E-08	-7,044
(6)Mg+2D(aq)	3,2532E-06	3,2532E-06	-5,488
(6)Ni+2D(aq)	9,9074E-11	9,9074E-11	-10,004
(6)NiCl+D(aq)	2,356E-14	2,356E-14	-13,628
(6)OH-D(aq)	1,7583E-14	1,7583E-14	-13,755
(6)SO4-2D(aq)	6,3978E-16	6,3978E-16	-15,194
(6)Zn+2D(aq)	2,4798E-08	2,4798E-08	-7,606
Ca+2	0,000053545	0,000016751	-4,776
CaCl+	0,000015852	0,000011855	-4,926
CaOH+	1,1732E-10	8,7742E-11	-10,057
CaSO4 (aq)	2,6485E-09	2,7628E-09	-8,559
Cl-1	0,36666	0,27421	-0,562
Cu(OH)2 (aq)	7,1926E-16	7,5031E-16	-15,125
Cu(OH)3-	3,5026E-19	2,6195E-19	-18,582
Cu(OH)4-2	3,8556E-24	1,2062E-24	-23,919
Cu+2	7,6043E-14	2,3789E-14	-13,624
Cu2(OH)2+2	2,7176E-23	8,5017E-24	-23,07
Cu2OH+3	3,0558E-26	2,2366E-27	-26,65
Cu3(OH)4+2	1,1694E-32	3,6582E-33	-32,437
CuCl+	1,8412E-14	1,377E-14	-13,861
CuCl2 (aq)	1,2717E-15	1,3266E-15	-14,877
CuCl3-	4,9611E-18	3,7103E-18	-17,431
CuCl4-2 1	1,3782E-20	4,3116E-21	-20,365
CuHSO4+	2,8115E-25	2,1026E-25	-24,677
CuOH+	2,1794E-14	1,6299E-14	-13,788
CuSO4 (aq)	3,8023E-18	3,9664E-18	-17,402
DOC (NICA-Donnan)	0,00049783	0,00049783	-3,303
FA1-Ca(6)(aq)	4,9062E-06	4,9062E-06	-5,309
FA1-Cu(6)(aq)	4,6294E-09	4,6294E-09	-8,334
FA1-Fe(II)(6)(aq)	2,8291E-07	2,8291E-07	-6,548
FA1-H(6)(aq)	3,3744E-06	3,3744E-06	-5,472
FA1-Mg(6)(aq)	1,8551E-06	1,8551E-06	-5,732
FA1-Ni(6)(aq)	3,8654E-09	3,8654E-09	-8,413
FA1-Zn(6)(aq)	7,5905E-09	7,5905E-09	-8,12
FA2-Ca(6)(aq)	1,6764E-10	1,6764E-10	-9,776
FA2-Cu(6)(aq)	9,0623E-09	9,0623E-09	-8,043
FA2-Fe(II)(6)(aq)	1,3555E-12	1,3555E-12	-11,868

FA2-H(6)(aq)	0,000018131	0,000018131	-4,742
FA2-Mg(6)(aq)	3,9843E-10	3,9843E-10	-9,4
FA2-Ni(6)(aq)	4,7893E-10	4,7893E-10	-9,32
FA2-Zn(6)(aq)	1,9239E-10	1,9239E-10	-9,716
Fe(OH)2 (aq)	2,1592E-18	2,2524E-18	-17,647
Fe(OH)3-	1,695E-21	1,2676E-21	-20,897
Fe+2	3,5022E-12	1,0956E-12	-11,96
FeCl+	2,5346E-13	1,8956E-13	-12,722
FeOH+	1,4472E-14	1,0823E-14	-13,966
FeSO4 (aq)	1,8675E-16	1,9481E-16	-15,71
H+1	7,8736E-08	5,8884E-08	-7,23
HFA1-(6)(aq)	0,000047525	0,000047525	-4,323
HFA2-(6)(aq)	1,945E-07	1,945E-07	-6,711
HSO4-	6,0907E-12	4,5551E-12	-11,342
K+1	0,000051724	0,000038683	-4,412
KCl (aq)	4,9599E-06	0,000005174	-5,286
KOH (aq)	1,5991E-11	1,6681E-11	-10,778
KSO4-	2,742E-10	2,0507E-10	-9,688
Mg+2	0,00001024	3,2035E-06	-5,494
MgCl+	4,8048E-06	3,5934E-06	-5,444
MgOH+	4,2932E-10	3,2107E-10	-9,493
MgSO4 (aq)	3,988E-10	4,1601E-10	-9,381
Ni(OH)2 (aq)	2,7007E-15	2,8173E-15	-14,55
Ni(OH)3-	6,4015E-19	4,7875E-19	-18,32
Ni(SO4)2-2	9,6992E-22	3,0343E-22	-21,518
Ni+2	3,1186E-10	9,756E-11	-10,011
NiCl+	1,3472E-11	1,0075E-11	-10,997
NiCl2 (aq)	9,0594E-14	9,4504E-14	-13,025
NiOH+	3,9662E-13	2,9662E-13	-12,528
NiSO4 (aq)	1,3317E-14	1,3892E-14	-13,857
OH-	3,3181E-07	2,4815E-07	-6,605
SO4-2	2,1932E-06	6,861E-07	-6,164
Z-(6)(aq)	-0,000040649	-0,000040649	0
Zn(OH)2 (aq)	8,5102E-11	8,8774E-11	-10,052
Zn(OH)3-	6,3788E-15	4,7705E-15	-14,321
Zn(OH)4-2	4,107E-20	1,2848E-20	-19,891
Zn(SO4)2-2	7,0015E-17	2,1903E-17	-16,659
Zn+2	7,8057E-08	2,4419E-08	-7,612
Zn2OH+3	2,1344E-16	1,5622E-17	-16,806
ZnCl+	2,6786E-08	2,0032E-08	-7,698
ZnCl2 (aq)	6,3161E-09	6,5887E-09	-8,181
ZnCl3-	2,7927E-09	2,0886E-09	-8,68
ZnCl4-2	9,5501E-10	2,9876E-10	-9,525
ZnOH+	8,1024E-10	6,0596E-10	-9,218
ZnSO4 (aq)	3,6647E-12	3,8228E-12	-11,418

Table 15 Chemical speciation of metals and some cations and ions estimated using Visual MINTEQ 3.1 in the sampled point P02 of the Maragogepe River in January of 2015. . The measured pH values, DOC (Dissolved Organic Carbon) and concentrations of Ca^{2+} , Cl^- , H^+ , K^+ , Mg^{2+} and SO_4^{2-} were used as a input parameters.

Especies Químicas	Concentration (mol / L)	Activity (mol / L)	Log activity (mol / L)
(6)Ca+2D(aq)	0,000014199	0,000014199	-4,848
(6)Cl-1D(aq)	1,718E-08	1,718E-08	-7,765
(6)Cu+2D(aq)	4,4543E-14	4,4543E-14	-13,351
(6)Fe+2D(aq)	1,3776E-13	1,3776E-13	-12,861
(6)H+1D(aq)	1,4236E-10	1,4236E-10	-9,847
(6)K+1D(aq)	7,4507E-08	7,4507E-08	-7,128
(6)Mg+2D(aq)	2,8251E-06	2,8251E-06	-5,549
(6)Ni+2D(aq)	6,5248E-11	6,5248E-11	-10,185
(6)NiCl+D(aq)	1,6476E-14	1,6476E-14	-13,783
(6)OH-D(aq)	1,1363E-14	1,1363E-14	-13,944
(6)SO4-2D(aq)	5,6489E-16	5,6489E-16	-15,248
(6)Zn+2D(aq)	8,368E-09	8,368E-09	-8,077
Ca+2	0,00005748	0,000017824	-4,749
CaCl+	0,000017532	0,000013083	-4,883
CaOH+	9,468E-11	7,0654E-11	-10,151
CaSO4 (aq)	2,8071E-09	2,9333E-09	-8,533
Cl-1	0,38169	0,28483	-0,545
Cu(OH)2 (aq)	9,7994E-16	1,024E-15	-14,99
Cu(OH)3-	3,8563E-19	2,8777E-19	-18,541
Cu(OH)4-2	3,0916E-24	9,5871E-25	-24,018
Cu+2	1,8032E-13	5,5917E-14	-13,252
Cu2(OH)2+2	8,8634E-23	2,7485E-23	-22,561
Cu2OH+3	1,3223E-25	9,4886E-27	-26,023
Cu3(OH)4+2	5,3296E-32	1,6527E-32	-31,782
CuCl+	4,4905E-14	3,3509E-14	-13,475
CuCl2 (aq)	3,1641E-15	3,3064E-15	-14,481
CuCl3-	1,2806E-17	9,5563E-18	-17,02
CuCl4-2 1	3,7561E-20	1,1648E-20	-19,934
CuHSO4+	8,537E-25	6,3706E-25	-24,196
CuOH+	3,9286E-14	2,9316E-14	-13,533
CuSO4 (aq)	8,8967E-18	9,2967E-18	-17,032
DOC (NICA-Donnan)	0,00042008	0,00042008	-3,377
FA1-Ca(6)(aq)	4,1004E-06	4,1004E-06	-5,387
FA1-Cu(6)(aq)	5,8661E-09	5,8661E-09	-8,232
FA1-Fe(II)(6)(aq)	1,325E-07	1,325E-07	-6,878
FA1-H(6)(aq)	3,2406E-06	3,2406E-06	-5,489
FA1-Mg(6)(aq)	1,5969E-06	1,5969E-06	-5,797
FA1-Ni(6)(aq)	2,7627E-09	2,7627E-09	-8,559
FA1-Zn(6)(aq)	3,4505E-09	3,4505E-09	-8,462
FA2-Ca(6)(aq)	1,204E-10	1,204E-10	-9,919
FA2-Cu(6)(aq)	8,6121E-09	8,6121E-09	-8,065
FA2-Fe(II)(6)(aq)	3,666E-13	3,666E-13	-12,436

FA2-H(6)(aq)	0,000015315	0,000015315	-4,815
FA2-Mg(6)(aq)	2,9219E-10	2,9219E-10	-9,534
FA2-Ni(6)(aq)	3,024E-10	3,024E-10	-9,519
FA2-Zn(6)(aq)	7,9347E-11	7,9347E-11	-10,1
Fe(OH)2 (aq)	1,955E-19	2,0429E-19	-18,69
Fe(OH)3-	1,1925E-22	8,8985E-23	-22,051
Fe+2	5,5767E-13	1,7293E-13	-12,762
FeCl+	4,1647E-14	3,1079E-14	-13,508
FeOH+	1,7381E-15	1,2971E-15	-14,887
FeSO4 (aq)	2,9351E-17	3,067E-17	-16,513
H+1	1,0165E-07	7,5858E-08	-7,12
HFA1-(6)(aq)	0,000039825	0,000039825	-4,4
HFA2-(6)(aq)	1,4784E-07	1,4784E-07	-6,83
HSO4-	7,8017E-12	5,8219E-12	-11,235
K+1	0,000053203	0,000039702	-4,401
KCl (aq)	5,2868E-06	5,5245E-06	-5,258
KOH (aq)	1,2439E-11	1,2999E-11	-10,886
KSO4-	2,8078E-10	2,0953E-10	-9,679
Mg+2	0,000011437	3,5466E-06	-5,45
MgCl+	5,5287E-06	4,1257E-06	-5,385
MgOH+	3,6036E-10	2,6891E-10	-9,57
MgSO4 (aq)	4,3999E-10	4,5977E-10	-9,337
Ni(OH)2 (aq)	1,3632E-15	1,4245E-15	-14,846
Ni(OH)3-	2,5174E-19	1,8786E-19	-18,726
Ni(SO4)2-2	8,2244E-22	2,5504E-22	-21,593
Ni+2	2,6414E-10	8,1909E-11	-10,087
NiCl+	1,1765E-11	8,7795E-12	-11,057
NiCl2 (aq)	8,1921E-14	8,5605E-14	-13,067
NiOH+	2,5377E-13	1,8937E-13	-12,723
NiSO4 (aq)	1,1142E-14	1,1643E-14	-13,934
OH-	2,5247E-07	1,884E-07	-6,725
SO4-2	2,2138E-06	6,8649E-07	-6,163
Z-(6)(aq)	-0,000034122	-0,000034122	0
Zn(OH)2 (aq)	2,201E-11	2,3E-11	-10,638
Zn(OH)3-	1,2853E-15	9,5916E-16	-15,018
Zn(OH)4-2	6,4648E-21	2,0047E-21	-20,698
Zn(SO4)2-2	3,042E-17	9,4333E-18	-17,025
Zn+2	3,3876E-08	1,0505E-08	-7,979
Zn2OH+3	3,0492E-17	2,1881E-18	-17,66
ZnCl+	1,197E-08	8,9323E-09	-8,049
ZnCl2 (aq)	2,8858E-09	3,0156E-09	-8,521
ZnCl3-	1,3283E-09	9,9122E-10	-9,004
ZnCl4-2	4,7384E-10	1,4694E-10	-9,833
ZnOH+	2,6521E-10	1,9791E-10	-9,704
ZnSO4 (aq)	1,5708E-12	1,6415E-12	-11,785

Table 16 Chemical speciation of metals and some cations and ions estimated using Visual MINTEQ 3.1 in the sampled point P03 of the Maragopipe River in January of 2015. . The measured pH values, DOC (Dissolved Organic Carbon) and concentrations of Ca^{2+} , Cl^- , H^+ , K^+ , Mg^{2+} and SO_4^{2-} were used as a input parameters.

Especies Químicas	Concentration (mol / L)	Activity (mol / L)	Log activity (mol / L)
(6)Ca+2D(aq)	0,000013771	0,000013771	-4,861
(6)Cl-1D(aq)	1,7182E-08	1,7182E-08	-7,765
(6)Cu+2D(aq)	1,4819E-15	1,4819E-15	-14,829
(6)Fe+2D(aq)	1,0493E-13	1,0493E-13	-12,979
(6)H+1D(aq)	1,7106E-11	1,7106E-11	-10,767
(6)K+1D(aq)	7,2479E-08	7,2479E-08	-7,14
(6)Mg+2D(aq)	0,000002592	0,000002592	-5,586
(6)Ni+2D(aq)	1,1731E-11	1,1731E-11	-10,931
(6)NiCl+D(aq)	3,1215E-15	3,1215E-15	-14,506
(6)OH-D(aq)	8,5883E-14	8,5883E-14	-13,066
(6)SO4-2D(aq)	6,1546E-16	6,1546E-16	-15,211
(6)Zn+2D(aq)	1,4622E-10	1,4622E-10	-9,835
Ca+2	0,000063555	0,000019612	-4,707
CaCl+	0,000019692	0,000014677	-4,833
CaOH+	8,0453E-10	5,9964E-10	-9,222
CaSO4 (aq)	3,2929E-09	3,444E-09	-8,463
Cl-1	0,38922	0,29009	-0,537
Cu(OH)2 (aq)	2,1785E-15	2,2785E-15	-14,642
Cu(OH)3-	6,3591E-18	4,7396E-18	-17,324
Cu(OH)4-2	4,0668E-22	1,255E-22	-21,901
Cu+2	6,8395E-15	2,1106E-15	-14,676
Cu2(OH)2+2	7,4418E-24	2,2965E-24	-23,639
Cu2OH+3	1,4549E-27	1,0326E-28	-27,986
Cu3(OH)4+2	9,8008E-33	3,0244E-33	-32,519
CuCl+	1,7321E-15	1,291E-15	-14,889
CuCl2 (aq)	1,2522E-16	1,3096E-16	-15,883
CuCl3-	5,1901E-19	3,8683E-19	-18,412
CuCl4-2 1	1,5461E-21	4,771E-22	-21,321
CuHSO4+	4,5297E-27	3,3761E-27	-26,472
CuOH+	1,1367E-14	8,4721E-15	-14,072
CuSO4 (aq)	3,5816E-19	3,7459E-19	-18,426
DOC (NICA-Donnan)	0,00040142	0,00040142	-3,396
FA1-Ca(6)(aq)	4,7743E-06	4,7743E-06	-5,321
FA1-Cu(6)(aq)	1,1338E-09	1,1338E-09	-8,945
FA1-Fe(II)(6)(aq)	1,4146E-07	1,4146E-07	-6,849
FA1-H(6)(aq)	9,4621E-07	9,4621E-07	-6,024
FA1-Mg(6)(aq)	1,7778E-06	1,7778E-06	-5,75
FA1-Ni(6)(aq)	1,07E-09	1,07E-09	-8,971
FA1-Zn(6)(aq)	2,7117E-10	2,7117E-10	-9,567
FA2-Ca(6)(aq)	5,5304E-10	5,5304E-10	-9,257
FA2-Cu(6)(aq)	1,1614E-08	1,1614E-08	-7,935
FA2-Fe(II)(6)(aq)	1,4775E-12	1,4775E-12	-11,83

FA2-H(6)(aq)	0,000014372	0,000014372	-4,842
FA2-Mg(6)(aq)	1,2918E-09	1,2918E-09	-8,889
FA2-Ni(6)(aq)	5,6457E-10	5,6457E-10	-9,248
FA2-Zn(6)(aq)	3,1295E-11	3,1295E-11	-10,505
Fe(OH)2 (aq)	1,002E-17	1,0479E-17	-16,98
Fe(OH)3-	4,6535E-20	3,4684E-20	-19,46
Fe+2	4,8427E-13	1,4944E-13	-12,826
FeCl+	3,67E-14	2,7353E-14	-13,563
FeOH+	1,1574E-14	8,6267E-15	-14,064
FeSO4 (aq)	2,7047E-17	2,8288E-17	-16,548
H+1	1,3417E-08	0,00000001	-8
HFA1-(6)(aq)	0,000039092	0,000039092	-4,408
HFA2-(6)(aq)	3,9871E-07	3,9871E-07	-6,399
HSO4-	1,1029E-12	8,2204E-13	-12,085
K+1	0,000056848	0,00004237	-4,373
KCl (aq)	5,7354E-06	5,9985E-06	-5,222
KOH (aq)	1,0208E-10	1,0677E-10	-9,972
KSO4-	3,2062E-10	2,3897E-10	-9,622
Mg+2	0,000011963	3,6915E-06	-5,433
MgCl+	5,8743E-06	4,3782E-06	-5,359
MgOH+	2,8972E-09	2,1594E-09	-8,666
MgSO4 (aq)	4,8809E-10	5,1048E-10	-9,292
Ni(OH)2 (aq)	1,5982E-14	1,6716E-14	-13,777
Ni(OH)3-	2,2433E-17	1,672E-17	-16,777
Ni(SO4)2-2	1,9123E-22	5,901E-23	-22,229
Ni+2	5,414E-11	1,6707E-11	-10,777
NiCl+	2,4483E-12	1,8248E-12	-11,739
NiCl2 (aq)	1,7318E-14	1,8112E-14	-13,742
NiOH+	3,9845E-13	2,9697E-13	-12,527
NiSO4 (aq)	2,4221E-15	2,5332E-15	-14,596
OH-	1,9455E-06	0,00000145	-5,839
SO4-2	2,3694E-06	7,3116E-07	-6,136
Z-(6)(aq)	-0,000032781	-0,000032781	0
Zn(OH)2 (aq)	2,508E-11	2,6231E-11	-10,581
Zn(OH)3-	1,1132E-14	8,297E-15	-14,081
Zn(OH)4-2	4,2624E-19	1,3153E-19	-18,881
Zn(SO4)2-2	6,8743E-19	2,1213E-19	-18,673
Zn+2	6,7485E-10	2,0825E-10	-9,681
Zn2OH+3	9,3445E-20	6,6322E-21	-20,178
ZnCl+	2,4231E-10	1,806E-10	-9,743
ZnCl2 (aq)	5,9847E-11	6,2593E-11	-10,203
ZnCl3-	2,8147E-11	2,0978E-11	-10,678
ZnCl4-2	1,028E-11	3,1722E-12	-11,499
ZnOH+	4,0515E-11	3,0197E-11	-10,52
ZnSO4 (aq)	3,3192E-14	3,4715E-14	-13,459

Table 17 Chemical speciation of metals and some cations and ions estimated using Visual MINTEQ 3.1 in the sampled point P04 of the Maragopipe River in January of 2015. . The measured pH values, DOC (Dissolved Organic Carbon) and concentrations of Ca^{2+} , Cl^- , H^+ , K^+ , Mg^{2+} and SO_4^{2-} were used as a input parameters.

Especies Químicas	Concentration (mol / L)	Activity (mol / L)	Log activity (mol / L)
(6)Ca+2D(aq)	0,000012444	0,000012444	-4,905
(6)Cl-1D(aq)	1,6722E-08	1,6722E-08	-7,777
(6)Cu+2D(aq)	1,9695E-15	1,9695E-15	-14,706
(6)Fe+2D(aq)	2,3192E-12	2,3192E-12	-11,635
(6)H+1D(aq)	1,8141E-11	1,8141E-11	-10,741
(6)K+1D(aq)	6,4376E-08	6,4376E-08	-7,191
(6)Mg+2D(aq)	2,1857E-06	2,1857E-06	-5,66
(6)Ni+2D(aq)	3,8394E-11	3,8394E-11	-10,416
(6)NiCl+D(aq)	1,2131E-14	1,2131E-14	-13,916
(6)OH-D(aq)	5,32E-14	5,32E-14	-13,274
(6)SO4-2D(aq)	4,4831E-16	4,4831E-16	-15,348
(6)Zn+2D(aq)	1,1991E-09	1,1991E-09	-8,921
Ca+2	0,000064524	0,000018746	-4,727
CaCl+	0,000025523	0,000018738	-4,727
CaOH+	6,6706E-10	4,8974E-10	-9,31
CaSO4 (aq)	3,1874E-09	3,3863E-09	-8,47
Cl-1	0,5253	0,38566	-0,414
Cu(OH)2 (aq)	2,1121E-15	2,2439E-15	-14,649
Cu(OH)3-	4,5166E-18	3,316E-18	-17,479
Cu(OH)4-2	2,9534E-22	8,5807E-23	-22,066
Cu+2	1,0212E-14	2,967E-15	-14,528
Cu2(OH)2+2	1,0692E-23	3,1065E-24	-23,508
Cu2OH+3	2,6935E-27	1,6692E-28	-27,777
Cu3(OH)4+2	1,2921E-32	3,754E-33	-32,426
CuCl+	3,3185E-15	2,4363E-15	-14,613
CuCl2 (aq)	3,2258E-16	3,4271E-16	-15,465
CuCl3-	1,8615E-18	1,3667E-18	-17,864
CuCl4-2	7,4922E-21	2,1767E-21	-20,662
CuHSO4+	8,302E-27	6,0951E-27	-26,215
CuOH+	1,3407E-14	9,8434E-15	-14,007
CuSO4 (aq)	5,1082E-19	5,427E-19	-18,265
DOC (NICA-Donnan)	0,00036833	0,00036833	-3,434
FA1-Ca(6)(aq)	4,5408E-06	4,5408E-06	-5,343
FA1-Cu(6)(aq)	1,2588E-09	1,2588E-09	-8,9
FA1-Fe(II)(6)(aq)	3,2229E-07	3,2229E-07	-6,492
FA1-H(6)(aq)	9,7107E-07	9,7107E-07	-6,013
FA1-Mg(6)(aq)	1,5833E-06	1,5833E-06	-5,8
FA1-Ni(6)(aq)	2,2773E-09	2,2773E-09	-8,643
FA1-Zn(6)(aq)	1,0992E-09	1,0992E-09	-8,959
FA2-Ca(6)(aq)	4,5399E-10	4,5399E-10	-9,343
FA2-Cu(6)(aq)	1,023E-08	1,023E-08	-7,99
FA2-Fe(II)(6)(aq)	5,9205E-12	5,9205E-12	-11,228

FA2-H(6)(aq)	0,000013241	0,000013241	-4,878
FA2-Mg(6)(aq)	9,8532E-10	9,8532E-10	-9,006
FA2-Ni(6)(aq)	8,7907E-10	8,7907E-10	-9,056
FA2-Zn(6)(aq)	9,5769E-11	9,5769E-11	-10,019
Fe(OH)2 (aq)	1,6668E-16	1,7708E-16	-15,752
Fe(OH)3-	6,3769E-19	4,6818E-19	-18,33
Fe+2	1,2026E-11	3,4939E-12	-11,457
FeCl+	1,158E-12	8,502E-13	-12,07
FeOH+	2,3245E-13	1,7066E-13	-12,768
FeSO4 (aq)	6,4105E-16	6,8105E-16	-15,167
H+1	1,7147E-08	1,2589E-08	-7,9
HFA1-(6)(aq)	0,000035461	0,000035461	-4,45
HFA2-(6)(aq)	3,1231E-07	3,1231E-07	-6,505
HSO4-	1,4751E-12	1,083E-12	-11,965
K+1	0,000060852	0,000044676	-4,35
KCl (aq)	7,8777E-06	8,3692E-06	-5,077
KOH (aq)	8,9663E-11	9,5258E-11	-10,021
KSO4-	3,5545E-10	2,6096E-10	-9,583
Mg+2	0,000011333	3,2928E-06	-5,482
MgCl+	7,1051E-06	5,2164E-06	-5,283
MgOH+	2,2437E-09	1,6473E-09	-8,783
MgSO4 (aq)	4,4021E-10	4,6768E-10	-9,33
Ni(OH)2 (aq)	3,4209E-14	3,6344E-14	-13,44
Ni(OH)3-	3,924E-17	2,8809E-17	-16,54
Ni(SO4)2-2	7,3177E-22	2,126E-22	-21,672
Ni+2	1,9908E-10	5,784E-11	-10,238
NiCl+	1,1467E-11	8,4186E-12	-11,075
NiCl2 (aq)	1,0432E-13	1,1083E-13	-12,955
NiOH+	1,1794E-12	8,6588E-13	-12,063
NiSO4 (aq)	8,4788E-15	9,0078E-15	-14,045
OH-	1,6712E-06	1,2269E-06	-5,911
SO4-2	2,5673E-06	7,4588E-07	-6,127
Z-(6)(aq)	-0,000029309	-0,000029309	0
Zn(OH)2 (aq)	1,345E-10	1,429E-10	-9,845
Zn(OH)3-	4,8789E-14	3,5819E-14	-13,446
Zn(OH)4-2	1,5489E-18	4,5001E-19	-18,347
Zn(SO4)2-2	6,5912E-18	1,915E-18	-17,718
Zn+2	6,2176E-09	1,8064E-09	-8,743
Zn2OH+3	6,8782E-18	4,2625E-19	-18,37
ZnCl+	2,8549E-09	2,096E-09	-8,679
ZnCl2 (aq)	9,4184E-10	1,0006E-09	-9
ZnCl3-	6,1042E-10	4,4816E-10	-9,349
ZnCl4-2	3,1225E-10	9,0718E-11	-10,042
ZnOH+	3,0189E-10	2,2164E-10	-9,654
ZnSO4 (aq)	2,9126E-13	3,0943E-13	-12,509

Table 18 Chemical speciation of metals and some cations and ions estimated using Visual MINTEQ 3.1 in the sampled point P05 of the Maragopipe River in January of 2015. . The measured pH values, DOC (Dissolved Organic Carbon) and concentrations of Ca^{2+} , Cl^- , H^+ , K^+ , Mg^{2+} and SO_4^{2-} were used as a input parameters.

Especies Químicas	Concentration (mol / L)	Activity (mol / L)	Log activity (mol / L)
(6)Ca+2D(aq)	0,000013516	0,000013516	-4,869
(6)Cl-1D(aq)	1,635E-08	1,635E-08	-7,786
(6)Cu+2D(aq)	2,3537E-15	2,3537E-15	-14,628
(6)Fe+2D(aq)	8,0526E-13	8,0526E-13	-12,094
(6)H+1D(aq)	2,7378E-11	2,7378E-11	-10,563
(6)K+1D(aq)	7,3589E-08	7,3589E-08	-7,133
(6)Mg+2D(aq)	2,5647E-06	2,5647E-06	-5,591
(6)Ni+2D(aq)	6,6816E-12	6,6816E-12	-11,175
(6)NiCl+D(aq)	1,6902E-15	1,6902E-15	-14,772
(6)OH-D(aq)	5,6402E-14	5,6402E-14	-13,249
(6)SO4-2D(aq)	6,2312E-16	6,2312E-16	-15,205
(6)Zn+2D(aq)	1,5634E-09	1,5634E-09	-8,806
Ca+2	0,000061769	0,000019369	-4,713
CaCl+	0,000018136	0,000013572	-4,867
CaOH+	5,1226E-10	3,8333E-10	-9,416
CaSO4 (aq)	3,28E-09	3,42E-09	-8,466
Cl-1	0,36242	0,2712	-0,567
Cu(OH)2 (aq)	1,4432E-15	1,5048E-15	-14,823
Cu(OH)3-	2,5459E-18	1,9051E-18	-17,72
Cu(OH)4-2	1,0891E-22	3,4152E-23	-22,467
Cu+2	1,0756E-14	3,3728E-15	-14,472
Cu2(OH)2+2	7,6699E-24	2,405E-24	-23,619
Cu2OH+3	2,2864E-27	1,6823E-28	-27,774
Cu3(OH)4+2	6,5155E-33	2,043E-33	-32,69
CuCl+	2,5858E-15	1,935E-15	-14,713
CuCl2 (aq)	1,785E-16	1,8611E-16	-15,73
CuCl3-	6,9034E-19	5,1658E-19	-18,287
CuCl4-2 1	1,8813E-21	5,899E-22	-21,229
CuHSO4+	1,1458E-26	8,574E-27	-26,067
CuOH+	1,1582E-14	8,667E-15	-14,062
CuSO4 (aq)	5,7765E-19	6,0229E-19	-18,22
DOC (NICA-Donnan)	0,00039233	0,00039233	-3,406
FA1-Ca(6)(aq)	4,3788E-06	4,3788E-06	-5,359
FA1-Cu(6)(aq)	1,3578E-09	1,3578E-09	-8,867
FA1-Fe(II)(6)(aq)	2,4531E-07	2,4531E-07	-6,61
FA1-H(6)(aq)	1,2067E-06	1,2067E-06	-5,918
FA1-Mg(6)(aq)	1,6455E-06	1,6455E-06	-5,784
FA1-Ni(6)(aq)	6,9403E-10	6,9403E-10	-9,159
FA1-Zn(6)(aq)	1,24E-09	1,24E-09	-8,907
FA2-Ca(6)(aq)	3,7442E-10	3,7442E-10	-9,427
FA2-Cu(6)(aq)	9,5015E-09	9,5015E-09	-8,022
FA2-Fe(II)(6)(aq)	2,8855E-12	2,8855E-12	-11,54

FA2-H(6)(aq)	0,00001413	0,00001413	-4,85
FA2-Mg(6)(aq)	8,8549E-10	8,8549E-10	-9,053
FA2-Ni(6)(aq)	2,8929E-10	2,8929E-10	-9,539
FA2-Zn(6)(aq)	9,1569E-11	9,1569E-11	-10,038
Fe(OH)2 (aq)	3,241E-17	3,3792E-17	-16,471
Fe(OH)3-	9,4599E-20	7,0789E-20	-19,15
Fe+2	3,68E-12	1,1539E-12	-11,938
FeCl+	2,6387E-13	1,9746E-13	-12,705
FeOH+	5,7435E-14	4,2979E-14	-13,367
FeSO4 (aq)	2,1073E-16	2,1971E-16	-15,658
H+1	2,118E-08	1,5849E-08	-7,8
HFA1-(6)(aq)	0,000038197	0,000038197	-4,418
HFA2-(6)(aq)	3,0895E-07	3,0895E-07	-6,51
HSO4-	1,7607E-12	1,3175E-12	-11,88
K+1	0,000056928	0,0000426	-4,371
KCl (aq)	5,3991E-06	5,6294E-06	-5,25
KOH (aq)	6,6427E-11	6,9261E-11	-10,16
KSO4-	3,2358E-10	2,4214E-10	-9,616
Mg+2	0,000011721	3,6752E-06	-5,435
MgCl+	5,4543E-06	4,0815E-06	-5,389
MgOH+	1,8603E-09	1,3921E-09	-8,856
MgSO4 (aq)	4,8988E-10	5,1078E-10	-9,292
Ni(OH)2 (aq)	3,661E-15	3,8172E-15	-14,418
Ni(OH)3-	3,2209E-18	2,4102E-18	-17,618
Ni(SO4)2-2	1,0844E-22	3,4003E-23	-22,468
Ni+2	3,0535E-11	9,5746E-12	-11,019
NiCl+	1,3075E-12	9,7845E-13	-12,009
NiCl2 (aq)	8,7011E-15	9,0722E-15	-14,042
NiOH+	1,4651E-13	1,0964E-13	-12,96
NiSO4 (aq)	1,3993E-15	1,459E-15	-14,836
OH-	1,2503E-06	9,3558E-07	-6,029
SO4-2	2,3382E-06	7,3316E-07	-6,135
Z-(6)(aq)	-0,000032222	-0,000032222	0
Zn(OH)2 (aq)	1,0784E-10	1,1244E-10	-9,949
Zn(OH)3-	3,0003E-14	2,2451E-14	-13,649
Zn(OH)4-2	7,1652E-19	2,2467E-19	-18,648
Zn(SO4)2-2	7,3178E-18	2,2946E-18	-17,639
Zn+2	7,1447E-09	2,2403E-09	-8,65
Zn2OH+3	6,7521E-18	4,9679E-19	-18,304
ZnCl+	2,4325E-09	1,8202E-09	-8,74
ZnCl2 (aq)	5,7239E-10	5,9681E-10	-9,224
ZnCl3-	2,5033E-10	1,8732E-10	-9,727
ZnCl4-2	8,4648E-11	2,6543E-11	-10,576
ZnOH+	2,801E-10	2,096E-10	-9,679
ZnSO4 (aq)	3,6003E-13	3,7539E-13	-12,426

Table 19 Chemical speciation of metals and some cations and ions estimated using Visual MINTEQ 3.1 in the sampled point P06 of the Maragopipe River in January of 2015. . The measured pH values, DOC (Dissolved Organic Carbon) and concentrations of Ca^{2+} , Cl^- , H^+ , K^+ , Mg^{2+} and SO_4^{2-} were used as a input parameters.

Especies Químicas	Concentration (mol / L)	Activity (mol / L)	Log activity (mol / L)
(6)Ca+2D(aq)	0,000014172	0,000014172	-4,849
(6)Cl-1D(aq)	1,7297E-08	1,7297E-08	-7,762
(6)Cu+2D(aq)	1,9153E-15	1,9153E-15	-14,718
(6)Fe+2D(aq)	3,7875E-13	3,7875E-13	-12,422
(6)H+1D(aq)	1,1281E-11	1,1281E-11	-10,948
(6)K+1D(aq)	7,5502E-08	7,5502E-08	-7,122
(6)Mg+2D(aq)	2,6158E-06	2,6158E-06	-5,582
(6)Ni+2D(aq)	2,4475E-11	2,4475E-11	-10,611
(6)NiCl+D(aq)	6,4603E-15	6,4603E-15	-14,19
(6)OH-D(aq)	1,7241E-13	1,7241E-13	-12,763
(6)SO4-2D(aq)	5,8566E-16	5,8566E-16	-15,232
(6)Zn+2D(aq)	5,2925E-09	5,2925E-09	-8,276
Ca+2	0,000060917	0,000018553	-4,732
CaCl+	0,000019472	0,000014465	-4,84
CaOH+	1,6175E-09	1,2016E-09	-8,92
CaSO4 (aq)	3,1713E-09	3,3207E-09	-8,479
Cl-1	0,39954	0,29681	-0,528
Cu(OH)2 (aq)	9,8942E-15	1,036E-14	-13,985
Cu(OH)3-	3,0157E-17	2,2403E-17	-16,65
Cu(OH)4-2	6,9259E-21	2,1094E-21	-20,676
Cu+2	8,2323E-15	2,5073E-15	-14,601
Cu2(OH)2+2	3,725E-23	1,1345E-23	-22,945
Cu2OH+3	3,7868E-27	2,6095E-28	-27,583
Cu3(OH)4+2	1,6982E-31	5,172E-32	-31,286
CuCl+	2,1932E-15	1,6293E-15	-14,788
CuCl2 (aq)	1,8999E-16	1,9894E-16	-15,701
CuCl3-	8,5877E-19	6,3797E-19	-18,195
CuCl4-2 1	2,3633E-21	7,1978E-22	-21,143
CuHSO4+	3,3622E-27	2,4977E-27	-26,602
CuOH+	2,5247E-14	1,8756E-14	-13,727
CuSO4 (aq)	4,3631E-19	4,5687E-19	-18,34
DOC (NICA-Donnan)	0,00041183	0,00041183	-3,385
FA1-Ca(6)(aq)	4,9847E-06	4,9847E-06	-5,302
FA1-Cu(6)(aq)	1,328E-09	1,328E-09	-8,877
FA1-Fe(II)(6)(aq)	2,1308E-07	2,1308E-07	-6,671
FA1-H(6)(aq)	7,3394E-07	7,3394E-07	-6,134
FA1-Mg(6)(aq)	1,8257E-06	1,8257E-06	-5,739
FA1-Ni(6)(aq)	1,7622E-09	1,7622E-09	-8,754
FA1-Zn(6)(aq)	3,0654E-09	3,0654E-09	-8,514
FA2-Ca(6)(aq)	7,903E-10	7,903E-10	-9,102
FA2-Cu(6)(aq)	1,7872E-08	1,7872E-08	-7,748
FA2-Fe(II)(6)(aq)	3,9832E-12	3,9832E-12	-11,4

FA2-H(6)(aq)	0,000014633	0,000014633	-4,835
FA2-Mg(6)(aq)	1,8178E-09	1,8178E-09	-8,74
FA2-Ni(6)(aq)	1,1676E-09	1,1676E-09	-8,933
FA2-Zn(6)(aq)	3,91E-10	3,91E-10	-9,408
Fe(OH)2 (aq)	1,4331E-16	1,5007E-16	-15,824
Fe(OH)3-	1,0926E-18	8,1168E-19	-18,091
Fe+2	1,628E-12	4,9582E-13	-12,305
FeCl+	1,2499E-13	9,2855E-14	-13,032
FeOH+	7,8606E-14	5,8395E-14	-13,234
FeSO4 (aq)	9,1731E-17	9,6053E-17	-16,017
H+1	8,4934E-09	6,3096E-09	-8,2
HFA1-(6)(aq)	0,000040184	0,000040184	-4,396
HFA2-(6)(aq)	5,1282E-07	5,1282E-07	-6,29
HSO4-	7,6123E-13	5,655E-13	-12,248
K+1	0,000056844	0,000042228	-4,374
KCl (aq)	5,7367E-06	0,000006007	-5,221
KOH (aq)	2,0733E-10	2,171E-10	-9,663
KSO4-	3,3546E-10	2,4921E-10	-9,603
Mg+2	0,000011243	3,4243E-06	-5,465
MgCl+	5,6959E-06	4,2314E-06	-5,374
MgOH+	5,7343E-09	4,2599E-09	-8,371
MgSO4 (aq)	4,5823E-10	4,7982E-10	-9,319
Ni(OH)2 (aq)	7,6874E-14	8,0496E-14	-13,094
Ni(OH)3-	1,7175E-16	1,2759E-16	-15,894
Ni(SO4)2-2	3,62E-22	1,1025E-22	-21,958
Ni+2	1,052E-10	3,2041E-11	-10,494
NiCl+	4,8638E-12	3,6133E-12	-11,442
NiCl2 (aq)	3,4727E-14	3,6364E-14	-13,439
NiOH+	1,5361E-12	1,1411E-12	-11,943
NiSO4 (aq)	4,7013E-15	4,9228E-15	-14,308
OH-	3,9823E-06	2,9584E-06	-5,529
SO4-2	2,3695E-06	7,2167E-07	-6,142
Z-(6)(aq)	-0,000033645	-0,000033645	0
Zn(OH)2 (aq)	2,0927E-09	2,1913E-09	-8,659
Zn(OH)3-	1,4785E-12	1,0983E-12	-11,959
Zn(OH)4-2	9,0593E-17	2,7592E-17	-16,559
Zn(SO4)2-2	2,2575E-17	6,8757E-18	-17,163
Zn+2	2,2749E-08	6,9285E-09	-8,159
Zn2OH+3	2,2537E-16	1,553E-17	-16,809
ZnCl+	8,4805E-09	6,3E-09	-8,201
ZnCl2 (aq)	2,4461E-09	2,5614E-09	-8,592
ZnCl3-	1,2062E-09	8,9603E-10	-9,048
ZnCl4-2	4,6749E-10	1,4238E-10	-9,847
ZnOH+	2,7591E-09	2,0497E-09	-8,688
ZnSO4 (aq)	1,1197E-12	1,1724E-12	-11,931

Table 20 Chemical speciation of metals and some cations and ions estimated using Visual MINTEQ 3.1 in the sampled point P01 of the Jaguaripe River in January of 2015. . The measured pH values, DOC (Dissolved Organic Carbon) and concentrations of Ca^{2+} , Cl^- , H^+ , K^+ , Mg^{2+} and SO_4^{2-} were used as a input parameters.

Especies Químicas	Concentration (mol / L)	Activity (mol / L)	Log activity (mol / L)
(6)Ca+2D(aq)	0,000014718	0,000014718	-4,832
(6)Cl-1D(aq)	1,7256E-08	1,7256E-08	-7,763
(6)Cu+2D(aq)	8,3429E-15	8,3429E-15	-14,079
(6)Fe+2D(aq)	2,7886E-12	2,7886E-12	-11,555
(6)H+1D(aq)	7,4397E-11	7,4397E-11	-10,128
(6)K+1D(aq)	7,9585E-08	7,9585E-08	-7,099
(6)Mg+2D(aq)	1,3571E-06	1,3571E-06	-5,867
(6)Ni+2D(aq)	1,2997E-23	1,2997E-23	-22,886
(6)NiCl+D(aq)	3,5522E-27	3,5522E-27	-26,449
(6)OH-D(aq)	1,5705E-14	1,5705E-14	-13,804
(6)SO4-2D(aq)	7,0627E-16	7,0627E-16	-15,151
(6)Zn+2D(aq)	1,6618E-09	1,6618E-09	-8,779
Ca+2	0,000073032	0,000022615	-4,646
CaCl+	0,000022556	0,000016826	-4,774
CaOH+	1,6553E-10	1,2348E-10	-9,908
CaSO4 (aq)	4,1815E-09	4,3746E-09	-8,359
Cl-1	0,39156	0,29209	-0,534
Cu(OH)2 (aq)	4,7147E-16	4,9324E-16	-15,307
Cu(OH)3-	4,0404E-19	3,014E-19	-18,521
Cu(OH)4-2	3,204E-24	9,9217E-25	-24,003
Cu+2	4,1398E-14	1,2819E-14	-13,892
Cu2(OH)2+2	1,0379E-23	3,214E-24	-23,493
Cu2OH+3	1,0696E-26	7,651E-28	-27,116
Cu3(OH)4+2	3,5809E-33	1,1089E-33	-32,955
CuCl+	1,0309E-14	7,6904E-15	-14,114
CuCl2 (aq)	6,7022E-16	7,0115E-16	-15,154
CuCl3-	2,6819E-18	2,0006E-18	-17,699
CuCl4-2 1	8,6764E-21	2,6868E-21	-20,571
CuHSO4+	1,4155E-25	1,056E-25	-24,976
CuOH+	1,3473E-14	1,0051E-14	-13,998
CuSO4 (aq)	2,3835E-18	2,4936E-18	-17,603
DOC (NICA-Donnan)	0,00039275	0,00039275	-3,406
FA1-Ca(6)(aq)	0,00000446	0,00000446	-5,351
FA1-Cu(6)(aq)	2,4812E-09	2,4812E-09	-8,605
FA1-Fe(II)(6)(aq)	3,2945E-07	3,2945E-07	-6,482
FA1-H(6)(aq)	2,1934E-06	2,1934E-06	-5,659
FA1-Mg(6)(aq)	9,5164E-07	9,5164E-07	-6,022
FA1-Ni(6)(aq)	1,5922E-17	1,5922E-17	-16,798
FA1-Zn(6)(aq)	1,2144E-09	1,2144E-09	-8,916
FA2-Ca(6)(aq)	1,8978E-10	1,8978E-10	-9,722
FA2-Cu(6)(aq)	6,9614E-09	6,9614E-09	-8,157
FA2-Fe(II)(6)(aq)	2,5422E-12	2,5422E-12	-11,595

FA2-H(6)(aq)	0,000014277	0,000014277	-4,845
FA2-Mg(6)(aq)	2,8539E-10	2,8539E-10	-9,545
FA2-Ni(6)(aq)	8,4086E-17	8,4086E-17	-16,075
FA2-Zn(6)(aq)	4,4633E-11	4,4633E-11	-10,35
Fe(OH) ₂ (aq)	9,4121E-18	9,8466E-18	-17,007
Fe(OH) ₃ ⁻	9,3534E-21	6,9774E-21	-20,156
Fe ⁺²	1,3837E-11	4,2848E-12	-11,368
FeCl ⁺	1,0586E-12	7,8967E-13	-12,103
FeOH ⁺	6,0789E-14	4,5347E-14	-13,343
FeSO ₄ (aq)	8,5158E-16	8,9089E-16	-15,05
H ⁺¹	6,1274E-08	4,5709E-08	-7,34
HFA1-(6)(aq)	0,000037787	0,000037787	-4,423
HFA2-(6)(aq)	1,813E-07	1,813E-07	-6,742
HSO ₄ ⁻	5,3038E-12	3,9565E-12	-11,403
K ⁺¹	0,000065547	0,000048896	-4,311
KCl (aq)	6,7474E-06	7,0589E-06	-5,151
KOH (aq)	2,1592E-11	2,2589E-11	-10,646
KSO ₄ ⁻	3,9982E-10	2,9826E-10	-9,525
Mg ⁺²	6,7338E-06	2,0852E-06	-5,681
MgCl ⁺	3,2961E-06	2,4588E-06	-5,609
MgOH ⁺	2,9137E-10	2,1735E-10	-9,663
MgSO ₄ (aq)	3,0487E-10	3,1895E-10	-9,496
Ni(OH) ₂ (aq)	9,141E-28	9,5629E-28	-27,019
Ni(OH) ₃ ⁻	2,8052E-31	2,0926E-31	-30,679
Ni(SO ₄) ₂ ⁻²	2,8912E-34	8,9529E-35	-34,048
Ni ⁺²	6,4493E-23	1,9971E-23	-22,7
NiCl ⁺	2,9257E-24	2,1825E-24	-23,661
NiCl ₂ (aq)	2,0981E-26	2,195E-26	-25,659
NiOH ⁺	8,8357E-26	6,5912E-26	-25,181
NiSO ₄ (aq)	3,2016E-27	3,3494E-27	-26,475
OH ⁻	3,5637E-07	2,6584E-07	-6,575
SO ₄ ⁻²	2,6601E-06	8,2372E-07	-6,084
Z ⁻⁽⁶⁾ (aq)	-0,000032216	-0,000032216	0
Zn(OH) ₂ (aq)	1,4714E-11	1,5393E-11	-10,813
Zn(OH) ₃ ⁻	1,4279E-15	1,0652E-15	-14,973
Zn(OH) ₄ ⁻²	1,1929E-20	3,6941E-21	-20,432
Zn(SO ₄) ₂ ⁻²	1,0661E-17	3,3013E-18	-17,481
Zn ⁺²	8,246E-09	2,5535E-09	-8,593
Zn ₂ OH ⁺³	2,4917E-18	1,7824E-19	-18,749
ZnCl ⁺	2,9383E-09	2,1919E-09	-8,659
ZnCl ₂ (aq)	6,6448E-10	6,9515E-10	-9,158
ZnCl ₃ ⁻	3,1013E-10	2,3134E-10	-9,636
ZnCl ₄ ⁻²	1,1164E-10	3,4571E-11	-10,461
ZnOH ⁺	9,0997E-11	6,7881E-11	-10,168
ZnSO ₄ (aq)	4,4947E-13	4,7022E-13	-12,328

Table 21 Chemical speciation of metals and some cations and ions estimated using Visual MINTEQ 3.1 in the sampled point P02 of the Jaguaripe River in January of 2015. . The measured pH values, DOC (Dissolved Organic Carbon) and concentrations of Ca^{2+} , Cl^- , H^+ , K^+ , Mg^{2+} and SO_4^{2-} were used as a input parameters.

Especies Químicas	Concentration (mol / L)	Activity (mol / L)	Log activity (mol / L)
(6)Ca+2D(aq)	0,000015384	0,000015384	-4,813
(6)Cl-1D(aq)	1,9768E-08	1,9768E-08	-7,704
(6)Cu+2D(aq)	7,5557E-15	7,5557E-15	-14,122
(6)Fe+2D(aq)	8,1396E-12	8,1396E-12	-11,089
(6)H+1D(aq)	1,3055E-10	1,3055E-10	-9,884
(6)K+1D(aq)	8,6432E-08	8,6432E-08	-7,063
(6)Mg+2D(aq)	2,7029E-06	2,7029E-06	-5,568
(6)Ni+2D(aq)	4,4449E-11	4,4449E-11	-10,352
(6)NiCl+D(aq)	1,2489E-14	1,2489E-14	-13,903
(6)OH-D(aq)	1,0602E-14	1,0602E-14	-13,975
(6)SO4-2D(aq)	6,9422E-16	6,9422E-16	-15,159
(6)Zn+2D(aq)	2,9962E-09	2,9962E-09	-8,523
Ca+2	0,000065716	0,000020044	-4,698
CaCl+	0,000021457	0,000015946	-4,797
CaOH+	9,2631E-11	6,8839E-11	-10,162
CaSO4 (aq)	3,444E-09	3,6152E-09	-8,442
Cl-1	0,42095	0,31283	-0,505
Cu(OH)2 (aq)	1,4479E-16	1,5198E-16	-15,818
Cu(OH)3-	8,3703E-20	6,2204E-20	-19,206
Cu(OH)4-2	4,0343E-25	1,2305E-25	-24,91
Cu+2	3,2276E-14	9,8445E-15	-14,007
Cu2(OH)2+2	2,5132E-24	7,6655E-25	-24,115
Cu2OH+3	4,1664E-27	2,8805E-28	-27,541
Cu3(OH)4+2	2,7368E-34	8,3475E-35	-34,078
CuCl+	8,483E-15	6,3042E-15	-14,2
CuCl2 (aq)	5,7808E-16	6,0681E-16	-15,217
CuCl3-	2,4822E-18	1,8447E-18	-17,734
CuCl4-2	8,7852E-21	2,6796E-21	-20,572
CuHSO4+	1,5803E-25	1,1744E-25	-24,93
CuOH+	6,6071E-15	4,9101E-15	-14,309
CuSO4 (aq)	1,6999E-18	1,7844E-18	-17,749
DOC (NICA-Donnan)	0,00044883	0,00044883	-3,348
FA1-Ca(6)(aq)	4,4755E-06	4,4755E-06	-5,349
FA1-Cu(6)(aq)	2,3434E-09	2,3434E-09	-8,63
FA1-Fe(II)(6)(aq)	4,6193E-07	4,6193E-07	-6,335
FA1-H(6)(aq)	3,1266E-06	3,1266E-06	-5,505
FA1-Mg(6)(aq)	1,5749E-06	1,5749E-06	-5,803
FA1-Ni(6)(aq)	2,1994E-09	2,1994E-09	-8,658
FA1-Zn(6)(aq)	1,7712E-09	1,7712E-09	-8,752
FA2-Ca(6)(aq)	1,4644E-10	1,4644E-10	-9,834
FA2-Cu(6)(aq)	5,2107E-09	5,2107E-09	-8,283
FA2-Fe(II)(6)(aq)	3,3585E-12	3,3585E-12	-11,474

FA2-H(6)(aq)	0,000016364	0,000016364	-4,786
FA2-Mg(6)(aq)	3,2543E-10	3,2543E-10	-9,488
FA2-Ni(6)(aq)	2,8224E-10	2,8224E-10	-9,549
FA2-Zn(6)(aq)	4,8471E-11	4,8471E-11	-10,315
Fe(OH) ₂ (aq)	9,2178E-18	9,6759E-18	-17,014
Fe(OH) ₃ ⁻	5,9378E-21	4,4127E-21	-20,355
Fe ⁺²	3,477E-11	1,0605E-11	-10,974
FeCl ⁺	2,8167E-12	2,0933E-12	-11,679
FeOH ⁺	9,5315E-14	7,0834E-14	-13,15
FeSO ₄ (aq)	1,958E-15	2,0553E-15	-14,687
H ⁺¹	9,5262E-08	7,0795E-08	-7,15
HFA1-(6)(aq)	0,00004261	0,00004261	-4,37
HFA2-(6)(aq)	1,6122E-07	1,6122E-07	-6,793
HSO ₄ ⁻	7,646E-12	5,6821E-12	-11,245
K ⁺¹	0,000063071	0,000046872	-4,329
KCl (aq)	6,9149E-06	7,2586E-06	-5,139
KOH (aq)	1,3019E-11	1,3666E-11	-10,864
KSO ₄ ⁻	3,579E-10	2,6597E-10	-9,575
Mg ⁺²	0,000011546	3,5216E-06	-5,453
MgCl ⁺	0,000005975	4,4403E-06	-5,353
MgOH ⁺	3,1062E-10	2,3084E-10	-9,637
MgSO ₄ (aq)	4,7873E-10	5,0252E-10	-9,299
Ni(OH) ₂ (aq)	1,1002E-15	1,1549E-15	-14,937
Ni(OH) ₃ ⁻	2,1945E-19	1,6308E-19	-18,788
Ni(SO ₄) ₂ ⁻²	7,4427E-22	2,2701E-22	-21,644
Ni ⁺²	1,8987E-10	5,7913E-11	-10,237
NiCl ⁺	9,1135E-12	6,7727E-12	-11,169
NiCl ₂ (aq)	6,9553E-14	7,3011E-14	-13,137
NiOH ⁺	1,6258E-13	1,2082E-13	-12,918
NiSO ₄ (aq)	8,6322E-15	9,0613E-15	-14,043
OH ⁻	2,2576E-07	1,6777E-07	-6,775
SO ₄ ⁻²	2,5253E-06	7,7025E-07	-6,113
Z ⁻⁽⁶⁾ (aq)	-0,000036246	-0,000036246	0
Zn(OH) ₂ (aq)	9,3362E-12	9,8003E-12	-11,009
Zn(OH) ₃ ⁻	5,8889E-16	4,3764E-16	-15,359
Zn(OH) ₄ ⁻²	3,2113E-21	9,7947E-22	-21,009
Zn(SO ₄) ₂ ⁻²	1,4469E-17	4,4132E-18	-17,355
Zn ⁺²	1,2799E-08	3,9038E-09	-8,409
Zn ₂ OH ⁺³	3,7908E-18	2,6208E-19	-18,582
ZnCl ⁺	4,819E-09	3,5812E-09	-8,446
ZnCl ₂ (aq)	1,1449E-09	1,2018E-09	-8,92
ZnCl ₃ ⁻	5,754E-10	4,2761E-10	-9,369
ZnCl ₄ ⁻²	2,2385E-10	6,8275E-11	-10,166
ZnOH ⁺	8,8132E-11	6,5495E-11	-10,184
ZnSO ₄ (aq)	6,388E-13	6,7056E-13	-12,174

Table 22 Chemical speciation of metals and some cations and ions estimated using Visual MINTEQ 3.1 in the sampled point P03 of the Jaguaripe River in January of 2015. . The measured pH values, DOC (Dissolved Organic Carbon) and concentrations of Ca^{2+} , Cl^- , H^+ , K^+ , Mg^{2+} and SO_4^{2-} were used as a input parameters.

Especies Químicas	Concentration (mol / L)	Activity (mol / L)	Log activity (mol / L)
(6)Ca+2D(aq)	0,000016963	0,000016963	-4,771
(6)Cl-1D(aq)	2,1173E-08	2,1173E-08	-7,674
(6)Cu+2D(aq)	3,5246E-15	3,5246E-15	-14,453
(6)Fe+2D(aq)	1,9287E-11	1,9287E-11	-10,715
(6)H+1D(aq)	1,4464E-10	1,4464E-10	-9,84
(6)K+1D(aq)	9,443E-08	9,443E-08	-7,025
(6)Mg+2D(aq)	2,9892E-06	2,9892E-06	-5,524
(6)Ni+2D(aq)	4,4119E-11	4,4119E-11	-10,355
(6)NiCl+D(aq)	1,1939E-14	1,1939E-14	-13,923
(6)OH-D(aq)	1,2229E-14	1,2229E-14	-13,913
(6)SO4-2D(aq)	7,3067E-16	7,3067E-16	-15,136
(6)Zn+2D(aq)	6,8881E-09	6,8881E-09	-8,162
Ca+2	0,000062925	0,000019305	-4,714
CaCl+	0,000020086	0,000014949	-4,825
CaOH+	9,3544E-11	6,9619E-11	-10,157
CaSO4 (aq)	3,2405E-09	3,3967E-09	-8,469
Cl-1	0,40848	0,30401	-0,517
Cu(OH)2 (aq)	6,4235E-17	6,7331E-17	-16,172
Cu(OH)3-	3,6515E-20	2,7176E-20	-19,566
Cu(OH)4-2	1,926E-25	5,9087E-26	-25,229
Cu+2	1,3075E-14	4,0112E-15	-14,397
Cu2(OH)2+2	4,4748E-25	1,3728E-25	-24,862
Cu2OH+3	7,0634E-28	4,9478E-29	-28,306
Cu3(OH)4+2	2,1075E-35	6,4655E-36	-35,189
CuCl+	3,3652E-15	2,5045E-15	-14,601
CuCl2 (aq)	2,2673E-16	2,3766E-16	-15,624
CuCl3-	9,4833E-19	7,0578E-19	-18,151
CuCl4-2 1	3,2156E-21	9,8651E-22	-21,006
CuHSO4+	6,1123E-26	4,549E-26	-25,342
CuOH+	2,791E-15	2,0772E-15	-14,683
CuSO4 (aq)	6,771E-19	7,0973E-19	-18,149
DOC (NICA-Donnan)	0,00049392	0,00049392	-3,306
FA1-Ca(6)(aq)	4,8134E-06	4,8134E-06	-5,318
FA1-Cu(6)(aq)	1,6053E-09	1,6053E-09	-8,794
FA1-Fe(II)(6)(aq)	6,3019E-07	6,3019E-07	-6,201
FA1-H(6)(aq)	3,3831E-06	3,3831E-06	-5,471
FA1-Mg(6)(aq)	1,6998E-06	1,6998E-06	-5,77
FA1-Ni(6)(aq)	2,2159E-09	2,2159E-09	-8,654
FA1-Zn(6)(aq)	3,125E-09	3,125E-09	-8,505
FA2-Ca(6)(aq)	1,6049E-10	1,6049E-10	-9,795
FA2-Cu(6)(aq)	4,2176E-09	4,2176E-09	-8,375
FA2-Fe(II)(6)(aq)	5,4609E-12	5,4609E-12	-11,263

FA2-H(6)(aq)	0,00001801	0,00001801	-4,744
FA2-Mg(6)(aq)	3,5841E-10	3,5841E-10	-9,446
FA2-Ni(6)(aq)	2,9375E-10	2,9375E-10	-9,532
FA2-Zn(6)(aq)	8,3398E-11	8,3398E-11	-10,079
Fe(OH)2 (aq)	2,0993E-17	2,2005E-17	-16,657
Fe(OH)3-	1,3839E-20	1,0299E-20	-19,987
Fe+2	7,1544E-11	2,1949E-11	-10,659
FeCl+	5,657E-12	4,2102E-12	-11,376
FeOH+	2,0616E-13	1,5343E-13	-12,814
FeSO4 (aq)	3,9603E-15	4,1512E-15	-14,382
H+1	9,2959E-08	6,9183E-08	-7,16
HFA1-(6)(aq)	0,00004697	0,00004697	-4,328
HFA2-(6)(aq)	1,7666E-07	1,7666E-07	-6,753
HSO4-	7,3192E-12	5,4472E-12	-11,264
K+1	0,000060691	0,000045168	-4,345
KCl (aq)	6,4746E-06	6,7867E-06	-5,168
KOH (aq)	1,3149E-11	1,3782E-11	-10,861
KSO4-	3,3674E-10	2,5061E-10	-9,601
Mg+2	0,000011089	3,4019E-06	-5,468
MgCl+	5,6098E-06	0,000004175	-5,379
MgOH+	3,147E-10	2,3421E-10	-9,63
MgSO4 (aq)	4,5155E-10	4,7331E-10	-9,325
Ni(OH)2 (aq)	1,0007E-15	1,0489E-15	-14,979
Ni(OH)3-	2,037E-19	1,516E-19	-18,819
Ni(SO4)2-2	6,0706E-22	1,8624E-22	-21,73
Ni+2	1,6366E-10	5,021E-11	-10,299
NiCl+	7,6735E-12	5,7109E-12	-11,243
NiCl2 (aq)	5,7031E-14	5,978E-14	-13,223
NiOH+	1,4707E-13	1,0945E-13	-12,961
NiSO4 (aq)	7,3076E-15	7,6598E-15	-14,116
OH-	2,3593E-07	1,7559E-07	-6,756
SO4-2	2,4423E-06	7,4928E-07	-6,125
Z-(6)(aq)	-0,000039992	-0,000039992	0
Zn(OH)2 (aq)	1,9668E-11	2,0616E-11	-10,686
Zn(OH)3-	1,2661E-15	9,4225E-16	-15,026
Zn(OH)4-2	7,0355E-21	2,1584E-21	-20,666
Zn(SO4)2-2	2,7334E-17	8,3859E-18	-17,076
Zn+2	2,5552E-08	7,8391E-09	-8,106
Zn2OH+3	1,584E-17	1,1095E-18	-17,955
ZnCl+	9,4105E-09	7,0037E-09	-8,155
ZnCl2 (aq)	2,2055E-09	2,3118E-09	-8,636
ZnCl3-	1,0759E-09	8,0074E-10	-9,097
ZnCl4-2	4,0594E-10	1,2454E-10	-9,905
ZnOH+	1,8495E-10	1,3764E-10	-9,861
ZnSO4 (aq)	1,2527E-12	1,3131E-12	-11,882

Table 23 Chemical speciation of metals and some cations and ions estimated using Visual MINTEQ 3.1 in the sampled point P04 of the Jaguaripe River in January of 2015. . The measured pH values, DOC (Dissolved Organic Carbon) and concentrations of Ca²⁺, Cl⁻, H⁺, K⁺, Mg²⁺ and SO₄²⁻ were used as a input parameters.

Especies Químicas	Concentration (mol / L)	Activity (mol / L)	Log activity (mol / L)
(6)Ca+2D(aq)	0,0000212	0,0000212	-4,674
(6)Cl-1D(aq)	2,049E-08	2,049E-08	-7,688
(6)Cu+2D(aq)	1,9879E-15	1,9879E-15	-14,702
(6)Fe+2D(aq)	8,6399E-11	8,6399E-11	-10,063
(6)H+1D(aq)	1,5195E-10	1,5195E-10	-9,818
(6)K+1D(aq)	1,2218E-07	1,2218E-07	-6,913
(6)Mg+2D(aq)	2,1248E-06	2,1248E-06	-5,673
(6)Ni+2D(aq)	1,4536E-23	1,4536E-23	-22,838
(6)NiCl+D(aq)	3,2037E-27	3,2037E-27	-26,494
(6)OH-D(aq)	1,7065E-14	1,7065E-14	-13,768
(6)SO4-2D(aq)	6,0871E-16	6,0871E-16	-15,216
(6)Zn+2D(aq)	1,7951E-08	1,7951E-08	-7,746
Ca+2	0,000049211	0,000015391	-4,813
CaCl+	0,000014696	0,00001099	-4,959
CaOH+	9,874E-11	7,3841E-11	-10,132
CaSO4 (aq)	2,3998E-09	2,5056E-09	-8,601
Cl-1	0,37464	0,28017	-0,553
Cu(OH)2 (aq)	4,0869E-17	4,2672E-17	-16,37
Cu(OH)3-	3,0004E-20	2,2438E-20	-19,649
Cu(OH)4-2	2,1069E-25	6,5894E-26	-25,181
Cu+2	4,6143E-15	1,4432E-15	-14,841
Cu2(OH)2+2	9,9825E-26	3,1221E-26	-25,506
Cu2OH+3	1,159E-28	8,4784E-30	-29,072
Cu3(OH)4+2	2,9557E-36	9,2444E-37	-36,034
CuCl+	1,1117E-15	8,3137E-16	-15,08
CuCl2 (aq)	6,9965E-17	7,3052E-17	-16,136
CuCl3-	2,6782E-19	2,0028E-19	-18,698
CuCl4-2	8,2218E-22	2,5715E-22	-21,59
CuHSO4+	1,5346E-26	1,1476E-26	-25,94
CuOH+	1,3245E-15	9,9048E-16	-15,004
CuSO4 (aq)	2,2632E-19	2,3631E-19	-18,627
DOC (NICA-Donnan)	0,00056967	0,00056967	-3,244
FA1-Ca(6)(aq)	5,7084E-06	5,7084E-06	-5,243
FA1-Cu(6)(aq)	1,2364E-09	1,2364E-09	-8,908
FA1-Fe(II)(6)(aq)	1,0776E-06	1,0776E-06	-5,968
FA1-H(6)(aq)	3,5566E-06	3,5566E-06	-5,449
FA1-Mg(6)(aq)	1,3022E-06	1,3022E-06	-5,885
FA1-Ni(6)(aq)	1,74E-17	1,74E-17	-16,759
FA1-Zn(6)(aq)	6,03E-09	6,03E-09	-8,22
FA2-Ca(6)(aq)	2,1135E-10	2,1135E-10	-9,675
FA2-Cu(6)(aq)	4,1144E-09	4,1144E-09	-8,386
FA2-Fe(II)(6)(aq)	1,3667E-11	1,3667E-11	-10,864

FA2-H(6)(aq)	0,000020759	0,000020759	-4,683
FA2-Mg(6)(aq)	3,3614E-10	3,3614E-10	-9,473
FA2-Ni(6)(aq)	8,2608E-17	8,2608E-17	-16,083
FA2-Zn(6)(aq)	1,7093E-10	1,7093E-10	-9,767
Fe(OH)2 (aq)	1,0647E-16	1,1116E-16	-15,954
Fe(OH)3-	9,1849E-20	6,8688E-20	-19,163
Fe+2	2,0055E-10	6,2725E-11	-10,203
FeCl+	1,4827E-11	1,1088E-11	-10,955
FeOH+	7,7912E-13	5,8265E-13	-12,235
FeSO4 (aq)	1,0514E-14	1,0977E-14	-13,96
H+1	7,0177E-08	5,2481E-08	-7,28
HFA1-(6)(aq)	0,000054671	0,000054671	-4,262
HFA2-(6)(aq)	2,1808E-07	2,1808E-07	-6,661
HSO4-	5,1218E-12	3,8303E-12	-11,417
K+1	0,000056429	0,000042199	-4,375
KCl (aq)	5,5936E-06	5,8403E-06	-5,234
KOH (aq)	1,6388E-11	1,7111E-11	-10,767
KSO4-	2,8991E-10	2,168E-10	-9,664
Mg+2	4,9322E-06	1,5426E-06	-5,812
MgCl+	2,3343E-06	1,7457E-06	-5,758
MgOH+	1,8894E-10	1,413E-10	-9,85
MgSO4 (aq)	1,9016E-10	1,9854E-10	-9,702
Ni(OH)2 (aq)	3,6735E-28	3,8355E-28	-27,416
Ni(OH)3-	9,7778E-32	7,3121E-32	-31,136
Ni(SO4)2-2	1,0694E-34	3,3446E-35	-34,476
Ni+2	3,3742E-23	1,0553E-23	-22,977
NiCl+	1,4796E-24	1,1065E-24	-23,956
NiCl2 (aq)	1,0221E-26	1,0672E-26	-25,972
NiOH+	4,0857E-26	3,0554E-26	-25,515
NiSO4 (aq)	1,4264E-27	1,4893E-27	-26,827
OH-	3,1201E-07	2,3333E-07	-6,632
SO4-2	2,2144E-06	6,9259E-07	-6,16
Z-(6)(aq)	-0,000046788	-0,000046788	0
Zn(OH)2 (aq)	5,7109E-11	5,9628E-11	-10,225
Zn(OH)3-	4,8069E-15	3,5948E-15	-14,444
Zn(OH)4-2	3,4728E-20	1,0862E-20	-19,964
Zn(SO4)2-2	3,8085E-17	1,1912E-17	-16,924
Zn+2	4,1668E-08	1,3032E-08	-7,885
Zn2OH+3	5,5763E-17	4,0792E-18	-17,389
ZnCl+	1,4359E-08	1,0738E-08	-7,969
ZnCl2 (aq)	3,1411E-09	3,2797E-09	-8,484
ZnCl3-	1,4008E-09	1,0475E-09	-8,98
ZnCl4-2	4,8045E-10	1,5027E-10	-9,823
ZnOH+	4,0661E-10	3,0408E-10	-9,517
ZnSO4 (aq)	1,9342E-12	2,0195E-12	-11,695

Table 24 Chemical speciation of metals and some cations and ions estimated using Visual MINTEQ 3.1 in the sampled point P05 of the Jaguaripe River in January of 2015. . The measured pH values, DOC (Dissolved Organic Carbon) and concentrations of Ca^{2+} , Cl^- , H^+ , K^+ , Mg^{2+} and SO_4^{2-} were used as a input parameters.

Especies Químicas	Concentration (mol / L)	Activity (mol / L)	Log activity (mol / L)
(6)Ca+2D(aq)	0,000020691	0,000020691	-4,684
(6)Cl-1D(aq)	2,3541E-08	2,3541E-08	-7,628
(6)Cu+2D(aq)	1,5583E-15	1,5583E-15	-14,807
(6)Fe+2D(aq)	5,2585E-11	5,2585E-11	-10,279
(6)H+1D(aq)	1,1914E-10	1,1914E-10	-9,924
(6)K+1D(aq)	1,1754E-07	1,1754E-07	-6,93
(6)Mg+2D(aq)	4,0978E-06	4,0978E-06	-5,387
(6)Ni+2D(aq)	9,5534E-24	9,5534E-24	-23,02
(6)NiCl+D(aq)	2,2335E-27	2,2335E-27	-26,651
(6)OH-D(aq)	2,647E-14	2,647E-14	-13,577
(6)SO4-2D(aq)	8,062E-16	8,062E-16	-15,094
(6)Zn+2D(aq)	2,4333E-10	2,4333E-10	-9,614
Ca+2	0,00005377	0,000017043	-4,768
CaCl+	0,00001537	0,000011533	-4,938
CaOH+	1,396E-10	1,0474E-10	-9,98
CaSO4 (aq)	2,6533E-09	2,7636E-09	-8,559
Cl-1	0,35348	0,26523	-0,576
Cu(OH)2 (aq)	5,9239E-17	6,1702E-17	-16,21
Cu(OH)3-	5,3126E-20	3,9862E-20	-19,399
Cu(OH)4-2	4,8771E-25	1,5459E-25	-24,811
Cu+2	4,0497E-15	1,2836E-15	-14,892
Cu2(OH)2+2	1,2602E-25	3,9944E-26	-25,399
Cu2OH+3	1,1286E-28	8,5077E-30	-29,07
Cu3(OH)4+2	5,3098E-36	1,683E-36	-35,774
CuCl+	9,35E-16	7,0156E-16	-15,154
CuCl2 (aq)	5,6566E-17	5,8918E-17	-16,23
CuCl3-	2,0451E-19	1,5345E-19	-18,814
CuCl4-2 1	5,8459E-22	1,853E-22	-21,732
CuHSO4+	1,0743E-26	8,0607E-27	-26,094
CuOH+	1,4928E-15	1,1201E-15	-14,951
CuSO4 (aq)	2,0108E-19	2,0944E-19	-18,679
DOC (NICA-Donnan)	0,00060525	0,00060525	-3,218
FA1-Ca(6)(aq)	5,7242E-06	5,7242E-06	-5,242
FA1-Cu(6)(aq)	1,1464E-09	1,1464E-09	-8,941
FA1-Fe(II)(6)(aq)	1,0007E-06	1,0007E-06	-6
FA1-H(6)(aq)	3,1566E-06	3,1566E-06	-5,501
FA1-Mg(6)(aq)	0,000002227	0,000002227	-5,652
FA1-Ni(6)(aq)	1,3816E-17	1,3816E-17	-16,86
FA1-Zn(6)(aq)	3,5183E-10	3,5183E-10	-9,454
FA2-Ca(6)(aq)	2,6341E-10	2,6341E-10	-9,579
FA2-Cu(6)(aq)	4,9914E-09	4,9914E-09	-8,302
FA2-Fe(II)(6)(aq)	1,3854E-11	1,3854E-11	-10,858

FA2-H(6)(aq)	0,00002201	0,00002201	-4,657
FA2-Mg(6)(aq)	6,4184E-10	6,4184E-10	-9,193
FA2-Ni(6)(aq)	8,6193E-17	8,6193E-17	-16,065
FA2-Zn(6)(aq)	1,6041E-11	1,6041E-11	-10,795
Fe(OH)2 (aq)	1,2066E-16	1,2568E-16	-15,901
Fe(OH)3-	1,3058E-19	9,7979E-20	-19,009
Fe+2	1,3666E-10	4,3315E-11	-10,363
FeCl+	9,6608E-12	7,2488E-12	-11,14
FeOH+	6,854E-13	5,1428E-13	-12,289
FeSO4 (aq)	7,2509E-15	7,5523E-15	-14,122
H+1	5,5558E-08	4,1687E-08	-7,38
HFA1-(6)(aq)	0,000058356	0,000058356	-4,234
HFA2-(6)(aq)	2,7595E-07	2,7595E-07	-6,559
HSO4-	4,0539E-12	3,0418E-12	-11,517
K+1	0,000054813	0,000041128	-4,386
KCl (aq)	0,000005168	5,3829E-06	-5,269
KOH (aq)	2,0465E-11	2,1316E-11	-10,671
KSO4-	2,8092E-10	2,1079E-10	-9,676
Mg+2	0,000010649	3,3754E-06	-5,472
MgCl+	4,8245E-06	3,6199E-06	-5,441
MgOH+	5,2792E-10	3,9612E-10	-9,402
MgSO4 (aq)	4,153E-10	4,3257E-10	-9,364
Ni(OH)2 (aq)	4,3551E-28	4,5362E-28	-27,343
Ni(OH)3-	1,4515E-31	1,0891E-31	-30,963
Ni(SO4)2-2	7,7769E-35	2,465E-35	-34,608
Ni+2	2,4827E-23	7,8693E-24	-23,104
NiCl+	1,0416E-24	7,8151E-25	-24,107
NiCl2 (aq)	6,8469E-27	7,1316E-27	-26,147
NiOH+	3,877E-26	2,909E-26	-25,536
NiSO4 (aq)	1,0616E-27	1,1058E-27	-26,956
OH-	3,9747E-07	2,9824E-07	-6,525
SO4-2	2,1723E-06	6,8856E-07	-6,162
Z-(6)(aq)	-0,000049672	-0,000049672	0
Zn(OH)2 (aq)	1,3965E-12	1,4545E-12	-11,837
Zn(OH)3-	1,4718E-16	1,1043E-16	-15,957
Zn(OH)4-2	1,3257E-21	4,2022E-22	-21,377
Zn(SO4)2-2	5,7126E-19	1,8107E-19	-18,742
Zn+2	6,3235E-10	2,0043E-10	-9,698
Zn2OH+3	1,6395E-20	1,2359E-21	-20,908
ZnCl+	2,0867E-10	1,5657E-10	-9,805
ZnCl2 (aq)	4,3813E-11	4,5635E-11	-10,341
ZnCl3-	1,8412E-11	1,3815E-11	-10,86
ZnCl4-2	5,9281E-12	1,879E-12	-11,726
ZnOH+	7,9667E-12	5,9776E-12	-11,223
ZnSO4 (aq)	2,9695E-14	3,093E-14	-13,51

Table 25 Chemical speciation of metals and some cations and ions estimated using Visual MINTEQ 3.1 in the sampled point P06 of the Jaguaripe River in January of 2015. . The measured pH values, DOC (Dissolved Organic Carbon) and concentrations of Ca^{2+} , Cl^- , H^+ , K^+ , Mg^{2+} and SO_4^{2-} were used as a input parameters.

Especies Químicas	Concentration (mol / L)	Activity (mol / L)	Log activity (mol / L)
(6)Ca+2D(aq)	0,000023328	0,000023328	-4,632
(6)Cl-1D(aq)	2,4186E-08	2,4186E-08	-7,616
(6)Cu+2D(aq)	1,5722E-15	1,5722E-15	-14,803
(6)Fe+2D(aq)	9,6189E-11	9,6189E-11	-10,017
(6)H+1D(aq)	1,5892E-10	1,5892E-10	-9,799
(6)K+1D(aq)	1,3642E-07	1,3642E-07	-6,865
(6)Mg+2D(aq)	4,5446E-06	4,5446E-06	-5,343
(6)Ni+2D(aq)	1,0703E-23	1,0703E-23	-22,971
(6)NiCl+D(aq)	2,2057E-27	2,2057E-27	-26,656
(6)OH-D(aq)	2,766E-14	2,766E-14	-13,558
(6)SO4-2D(aq)	8,4552E-16	8,4552E-16	-15,073
(6)Zn+2D(aq)	3,3982E-20	3,3982E-20	-19,469
Ca+2	0,000048599	0,000015999	-4,796
CaCl+	0,000012425	9,4115E-06	-5,026
CaOH+	1,1451E-10	8,6738E-11	-10,062
CaSO4 (aq)	2,3187E-09	2,4017E-09	-8,619
Cl-1	0,30506	0,23107	-0,636
Cu(OH)2 (aq)	3,9677E-17	4,1097E-17	-16,386
Cu(OH)3-	3,3617E-20	2,5464E-20	-19,594
Cu(OH)4-2	2,4902E-25	8,1976E-26	-25,086
Cu+2	3,2754E-15	1,0782E-15	-14,967
Cu2(OH)2+2	6,8602E-26	2,2584E-26	-25,646
Cu2OH+3	6,58E-29	5,4013E-30	-29,268
Cu3(OH)4+2	1,9879E-36	6,5441E-37	-36,184
CuCl+	6,7482E-16	5,1116E-16	-15,291
CuCl2 (aq)	3,5425E-17	3,6692E-17	-16,435
CuCl3-	1,0915E-19	8,268E-20	-19,083
CuCl4-2 1	2,6771E-22	8,8131E-23	-22,055
CuHSO4+	9,1085E-27	6,8994E-27	-26,161
CuOH+	1,1124E-15	8,4259E-16	-15,074
CuSO4 (aq)	1,5711E-19	1,6274E-19	-18,789
DOC (NICA-Donnan)	0,00067292	0,00067292	-3,172
FA1-Ca(6)(aq)	0,000005965	0,000005965	-5,224
FA1-Cu(6)(aq)	1,1518E-09	1,1518E-09	-8,939
FA1-Fe(II)(6)(aq)	1,2531E-06	1,2531E-06	-5,902
FA1-H(6)(aq)	3,7248E-06	3,7248E-06	-5,429
FA1-Mg(6)(aq)	2,3044E-06	2,3044E-06	-5,637
FA1-Ni(6)(aq)	1,454E-17	1,454E-17	-16,837
FA1-Zn(6)(aq)	8,5504E-17	8,5504E-17	-16,068
FA2-Ca(6)(aq)	2,5717E-10	2,5717E-10	-9,59
FA2-Cu(6)(aq)	4,8286E-09	4,8286E-09	-8,316
FA2-Fe(II)(6)(aq)	1,7667E-11	1,7667E-11	-10,753

FA2-H(6)(aq)	0,000024488	0,000024488	-4,611
FA2-Mg(6)(aq)	6,2977E-10	6,2977E-10	-9,201
FA2-Ni(6)(aq)	8,5469E-17	8,5469E-17	-16,068
FA2-Zn(6)(aq)	1,4365E-17	1,4365E-17	-16,843
Fe(OH)2 (aq)	1,4448E-16	1,4965E-16	-15,825
Fe(OH)3-	1,4007E-19	1,061E-19	-18,974
Fe+2	2,0039E-10	6,5969E-11	-10,181
FeCl+	1,2698E-11	9,6181E-12	-11,017
FeOH+	9,1625E-13	6,9403E-13	-12,159
FeSO4 (aq)	1,0276E-14	1,0644E-14	-13,973
H+1	6,0344E-08	4,5709E-08	-7,34
HFA1-(6)(aq)	0,000065095	0,000065095	-4,186
HFA2-(6)(aq)	0,000000291	0,000000291	-6,536
HSO4-	4,0462E-12	3,0648E-12	-11,514
K+1	0,000051798	0,000039235	-4,406
KCl (aq)	4,3284E-06	4,4833E-06	-5,348
KOH (aq)	1,7396E-11	1,8018E-11	-10,744
KSO4-	2,4501E-10	1,8559E-10	-9,731
Mg+2	9,4679E-06	3,1168E-06	-5,506
MgCl+	3,8364E-06	2,9059E-06	-5,537
MgOH+	4,2585E-10	3,2257E-10	-9,491
MgSO4 (aq)	3,5726E-10	3,7004E-10	-9,432
Ni(OH)2 (aq)	3,4033E-28	3,5251E-28	-27,453
Ni(OH)3-	1,0199E-31	7,7252E-32	-31,112
Ni(SO4)2-2	6,0317E-35	1,9856E-35	-34,702
Ni+2	2,2297E-23	7,3401E-24	-23,134
NiCl+	8,3753E-25	6,344E-25	-24,198
NiCl2 (aq)	4,8745E-27	5,0489E-27	-26,297
NiOH+	3,1809E-26	2,4094E-26	-25,618
NiSO4 (aq)	9,2253E-28	9,5554E-28	-27,02
OH-	3,4888E-07	2,6426E-07	-6,578
SO4-2	1,9437E-06	6,3987E-07	-6,194
Z-(6)(aq)	-0,000055857	-0,000055857	0
Zn(OH)2 (aq)	1,3604E-22	1,4091E-22	-21,851
Zn(OH)3-	1,2891E-26	9,7649E-27	-26,01
Zn(OH)4-2	1,0303E-31	3,3916E-32	-31,47
Zn(SO4)2-2	5,5233E-29	1,8182E-29	-28,74
Zn+2	7,0796E-20	2,3306E-20	-19,633
Zn2OH+3	1,7962E-40	1,4744E-41	-40,831
ZnCl+	2,0879E-20	1,5815E-20	-19,801
ZnCl2 (aq)	3,8155E-21	3,952E-21	-20,403
ZnCl3-	1,3728E-21	1,0399E-21	-20,983
ZnCl4-2	3,7314E-22	1,2283E-22	-21,911
ZnOH+	8,1309E-22	6,1589E-22	-21,21
ZnSO4 (aq)	3,216E-24	3,3311E-24	-23,477

Table 26 Chemical speciation of metals and some cations and ions estimated using Visual MINTEQ 3.1 in the sampled point P01 of the São Paulo River in January of 2015. . The measured pH values, DOC (Dissolved Organic Carbon) and concentrations of Ca^{2+} , Cl^- , H^+ , K^+ , Mg^{2+} and SO_4^{2-} were used as a input parameters.

Especies Químicas	Concentration (mol / L)	Activity (mol / L)	Log activity (mol / L)
(6)Ca+2D(aq)	0,000010833	0,000010833	-4,965
(6)Cl-1D(aq)	1,6432E-08	1,6432E-08	-7,784
(6)Cu+2D(aq)	5,5308E-15	5,5308E-15	-14,257
(6)Fe+2D(aq)	1,8976E-12	1,8976E-12	-11,722
(6)H+1D(aq)	2,2981E-11	2,2981E-11	-10,639
(6)K+1D(aq)	5,9264E-08	5,9264E-08	-7,227
(6)Mg+2D(aq)	9,319E-07	9,319E-07	-6,031
(6)Ni+2D(aq)	1,5719E-11	1,5719E-11	-10,804
(6)NiCl+D(aq)	6,1682E-15	6,1682E-15	-14,21
(6)OH-D(aq)	2,0961E-14	2,0961E-14	-13,679
(6)SO4-2D(aq)	7,2998E-16	7,2998E-16	-15,137
(6)Zn+2D(aq)	1,6157E-09	1,6157E-09	-8,792
Ca+2	0,00010454	0,000030405	-4,517
CaCl+	0,000042136	0,000030944	-4,509
CaOH+	4,3439E-10	3,1901E-10	-9,496
CaSO4 (aq)	7,1181E-09	7,5778E-09	-8,12
Cl-1	0,54291	0,3987	-0,399
Cu(OH)2 (aq)	2,0335E-15	2,1648E-15	-14,665
Cu(OH)3-	3,1841E-18	2,3383E-18	-17,631
Cu(OH)4-2	5,404E-23	1,5718E-23	-22,804
Cu+2	5,3373E-14	1,5524E-14	-13,809
Cu2(OH)2+2	5,8118E-23	1,6904E-23	-22,772
Cu2OH+3	3,4026E-26	2,1139E-27	-26,675
Cu3(OH)4+2	8,523E-32	2,479E-32	-31,606
CuCl+	1,7386E-14	1,2768E-14	-13,894
CuCl2 (aq)	1,5213E-15	1,6196E-15	-14,791
CuCl3-	8,6494E-18	6,352E-18	-17,197
CuCl4-2 1	3,9512E-20	1,1492E-20	-19,94
CuHSO4+	1,2003E-25	8,8146E-26	-25,055
CuOH+	3,1372E-14	2,3039E-14	-13,638
CuSO4 (aq)	3,6577E-18	3,8939E-18	-17,41
DOC (NICA-Donnan)	0,00029508	0,00029508	-3,53
FA1-Ca(6)(aq)	3,9144E-06	3,9144E-06	-5,407
FA1-Cu(6)(aq)	1,9538E-09	1,9538E-09	-8,709
FA1-Fe(II)(6)(aq)	2,5782E-07	2,5782E-07	-6,589
FA1-H(6)(aq)	1,0517E-06	1,0517E-06	-5,978
FA1-Mg(6)(aq)	7,8136E-07	7,8136E-07	-6,107
FA1-Ni(6)(aq)	1,178E-09	1,178E-09	-8,929
FA1-Zn(6)(aq)	1,2466E-09	1,2466E-09	-8,904
FA2-Ca(6)(aq)	2,7594E-10	2,7594E-10	-9,559
FA2-Cu(6)(aq)	9,0627E-09	9,0627E-09	-8,043
FA2-Fe(II)(6)(aq)	3,3848E-12	3,3848E-12	-11,47

FA2-H(6)(aq)	0,00001066	0,00001066	-4,972
FA2-Mg(6)(aq)	3,8471E-10	3,8471E-10	-9,415
FA2-Ni(6)(aq)	3,4848E-10	3,4848E-10	-9,458
FA2-Zn(6)(aq)	7,4525E-11	7,4525E-11	-10,128
Fe(OH)2 (aq)	4,2261E-17	4,499E-17	-16,347
Fe(OH)3-	8,0919E-20	5,9425E-20	-19,226
Fe+2	1,8312E-11	5,3262E-12	-11,274
FeCl+	1,8245E-12	1,3399E-12	-11,873
FeOH+	1,4685E-13	1,0784E-13	-12,967
FeSO4 (aq)	1,3409E-15	1,4275E-15	-14,845
H+1	3,3426E-08	2,4547E-08	-7,61
HFA1-(6)(aq)	0,000028345	0,000028345	-4,548
HFA2-(6)(aq)	1,9815E-07	1,9815E-07	-6,703
HSO4-	3,7557E-12	2,7581E-12	-11,559
K+1	0,000086197	0,000063301	-4,199
KCl (aq)	0,000011692	0,000012447	-4,905
KOH (aq)	5,2554E-11	5,5947E-11	-10,252
KSO4-	6,7952E-10	4,9902E-10	-9,302
Mg+2	8,9929E-06	2,6156E-06	-5,582
MgCl+	0,000005745	0,000004219	-5,375
MgOH+	7,1364E-10	5,2408E-10	-9,281
MgSO4 (aq)	4,8387E-10	5,1512E-10	-9,288
Ni(OH)2 (aq)	6,8454E-15	7,2874E-15	-14,137
Ni(OH)3-	4,033E-18	2,9617E-18	-17,528
Ni(SO4)2-2	1,1204E-21	3,2588E-22	-21,487
Ni+2	1,5169E-10	4,412E-11	-10,355
NiCl+	8,9714E-12	6,5884E-12	-11,181
NiCl2 (aq)	8,4871E-14	9,0352E-14	-13,044
NiOH+	3,7854E-13	2,7799E-13	-12,556
NiSO4 (aq)	8,9493E-15	9,5272E-15	-14,021
OH-	6,9255E-07	5,0859E-07	-6,294
SO4-2	3,6352E-06	1,0573E-06	-5,976
Z-(6)(aq)	-0,000023575	-0,000023575	0
Zn(OH)2 (aq)	8,8579E-11	9,4299E-11	-10,025
Zn(OH)3-	1,6503E-14	1,2119E-14	-13,917
Zn(OH)4-2	2,6839E-19	7,8063E-20	-19,108
Zn(SO4)2-2	3,3213E-17	9,6601E-18	-17,015
Zn+2	1,5592E-08	4,5349E-09	-8,343
Zn2OH+3	1,7386E-17	1,0801E-18	-17,967
ZnCl+	7,2565E-09	5,329E-09	-8,273
ZnCl2 (aq)	2,202E-09	2,3442E-09	-8,63
ZnCl3-	1,4535E-09	1,0674E-09	-8,972
ZnCl4-2	7,5092E-10	2,1841E-10	-9,661
ZnOH+	3,1407E-10	2,3064E-10	-9,637
ZnSO4 (aq)	1,0102E-12	1,0755E-12	-11,968

Table 27 Chemical speciation of metals and some cations and ions estimated using Visual MINTEQ 3.1 in the sampled point P02 of the São Paulo River in January of 2015. . The measured pH values, DOC (Dissolved Organic Carbon) and concentrations of Ca^{2+} , Cl^- , H^+ , K^+ , Mg^{2+} and SO_4^{2-} were used as a input parameters.

Especies Químicas	Concentration (mol / L)	Activity (mol / L)	Log activity (mol / L)
(6)Ca+2D(aq)	0,000011624	0,000011624	-4,935
(6)Cl-1D(aq)	1,7524E-08	1,7524E-08	-7,756
(6)Cu+2D(aq)	2,6807E-14	2,6807E-14	-13,572
(6)Fe+2D(aq)	2,7048E-11	2,7048E-11	-10,568
(6)H+1D(aq)	4,7282E-11	4,7282E-11	-10,325
(6)K+1D(aq)	6,3891E-08	6,3891E-08	-7,195
(6)Mg+2D(aq)	1,0071E-06	1,0071E-06	-5,997
(6)Ni+2D(aq)	1,1523E-10	1,1523E-10	-9,938
(6)NiCl+D(aq)	4,4463E-14	4,4463E-14	-13,352
(6)OH-D(aq)	1,1609E-14	1,1609E-14	-13,935
(6)SO4-2D(aq)	7,9674E-16	7,9674E-16	-15,099
(6)Zn+2D(aq)	2,5011E-09	2,5011E-09	-8,602
Ca+2	0,00010448	0,000030548	-4,515
CaCl+	0,00004107	0,0000302	-4,52
CaOH+	2,1926E-10	1,6123E-10	-9,793
CaSO4 (aq)	7,0854E-09	7,5301E-09	-8,123
Cl-1	0,52811	0,38834	-0,411
Cu(OH)2 (aq)	2,3945E-15	2,5448E-15	-14,594
Cu(OH)3-	2,0875E-18	1,535E-18	-17,814
Cu(OH)4-2	1,6454E-23	4,8108E-24	-23,318
Cu+2	2,4095E-13	7,0448E-14	-13,152
Cu2(OH)2+2	3,125E-22	9,1367E-23	-22,039
Cu2OH+3	3,5709E-25	2,2447E-26	-25,649
Cu3(OH)4+2	5,6072E-31	1,6394E-31	-30,785
CuCl+	7,6328E-14	5,6127E-14	-13,251
CuCl2 (aq)	6,3711E-15	6,7709E-15	-14,169
CuCl3-	3,487E-17	2,5641E-17	-16,591
CuCl4-2	1,571E-19	4,5932E-20	-19,338
CuHSO4+	1,0301E-24	7,5744E-25	-24,121
CuOH+	7,2883E-14	5,3594E-14	-13,271
CuSO4 (aq)	1,6428E-17	1,7459E-17	-16,758
DOC (NICA-Donnan)	0,00031625	0,00031625	-3,5
FA1-Ca(6)(aq)	3,7466E-06	3,7466E-06	-5,426
FA1-Cu(6)(aq)	4,1779E-09	4,1779E-09	-8,379
FA1-Fe(II)(6)(aq)	5,4046E-07	5,4046E-07	-6,267
FA1-H(6)(aq)	1,5512E-06	1,5512E-06	-5,809
FA1-Mg(6)(aq)	7,5286E-07	7,5286E-07	-6,123
FA1-Ni(6)(aq)	3,9428E-09	3,9428E-09	-8,404
FA1-Zn(6)(aq)	1,5293E-09	1,5293E-09	-8,816
FA2-Ca(6)(aq)	1,8109E-10	1,8109E-10	-9,742
FA2-Cu(6)(aq)	1,03E-08	1,03E-08	-7,987
FA2-Fe(II)(6)(aq)	8,3433E-12	8,3433E-12	-11,079

FA2-H(6)(aq)	0,00001148	0,00001148	-4,94
FA2-Mg(6)(aq)	2,5431E-10	2,5431E-10	-9,595
FA2-Ni(6)(aq)	6,3571E-10	6,3571E-10	-9,197
FA2-Zn(6)(aq)	6,1328E-11	6,1328E-11	-10,212
Fe(OH)2 (aq)	1,4379E-16	1,5282E-16	-15,816
Fe(OH)3-	1,4345E-19	1,0548E-19	-18,977
Fe+2	2,4312E-10	7,1082E-11	-10,148
FeCl+	2,3686E-11	1,7417E-11	-10,759
FeOH+	9,9005E-13	7,2802E-13	-12,138
FeSO4 (aq)	1,772E-14	1,8832E-14	-13,725
H+1	6,3608E-08	4,6774E-08	-7,33
HFA1-(6)(aq)	0,000030218	0,000030218	-4,52
HFA2-(6)(aq)	1,5629E-07	1,5629E-07	-6,806
HSO4-	7,0033E-12	5,1498E-12	-11,288
K+1	0,000085952	0,000063204	-4,199
KCl (aq)	0,000011421	0,000012137	-4,916
KOH (aq)	2,6588E-11	2,8257E-11	-10,549
KSO4-	6,6761E-10	4,9091E-10	-9,309
Mg+2	9,0522E-06	2,6467E-06	-5,577
MgCl+	5,6396E-06	0,000004147	-5,382
MgOH+	3,6263E-10	2,6666E-10	-9,574
MgSO4 (aq)	4,855E-10	5,1597E-10	-9,287
Ni(OH)2 (aq)	1,2969E-14	1,3783E-14	-13,861
Ni(OH)3-	3,9988E-18	2,9404E-18	-17,532
Ni(SO4)2-2	7,5542E-21	2,2087E-21	-20,656
Ni+2	1,0357E-09	3,0282E-10	-9,519
NiCl+	5,9815E-11	4,3984E-11	-10,357
NiCl2 (aq)	5,5355E-13	5,8829E-13	-12,23
NiOH+	1,316E-12	9,6768E-13	-12,014
NiSO4 (aq)	6,0907E-14	6,473E-14	-13,189
OH-	3,4986E-07	2,5726E-07	-6,59
SO4-2	3,5936E-06	1,0507E-06	-5,979
Z-(6)(aq)	-0,000025314	-0,000025314	0
Zn(OH)2 (aq)	3,5438E-11	3,7663E-11	-10,424
Zn(OH)3-	3,4554E-15	2,5409E-15	-14,595
Zn(OH)4-2	2,9385E-20	8,5914E-21	-20,066
Zn(SO4)2-2	4,7289E-17	1,3826E-17	-16,859
Zn+2	2,2481E-08	6,5728E-09	-8,182
Zn2OH+3	1,8162E-17	1,1417E-18	-17,942
ZnCl+	1,0194E-08	7,496E-09	-8,125
ZnCl2 (aq)	2,9621E-09	3,148E-09	-8,502
ZnCl3-	1,893E-09	1,392E-09	-8,856
ZnCl4-2	9,4515E-10	2,7634E-10	-9,559
ZnOH+	2,2996E-10	1,691E-10	-9,772
ZnSO4 (aq)	1,4515E-12	1,5426E-12	-11,812

Table 28 Chemical speciation of metals and some cations and ions estimated using Visual MINTEQ 3.1 in the sampled point P03 of the São Paulo River in January of 2015. . The measured pH values, DOC (Dissolved Organic Carbon) and concentrations of Ca^{2+} , Cl^- , H^+ , K^+ , Mg^{2+} and SO_4^{2-} were used as a input parameters.

Especies Químicas	Concentration (mol / L)	Activity (mol / L)	Log activity (mol / L)
(6)Ca+2D(aq)	0,000012355	0,000012355	-4,908
(6)Cl-1D(aq)	1,8864E-08	1,8864E-08	-7,724
(6)Cu+2D(aq)	5,4042E-14	5,4042E-14	-13,267
(6)Fe+2D(aq)	5,0392E-13	5,0392E-13	-12,298
(6)H+1D(aq)	7,8915E-11	7,8915E-11	-10,103
(6)K+1D(aq)	6,4762E-08	6,4762E-08	-7,189
(6)Mg+2D(aq)	1,1407E-06	1,1407E-06	-5,943
(6)Ni+2D(aq)	9,6148E-11	9,6148E-11	-10,017
(6)NiCl+D(aq)	3,8649E-14	3,8649E-14	-13,413
(6)OH-D(aq)	7,0877E-15	7,0877E-15	-14,149
(6)SO4-2D(aq)	6,9679E-16	6,9679E-16	-15,157
(6)Zn+2D(aq)	6,4341E-10	6,4341E-10	-9,192
Ca+2	0,000098022	0,000028246	-4,549
CaCl+	0,000042319	0,000031006	-4,509
CaOH+	1,2792E-10	9,3722E-11	-10,028
CaSO4 (aq)	6,1174E-09	6,5474E-09	-8,184
Cl-1	0,58945	0,43187	-0,365
Cu(OH)2 (aq)	1,6713E-15	1,7888E-15	-14,747
Cu(OH)3-	9,8583E-19	7,2228E-19	-18,141
Cu(OH)4-2	4,718E-24	1,3595E-24	-23,867
Cu+2	4,2876E-13	1,2355E-13	-12,908
Cu2(OH)2+2	3,9397E-22	1,1353E-22	-21,945
Cu2OH+3	7,2409E-25	4,4051E-26	-25,356
Cu3(OH)4+2	5,09E-31	1,4667E-31	-30,834
CuCl+	1,4892E-13	1,0911E-13	-12,962
CuCl2 (aq)	1,3482E-14	1,443E-14	-13,841
CuCl3-	8,2511E-17	6,0453E-17	-16,219
CuCl4-2	4,221E-19	1,2163E-19	-18,915
CuHSO4+	2,6481E-24	1,9402E-24	-23,712
CuOH+	8,1566E-14	5,9761E-14	-13,224
CuSO4 (aq)	2,6885E-17	2,8775E-17	-16,541
DOC (NICA-Donnan)	0,00034258	0,00034258	-3,465
FA1-Ca(6)(aq)	4,2343E-06	4,2343E-06	-5,373
FA1-Cu(6)(aq)	6,537E-09	6,537E-09	-8,185
FA1-Fe(II)(6)(aq)	1,7726E-07	1,7726E-07	-6,751
FA1-H(6)(aq)	2,3418E-06	2,3418E-06	-5,63
FA1-Mg(6)(aq)	8,9046E-07	8,9046E-07	-6,05
FA1-Ni(6)(aq)	3,7744E-09	3,7744E-09	-8,423
FA1-Zn(6)(aq)	6,6285E-10	6,6285E-10	-9,179
FA2-Ca(6)(aq)	1,399E-10	1,399E-10	-9,854
FA2-Cu(6)(aq)	9,8294E-09	9,8294E-09	-8,007
FA2-Fe(II)(6)(aq)	8,0923E-13	8,0923E-13	-12,092

FA2-H(6)(aq)	0,000012475	0,000012475	-4,904
FA2-Mg(6)(aq)	2,0212E-10	2,0212E-10	-9,694
FA2-Ni(6)(aq)	4,2693E-10	4,2693E-10	-9,37
FA2-Zn(6)(aq)	1,9776E-11	1,9776E-11	-10,704
Fe(OH)2 (aq)	9,1774E-19	9,8225E-19	-18,008
Fe(OH)3-	5,9522E-22	4,361E-22	-21,36
Fe+2	3,9981E-12	1,1521E-12	-11,939
FeCl+	4,2848E-13	3,1393E-13	-12,503
FeOH+	1,0158E-14	7,4425E-15	-14,128
FeSO4 (aq)	2,6807E-16	2,8691E-16	-15,542
H+1	9,8876E-08	7,2444E-08	-7,14
HFA1-(6)(aq)	0,00003223	0,00003223	-4,492
HFA2-(6)(aq)	1,3212E-07	1,3212E-07	-6,879
HSO4-	1,018E-11	7,4587E-12	-11,127
K+1	0,000081143	0,000059451	-4,226
KCl (aq)	0,000011882	0,000012717	-4,896
KOH (aq)	1,5664E-11	1,6765E-11	-10,776
KSO4-	5,9129E-10	4,3322E-10	-9,363
Mg+2	9,0505E-06	0,000002608	-5,584
MgCl+	6,1928E-06	4,5373E-06	-5,343
MgOH+	2,2541E-10	1,6515E-10	-9,782
MgSO4 (aq)	4,4694E-10	4,7836E-10	-9,32
Ni(OH)2 (aq)	3,8886E-15	4,1619E-15	-14,381
Ni(OH)3-	7,8165E-19	5,7269E-19	-18,242
Ni(SO4)2-2	4,948E-21	1,4258E-21	-20,846
Ni+2	7,6282E-10	2,1981E-10	-9,658
NiCl+	4,8425E-11	3,5479E-11	-10,45
NiCl2 (aq)	4,9348E-13	5,2816E-13	-12,277
NiOH+	6,0569E-13	4,4377E-13	-12,353
NiSO4 (aq)	4,1305E-14	4,4208E-14	-13,354
OH-	2,2148E-07	1,6227E-07	-6,79
SO4-2	3,4385E-06	9,9084E-07	-6,004
Z-(6)(aq)	-0,000027039	-0,000027039	0
Zn(OH)2 (aq)	3,276E-12	3,5063E-12	-11,455
Zn(OH)3-	2,0824E-16	1,5257E-16	-15,817
Zn(OH)4-2	1,1547E-21	3,3273E-22	-21,478
Zn(SO4)2-2	9,5495E-18	2,7518E-18	-17,56
Zn+2	5,1047E-09	1,471E-09	-8,832
Zn2OH+3	5,9094E-19	3,5951E-20	-19,444
ZnCl+	2,5409E-09	1,8616E-09	-8,73
ZnCl2 (aq)	8,026E-10	8,5901E-10	-9,066
ZnCl3-	5,7557E-10	4,217E-10	-9,375
ZnCl4-2	3,2233E-10	9,2882E-11	-10,032
ZnOH+	3,2579E-11	2,3869E-11	-10,622
ZnSO4 (aq)	3,0343E-13	3,2476E-13	-12,488

Table 29 Chemical speciation of metals and some cations and ions estimated using Visual MINTEQ 3.1 in the sampled point P04 of the São Paulo River in January of 2015. . The measured pH values, DOC (Dissolved Organic Carbon) and concentrations of Ca^{2+} , Cl^- , H^+ , K^+ , Mg^{2+} and SO_4^{2-} were used as a input parameters.

Especies Químicas	Concentration (mol / L)	Activity (mol / L)	Log activity (mol / L)
(6)Ca+2D(aq)	0,000012175	0,000012175	-4,915
(6)Cl-1D(aq)	1,8035E-08	1,8035E-08	-7,744
(6)Cu+2D(aq)	1,1668E-13	1,1668E-13	-12,933
(6)Fe+2D(aq)	4,0079E-12	4,0079E-12	-11,397
(6)H+1D(aq)	4,6695E-10	4,6695E-10	-9,331
(6)K+1D(aq)	6,524E-08	6,524E-08	-7,185
(6)Mg+2D(aq)	1,1602E-06	1,1602E-06	-5,935
(6)Ni+2D(aq)	4,2537E-11	4,2537E-11	-10,371
(6)NiCl+D(aq)	1,5489E-14	1,5489E-14	-13,81
(6)OH-D(aq)	1,3334E-15	1,3334E-15	-14,875
(6)SO4-2D(aq)	7,1907E-16	7,1907E-16	-15,143
(6)Zn+2D(aq)	1,7059E-09	1,7059E-09	-8,768
Ca+2	0,000092906	0,000027311	-4,564
CaCl+	0,000035685	0,000026276	-4,58
CaOH+	2,1176E-11	1,5592E-11	-10,807
CaSO4 (aq)	5,6234E-09	5,9674E-09	-8,224
Cl-1	0,51517	0,37933	-0,421
Cu(OH)2 (aq)	1,0772E-16	1,1431E-16	-15,942
Cu(OH)3-	1,1731E-20	8,6376E-21	-20,064
Cu(OH)4-2	8,9523E-27	2,6317E-27	-26,58
Cu+2	8,9038E-13	2,6174E-13	-12,582
Cu2(OH)2+2	5,2837E-23	1,5532E-23	-22,809
Cu2OH+3	5,453E-25	3,4698E-26	-25,46
Cu3(OH)4+2	4,5051E-33	1,3244E-33	-32,878
CuCl+	2,745E-13	2,0212E-13	-12,694
CuCl2 (aq)	2,1706E-14	2,3034E-14	-13,638
CuCl3-	1,1431E-16	8,4169E-17	-16,075
CuCl4-2	5,1272E-19	1,5072E-19	-18,822
CuHSO4+	2,9702E-23	2,187E-23	-22,66
CuOH+	3,0034E-14	2,2115E-14	-13,655
CuSO4 (aq)	5,4102E-17	5,7411E-17	-16,241
DOC (NICA-Donnan)	0,00034125	0,00034125	-3,467
FA1-Ca(6)(aq)	2,9407E-06	2,9407E-06	-5,532
FA1-Cu(6)(aq)	7,0753E-09	7,0753E-09	-8,15
FA1-Fe(II)(6)(aq)	2,4169E-07	2,4169E-07	-6,617
FA1-H(6)(aq)	5,3981E-06	5,3981E-06	-5,268
FA1-Mg(6)(aq)	6,3808E-07	6,3808E-07	-6,195
FA1-Ni(6)(aq)	1,585E-09	1,585E-09	-8,8
FA1-Zn(6)(aq)	9,0763E-10	9,0763E-10	-9,042
FA2-Ca(6)(aq)	3,5802E-11	3,5802E-11	-10,446
FA2-Cu(6)(aq)	3,4672E-09	3,4672E-09	-8,46
FA2-Fe(II)(6)(aq)	6,1621E-13	6,1621E-13	-12,21

FA2-H(6)(aq)	0,000012512	0,000012512	-4,903
FA2-Mg(6)(aq)	5,3675E-11	5,3675E-11	-10,27
FA2-Ni(6)(aq)	7,3179E-11	7,3179E-11	-10,136
FA2-Zn(6)(aq)	9,4116E-12	9,4116E-12	-11,026
Fe(OH)2 (aq)	2,1484E-19	2,2798E-19	-18,642
Fe(OH)3-	2,4387E-23	1,7957E-23	-22,746
Fe+2	3,0584E-11	8,9905E-12	-11,046
FeCl+	2,9224E-12	2,1518E-12	-11,667
FeOH+	1,3632E-14	1,0038E-14	-13,998
FeSO4 (aq)	1,9879E-15	2,1095E-15	-14,676
H+1	5,5326E-07	4,0738E-07	-6,39
HFA1-(6)(aq)	0,000030502	0,000030502	-4,516
HFA2-(6)(aq)	5,3605E-08	5,3605E-08	-7,271
HSO4-	5,3297E-11	3,9245E-11	-10,406
K+1	0,000077299	0,000056918	-4,245
KCl (aq)	0,000010099	0,000010717	-4,97
KOH (aq)	2,614E-12	2,7739E-12	-11,557
KSO4-	5,2931E-10	3,8975E-10	-9,409
Mg+2	8,8532E-06	2,6025E-06	-5,585
MgCl+	5,3895E-06	3,9685E-06	-5,401
MgOH+	3,8498E-11	2,8347E-11	-10,547
MgSO4 (aq)	4,2431E-10	4,5027E-10	-9,347
Ni(OH)2 (aq)	5,3976E-17	5,7278E-17	-16,242
Ni(OH)3-	1,9058E-21	1,4033E-21	-20,853
Ni(SO4)2-2	1,885E-21	5,5411E-22	-21,256
Ni+2	3,2459E-10	9,5419E-11	-10,02
NiCl+	1,8352E-11	1,3513E-11	-10,869
NiCl2 (aq)	1,6668E-13	1,7688E-13	-12,752
NiOH+	4,5311E-14	3,3364E-14	-13,477
NiSO4 (aq)	1,7058E-14	1,8101E-14	-13,742
OH-	3,8087E-08	2,8045E-08	-7,552
SO4-2	3,1892E-06	9,3752E-07	-6,028
Z-(6)(aq)	-0,000026722	-0,000026722	0
Zn(OH)2 (aq)	2,7251E-13	2,8918E-13	-12,539
Zn(OH)3-	3,0428E-18	2,2405E-18	-17,65
Zn(OH)4-2	2,9596E-24	8,7E-25	-24,06
Zn(SO4)2-2	2,1802E-17	6,4089E-18	-17,193
Zn+2	1,3018E-08	3,8267E-09	-8,417
Zn2OH+3	6,5802E-19	4,187E-20	-19,378
ZnCl+	5,7603E-09	4,2415E-09	-8,372
ZnCl2 (aq)	1,5941E-09	1,6916E-09	-8,772
ZnCl3-	9,8825E-10	7,2768E-10	-9,138
ZnCl4-2	4,7738E-10	1,4033E-10	-9,853
ZnOH+	1,4575E-11	1,0732E-11	-10,969
ZnSO4 (aq)	7,5082E-13	7,9675E-13	-12,099

Table 30 Chemical speciation of metals and some cations and ions estimated using Visual MINTEQ 3.1 in the sampled point P05 of the São Paulo River in January of 2015. . The measured pH values, DOC (Dissolved Organic Carbon) and concentrations of Ca^{2+} , Cl^- , H^+ , K^+ , Mg^{2+} and SO_4^{2-} were used as a input parameters.

Especies Químicas	Concentration (mol / L)	Activity (mol / L)	Log activity (mol / L)
(6)Ca+2D(aq)	0,000014716	0,000014716	-4,832
(6)Cl-1D(aq)	2,1625E-08	2,1625E-08	-7,665
(6)Cu+2D(aq)	6,961E-14	6,961E-14	-13,157
(6)Fe+2D(aq)	2,9729E-10	2,9729E-10	-9,527
(6)H+1D(aq)	1,1649E-10	1,1649E-10	-9,934
(6)K+1D(aq)	8,2119E-08	8,2119E-08	-7,086
(6)Mg+2D(aq)	1,3674E-06	1,3674E-06	-5,864
(6)Ni+2D(aq)	2,6553E-10	2,6553E-10	-9,576
(6)NiCl+D(aq)	9,7406E-14	9,7406E-14	-13,011
(6)OH-D(aq)	7,8442E-15	7,8442E-15	-14,105
(6)SO4-2D(aq)	9,7417E-16	9,7417E-16	-15,011
(6)Zn+2D(aq)	1,3037E-09	1,3037E-09	-8,885
Ca+2	0,000098379	0,000028983	-4,538
CaCl+	0,000037259	0,00002745	-4,561
CaOH+	1,0873E-10	8,0105E-11	-10,096
CaSO4 (aq)	6,5181E-09	6,9094E-09	-8,161
Cl-1	0,50577	0,37262	-0,429
Cu(OH)2 (aq)	1,2992E-15	1,3771E-15	-14,861
Cu(OH)3-	6,287E-19	4,6319E-19	-18,334
Cu(OH)4-2	2,465E-24	7,262E-25	-24,139
Cu+2	4,6535E-13	1,371E-13	-12,863
Cu2(OH)2+2	3,2919E-22	9,6983E-23	-22,013
Cu2OH+3	7,0654E-25	4,5179E-26	-25,345
Cu3(OH)4+2	3,2744E-31	9,6466E-32	-31,016
CuCl+	1,4178E-13	1,0446E-13	-12,981
CuCl2 (aq)	1,1244E-14	1,1919E-14	-13,924
CuCl3-	5,848E-17	4,3084E-17	-16,366
CuCl4-2 1	2,5387E-19	7,4792E-20	-19,126
CuHSO4+	3,6132E-24	2,662E-24	-23,575
CuOH+	7,4974E-14	5,5236E-14	-13,258
CuSO4 (aq)	3,0978E-17	3,2837E-17	-16,484
DOC (NICA-Donnan)	0,00040325	0,00040325	-3,394
FA1-Ca(6)(aq)	4,0796E-06	4,0796E-06	-5,389
FA1-Cu(6)(aq)	6,7251E-09	6,7251E-09	-8,172
FA1-Fe(II)(6)(aq)	1,1453E-06	1,1453E-06	-5,941
FA1-H(6)(aq)	2,6369E-06	2,6369E-06	-5,579
FA1-Mg(6)(aq)	8,6735E-07	8,6735E-07	-6,062
FA1-Ni(6)(aq)	6,3771E-09	6,3771E-09	-8,195
FA1-Zn(6)(aq)	9,2411E-10	9,2411E-10	-9,034
FA2-Ca(6)(aq)	1,3959E-10	1,3959E-10	-9,855
FA2-Cu(6)(aq)	1,0428E-08	1,0428E-08	-7,982
FA2-Fe(II)(6)(aq)	1,9543E-11	1,9543E-11	-10,709

FA2-H(6)(aq)	0,000014696	0,000014696	-4,833
FA2-Mg(6)(aq)	2,0566E-10	2,0566E-10	-9,687
FA2-Ni(6)(aq)	6,7891E-10	6,7891E-10	-9,168
FA2-Zn(6)(aq)	2,7679E-11	2,7679E-11	-10,558
Fe(OH)2 (aq)	3,2675E-16	3,4636E-16	-15,46
Fe(OH)3-	1,7386E-19	1,2809E-19	-18,892
Fe+2	1,9875E-09	5,8552E-10	-9,232
FeCl+	1,8685E-10	1,3766E-10	-9,861
FeOH+	4,2765E-12	3,1507E-12	-11,502
FeSO4 (aq)	1,4147E-13	1,4996E-13	-12,824
H+1	1,1822E-07	8,7096E-08	-7,06
HFA1-(6)(aq)	0,000038205	0,000038205	-4,418
HFA2-(6)(aq)	1,4437E-07	1,4437E-07	-6,841
HSO4-	1,2518E-11	9,2224E-12	-11,035
K+1	0,00008334	0,000061399	-4,212
KCl (aq)	0,00001069	0,000011332	-4,946
KOH (aq)	1,3605E-11	1,4422E-11	-10,841
KSO4-	6,2457E-10	4,6014E-10	-9,337
Mg+2	9,1414E-06	2,6931E-06	-5,57
MgCl+	5,4871E-06	4,0425E-06	-5,393
MgOH+	1,9281E-10	1,4205E-10	-9,848
MgSO4 (aq)	4,7925E-10	5,0802E-10	-9,294
Ni(OH)2 (aq)	6,481E-15	6,8701E-15	-14,163
Ni(OH)3-	1,0688E-18	7,8742E-19	-18,104
Ni(SO4)2-2	1,2178E-20	3,5878E-21	-20,445
Ni+2	1,7751E-09	5,2297E-10	-9,282
NiCl+	9,8854E-11	7,2829E-11	-10,138
NiCl2 (aq)	8,8244E-13	9,3541E-13	-12,029
NiOH+	1,1937E-12	8,7943E-13	-12,056
NiSO4 (aq)	1,0204E-13	1,0817E-13	-12,966
OH-	1,8346E-07	1,3516E-07	-6,869
SO4-2	3,4589E-06	0,000001019	-5,992
Z-(6)(aq)	-0,000032231	-0,000032231	0
Zn(OH)2 (aq)	4,0058E-12	4,2463E-12	-11,372
Zn(OH)3-	2,089E-16	1,539E-16	-15,813
Zn(OH)4-2	9,4897E-22	2,7957E-22	-21,554
Zn(SO4)2-2	1,7244E-17	5,0802E-18	-17,294
Zn+2	8,7152E-09	2,5676E-09	-8,59
Zn2OH+3	1,4268E-18	9,1236E-20	-19,04
ZnCl+	3,8054E-09	2,8036E-09	-8,552
ZnCl2 (aq)	1,053E-09	1,1162E-09	-8,952
ZnCl3-	6,417E-10	4,7276E-10	-9,325
ZnCl4-2	3,0496E-10	8,9842E-11	-10,047
ZnOH+	4,7105E-11	3,4704E-11	-10,46
ZnSO4 (aq)	5,4997E-13	5,8298E-13	-12,234

Table 31 Chemical speciation of metals and some cations and ions estimated using Visual MINTEQ 3.1 in the sampled point P06 of the São Paulo River in January of 2015. . The measured pH values, DOC (Dissolved Organic Carbon) and concentrations of Ca^{2+} , Cl^- , H^+ , K^+ , Mg^{2+} and SO_4^{2-} were used as a input parameters.

Especies Químicas	Concentration (mol / L)	Activity (mol / L)	Log activity (mol / L)
(6)Ca+2D(aq)	0,000013308	0,000013308	-4,876
(6)Cl-1D(aq)	1,958E-08	1,958E-08	-7,708
(6)Cu+2D(aq)	3,3698E-15	3,3698E-15	-14,472
(6)Fe+2D(aq)	3,4667E-13	3,4667E-13	-12,46
(6)H+1D(aq)	2,478E-11	2,478E-11	-10,606
(6)K+1D(aq)	7,2744E-08	7,2744E-08	-7,138
(6)Mg+2D(aq)	1,1733E-06	1,1733E-06	-5,931
(6)Ni+2D(aq)	5,2131E-11	5,2131E-11	-10,283
(6)NiCl+D(aq)	1,9379E-14	1,9379E-14	-13,713
(6)OH-D(aq)	2,9151E-14	2,9151E-14	-13,535
(6)SO4-2D(aq)	8,9089E-16	8,9089E-16	-15,05
(6)Zn+2D(aq)	1,969E-09	1,969E-09	-8,706
Ca+2	0,00010099	0,000029719	-4,527
CaCl+	0,000038504	0,000028359	-4,547
CaOH+	4,6091E-10	3,3947E-10	-9,469
CaSO4 (aq)	6,7459E-09	7,1543E-09	-8,145
Cl-1	0,51	0,37562	-0,425
Cu(OH)2 (aq)	1,2232E-15	1,2973E-15	-14,887
Cu(OH)3-	2,5003E-18	1,8415E-18	-17,735
Cu(OH)4-2	3,9937E-23	1,1752E-23	-22,93
Cu+2	2,5574E-14	7,5255E-15	-14,123
Cu2(OH)2+2	1,7087E-23	5,0281E-24	-23,299
Cu2OH+3	8,8657E-27	5,6541E-28	-27,248
Cu3(OH)4+2	1,614E-32	4,7493E-33	-32,323
CuCl+	7,8392E-15	5,7737E-15	-14,239
CuCl2 (aq)	6,2323E-16	6,6097E-16	-15,18
CuCl3-	3,2644E-18	2,4043E-18	-17,619
CuCl4-2 1	1,4345E-20	4,2212E-21	-20,375
CuHSO4+	4,8105E-26	3,543E-26	-25,451
CuOH+	1,7078E-14	1,2578E-14	-13,9
CuSO4 (aq)	1,7159E-18	1,8198E-18	-17,74
DOC (NICA-Donnan)	0,0003615	0,0003615	-3,442
FA1-Ca(6)(aq)	0,000004871	0,000004871	-5,312
FA1-Cu(6)(aq)	1,6943E-09	1,6943E-09	-8,771
FA1-Fe(II)(6)(aq)	1,8443E-07	1,8443E-07	-6,734
FA1-H(6)(aq)	1,2083E-06	1,2083E-06	-5,918
FA1-Mg(6)(aq)	9,9347E-07	9,9347E-07	-6,003
FA1-Ni(6)(aq)	2,8138E-09	2,8138E-09	-8,551
FA1-Zn(6)(aq)	1,5521E-09	1,5521E-09	-8,809
FA2-Ca(6)(aq)	3,7227E-10	3,7227E-10	-9,429
FA2-Cu(6)(aq)	9,637E-09	9,637E-09	-8,016
FA2-Fe(II)(6)(aq)	1,7443E-12	1,7443E-12	-11,758

FA2-H(6)(aq)	0,000013041	0,000013041	-4,885
FA2-Mg(6)(aq)	5,3023E-10	5,3023E-10	-9,276
FA2-Ni(6)(aq)	8,0291E-10	8,0291E-10	-9,095
FA2-Zn(6)(aq)	1,0068E-10	1,0068E-10	-9,997
Fe(OH)2 (aq)	7,3844E-18	7,8315E-18	-17,106
Fe(OH)3-	1,6376E-20	1,2061E-20	-19,919
Fe+2	2,6309E-12	7,7418E-13	-12,111
FeCl+	2,4912E-13	1,8348E-13	-12,736
FeOH+	2,3402E-14	1,7236E-14	-13,764
FeSO4 (aq)	1,8878E-16	2,0021E-16	-15,699
H+1	2,8367E-08	2,0893E-08	-7,68
HFA1-(6)(aq)	0,000034824	0,000034824	-4,458
HFA2-(6)(aq)	2,6167E-07	2,6167E-07	-6,582
HSO4-	3,0276E-12	2,2299E-12	-11,652
K+1	0,000083274	0,000061333	-4,212
KCl (aq)	0,000010765	0,000011417	-4,942
KOH (aq)	5,6203E-11	5,9606E-11	-10,225
KSO4-	6,2973E-10	4,638E-10	-9,334
Mg+2	8,9041E-06	2,6201E-06	-5,582
MgCl+	5,3802E-06	3,9626E-06	-5,402
MgOH+	7,7545E-10	5,7113E-10	-9,243
MgSO4 (aq)	4,707E-10	4,9919E-10	-9,302
Ni(OH)2 (aq)	2,5056E-14	2,6573E-14	-13,576
Ni(OH)3-	1,7237E-17	1,2696E-17	-16,896
Ni(SO4)2-2	2,7731E-21	8,1601E-22	-21,088
Ni+2	3,9563E-10	1,1642E-10	-9,934
NiCl+	2,2184E-11	1,6339E-11	-10,787
NiCl2 (aq)	1,9953E-13	2,1161E-13	-12,674
NiOH+	1,1004E-12	8,1043E-13	-12,091
NiSO4 (aq)	2,2932E-14	2,432E-14	-13,614
OH-	7,593E-07	5,5924E-07	-6,252
SO4-2	3,5003E-06	0,00000103	-5,987
Z-(6)(aq)	-0,000029019	-0,000029019	0
Zn(OH)2 (aq)	1,1914E-10	1,2636E-10	-9,898
Zn(OH)3-	2,5919E-14	1,909E-14	-13,719
Zn(OH)4-2	4,9123E-19	1,4455E-19	-18,84
Zn(SO4)2-2	3,0208E-17	8,8889E-18	-17,051
Zn+2	1,4943E-08	4,3971E-09	-8,357
Zn2OH+3	1,7342E-17	1,106E-18	-17,956
ZnCl+	6,5669E-09	4,8366E-09	-8,315
ZnCl2 (aq)	1,8229E-09	1,9333E-09	-8,714
ZnCl3-	1,1201E-09	8,2498E-10	-9,084
ZnCl4-2	5,3666E-10	1,5792E-10	-9,802
ZnOH+	3,3388E-10	2,4591E-10	-9,609
ZnSO4 (aq)	9,5078E-13	1,0083E-12	-11,996

APÊNDICE B – JUSTIFICATIVA DA PARTICIPAÇÃO DOS AUTORES

CAPÍTULO 2 - ARTIGO 1: PHYSICOCHEMICAL PARAMETERS IN ESTUARINE ZONES OF THE TODOS OS SANTOS BAY IN BAHIA, BRAZIL.

- Eduardo Gomes Vieira de Melo, Biólogo e Mestre em Geoquímica Petróleo e Meio Ambiente (UFBA/IGEO), participou significativamente na elaboração do artigo, principalmente na Introdução e Discussão. Em discussões com o primeiro autor, Eduardo contribuiu com idéias, busca por referências e análise de resultados.

CAPÍTULO 3 - ARTIGO 2: SPATIAL AND TEMPORAL VARIATION OF METAL CONCENTRATIONS IN ESTUARINE ZONES OF THE TODOS OS SANTOS BAY IN BAHIA, BRAZIL

- Cornelis A.M. van Gestel, Professor at Vrije University and supervisor of Alexandre Dacorso Daltro Milazzo during his PhD Sandwich from march 2015 to february 2016 at the same University in Amsterdam. He helped during all PhD sandwich and with the paper, mainly about the english written.

ANEXO A - REGRAS DE FORMATAÇÃO DA REVISTA - GEOCHIMICA BRASILIENSIS

INSTRUCTIONS TO AUTHORS

Manuscripts submitted for publication to *Geochimica Brasiliensis* should not have been published previously or being considered for publication in any other scientific journal. On submitting a manuscript, authors agree that the copyright of the article is transferred to the Sociedade Brasileira de Geoquímica (SBGq) when the article is accepted for publication. The content of articles is the sole responsibility of the respective author(s).

1. PREPARATION FOR SUBMISSION

a) Type and Size of File: For initial submission the manuscript must be submitted as a single file in pdf format with lines numbered in sequence. Tables and Figures must be in the text body in the appropriate place of insertion. The manuscript cannot contain more than 8,000 words, including, title, authors, institutions and e-mail, abstract, keywords, text, references and subtitles. Files cannot be larger than 10Mb.

b) Sending the file: Text, figures and tables must be sent through the submission system of the *Geochimica Brasiliensis* homepage (www.geobrasiliensis.com.br).

2. ARTICLES

a) Articles written in Portuguese and English will be accepted.

b) Manuscript Organization: The *Geochimica Brasiliensis* Editorial Board suggests the author(s) to present the text in the following sequence: title, complete name of the author(s), complete address and e-mail, abstract, keywords, complete text, acknowledgments and references. The text should have the following items **Introduction, Materials and Methods, Results and Discussion, Conclusions**. These items must be numbered. The use of subitems should be avoided as far as possible. Indication of the **Figure Insertion Position** in the text should be made after its first mention.

c) Abstract: The author(s) should provide an abstract of 150 to 250 words, Times New Roman font, size 10, **space 1**, justified.

d) Keywords: The author(s) should provide 3 to 5 keywords

e) Full Text: For the full text use Times New Roman font, size 11, line space 1.5, paper A4, picture orientation and edited in one column. Lines must be numbered in sequence. Margins: superior: 2.0; inferior 2.0; left 3.0 and right 2.0. Tables, graphics and figures must be inserted in the text after the first time they are referred. They must be numbered in crescent order and centralized. Table captions must be written above the tables. They must also be centralized. Graphic and figure captions must be written below. They must also be centralized. All references must be cited in the text, identified by their author(s) and date of publication (see model below). They must be listed in alphabetical order in the item References.

f) Abbreviations: Must be avoided or kept to a minimum. If used, they must be defined the first time they are mentioned, and must not be used in the title or abstract, unless absolutely necessary.

g) Figures: The printed version of *Geochimica Brasiliensis* publishes figures in black and white and shades of grey.

Colored figures may be published as long as the author(s) pay R\$ 5000,00 (five hundred reais) per colored page. The author(s) will be informed about the number of colored pages after the design of the accepted manuscript. The payment must be done to the SBGq account. For detailed information, please contact the secretary (secretaria@sbq.org.br)

Graphical Illustrations, photos and photomicrography must be numbered in sequence as they are mentioned in the text and will be all considered Figures. They must be separated from the text by one line. Inserts will not be accepted. Outcrop pictures must have scale and indication of North.

Illustration symbols and writings must have adequate dimensions to allow legibility. Figures must be maximum 18 cm width and maximum 25 cm height in order to allow design in two columns. All symbols must be clearly explained. Graphical scale s, if necessary, must be allocated inside the illustration area.

Tables must be self-explaining, with open sides, concise and sequentially numbered. They must be written in Times New Roman, size 9.

h) Equations: They must be numbered sequentially on the right, with arabic figures between brackets.

i) Citations in the text: The following example format must be adopted: ..."Cunha (1985) interpret the feature as an early magmatic cooling structure, but other authors (Lima 1986, Fonseca *et al.* 1989, Ferreira & Araújo 1994) as a late feature".

j) Acknowledgments. It must be in a separate paragraph just before the References.

k) References: Internal reports will NOT be accepted as references, except those which are broadly known by the scientific community and with the GB referees authorization. References must be written with Times New Roman font size 10, line space 1. Automatic space must be used between paragraphs. References must be ordered in alphabetical order of the first author surname, using the following directions:

Books:

Arndt N.T. & Nisbet E.G. (Eds.) 1982. *Komatiites*. George Allen & Unwin, London, 526 pp.

Book Chapter:

Pollack H.N. 1997. Thermal characteristics of the Archean. *In*: M. de Wit & L.D. Ashwal (eds.) *Greenstone belts*. Oxford Monographs on Geology and Geophysics, 25, Oxford University Press, p.: 223-232.

Articles:

Resende M.G. & Jost H. 1995. Petrogênese de formações ferríferas e metahidrotermalitos da Formação Aimbé, Grupo Guarinos (Arqueano), Goiás. *Rev. Bras. Geoc.*, **25**:41-50.

Resende M.G., Jost H., Osborne G.A., Mol A. 1998. The stratigraphy of the Goiás and Faina greenstone belts, Central Brazil: a new proposal. *Rev. Bras. Geoc.*, **28**:1-15.

Sabóia L. A. 1979. Os *greenstone belts* de Crixás e Goiás, Go. *In*: SBG, Núcleo Centro-Oeste, *Boletim Informativo*, **9**:44-72.

Articles in Seral Publications:

Barbosa O., Braun O.P.G., Dyer R.C., Cunha C.A.B.R. 1970. *Geologia da região do Triângulo Mineiro*. Rio de Janeiro, DNPM/DFPM, Boletim 136, 140 p.

Theses and Dissertations:

Resende L. 1995. Estratigrafia, petrografia e geoquímica da seqüência sedimentar do greenstone Belt de Pilar de Goiás, GO. Dissertação de Mestrado, Instituto de Geociências, Universidade de Brasília, 124 p.

Articles published in conferences:

Tassinari C.C.G., Siga Jr. O, Teixeira W. 1981. Panorama geocronológico do centro-oeste brasileiro: solução, problemática e sugestões. *In: SBG, Simp. Geol. Centro-Oeste,1, Atas*, p. 175.

Aerial Photos:

IGC - INSTITUTO GEOGRÁFICO E CARTOGRÁFICO 1986. (São Paulo). Projeto Lins Tupã. Foto aérea. Escala 1:25.000, São Paulo, Fx28, n. 15.

Maps:

INPE - INSTITUTO DE PESQUISAS ESPACIAIS 1987. São José dos Campos (SP): atualização do uso da terra. SF-23-Y-D-II-1 MI-2769/1. São José dos Campos, Mapa Topográfico, escala 1:100.000. Silva A.J. 1999. Mapa geológico da Bacia de Campos. Rio de Janeiro, Petrobrás, 1 mapa geológico, escala 1:50.000.

Softwares:

MICROSOFT 1995. Project for Windows 95, version 4.1: project planning software. Redmond, Wa, Microsoft Corporation. Conjunto de programas 1 CD-ROM.

Internet Pages:

Moura G.A.C. de M. 1996. Citação de referencias e documentos eletrônicos. Disponível em: <http://www.elogica.com.br/users/gmoura/refere.html>. Acessado em 9 out 1996.

INPE - INSTITUTO DE PESQUISAS ESPACIAIS 2000. El Ninho. Disponível em <http://www.inpe.dpi/elninho.html>. Acessado em 14 jun 2000.

3 REVIEW ARTICLES

Review Articles are published by invitation and must be organized as a common article (see item 2). Their purpose is to communicate progress in a specific field of geochemistry, with the objective of providing a critical account of the state of the art from the point of view of the highly qualified and experienced specialist.

4 BOOK REVIEWS

They are published by invitation and must not be larger than one page.

5 NOTES

Their main purpose is to convey short communications which deserve quick publication. They must have the same structure of a common article (see Item 2) e must not have more that 4000 words.

6 FINAL VERSION

Once accepted the author(s) will receive specific instructions concerning the file sending of files for final version design.

pdf files will not be required at this stage.

The text and tables must be sent as Word files.

Figures must be sent as tif files. Colored figures must be as cmyk (not rgb) and shades of gray must be in gray-scale.

Figures (colored, black and white and shades of gray) must have minimum resolution of 300 dpi.

ANEXO B - REGRAS DE FORMATAÇÃO DAS REVISTAS - ENVIRONMENTAL MONITORING AND ASSESSMENT and ENVIRONMENTAL EARTH SCIENCES (Revistas Qualis B2 da CAPES), que serviram como referência para os artigos 2 e 3 (capítulos 3 e 4 respectivamente) desta Tese de Doutorado.

Instructions for Authors

Title Page

The title page should include:

- The name(s) of the author(s)
- A concise and informative title
- The affiliation(s) and address(es) of the author(s)
- The e-mail address, and telephone number(s) of the corresponding author
- If available, the 16-digit ORCID of the author(s)

Abstract

Please provide an abstract of 150 to 250 words. The abstract should not contain any undefined abbreviations or unspecified references.

Keywords

Please provide 4 to 6 keywords which can be used for indexing purposes.

Text

Text Formatting

Manuscripts should be submitted in Word.

- Use a normal, plain font (e.g., 10-point Times Roman) for text.
- Use italics for emphasis.
- Use the automatic page numbering function to number the pages.
- Do not use field functions.
- Use tab stops or other commands for indents, not the space bar.
- Use the table function, not spreadsheets, to make tables.
- Use the equation editor or MathType for equations.
- Save your file in docx format (Word 2007 or higher) or doc format (older Word versions).

Manuscripts with mathematical content can also be submitted in LaTeX.

- [LaTeX macro package \(zip, 182 kB\)](#)

Headings

Please use no more than three levels of displayed headings.

Abbreviations

Abbreviations should be defined at first mention and used consistently thereafter.

Footnotes

Footnotes can be used to give additional information, which may include the citation of a reference included in the reference list. They should not consist solely of a reference citation, and they should never include the bibliographic details of a reference. They should also not contain any figures or tables.

Footnotes to the text are numbered consecutively; those to tables should be indicated by superscript lower-case letters (or asterisks for significance values and other statistical data). Footnotes to the title or the authors of the article are not given reference symbols.

Always use footnotes instead of endnotes.

Acknowledgments

Acknowledgments of people, grants, funds, etc. should be placed in a separate section on the title page.

The names of funding organizations should be written in full.

References

Citation

Cite references in the text by name and year in parentheses. Some examples:

- Negotiation research spans many disciplines (Thompson 1990).
- This result was later contradicted by Becker and Seligman (1996).
- This effect has been widely studied (Abbott 1991; Barakat et al. 1995a, b; Kelso and Smith 1998; Medvec et al. 1999, 2000).

Reference list

The list of references should only include works that are cited in the text and that have been published or accepted for publication. Personal communications and unpublished works should only be mentioned in the text. Do not use footnotes or endnotes as a substitute for a reference list.

Reference list entries should be alphabetized by the last names of the first author of each work. Order multi-author publications of the same first author alphabetically with respect to second, third, etc. author. Publications of exactly the same author(s) must be ordered chronologically.

- Journal article

Gamelin FX, Baquet G, Berthoin S, Thevenet D, Nourry C, Nottin S, Bosquet L (2009) Effect of high intensity intermittent training on heart rate variability in prepubescent children. *Eur J Appl Physiol* 105:731-738. doi: 10.1007/s00421-008-0955-8

Ideally, the names of all authors should be provided, but the usage of “et al” in long author lists will also be accepted:

Smith J, Jones M Jr, Houghton L et al (1999) Future of health insurance. *N Engl J Med* 341:325–329

- Article by DOI

Slifka MK, Whitton JL (2000) Clinical implications of dysregulated cytokine production. *J Mol Med*. doi:10.1007/s001090000086

- Book

South J, Blass B (2001) *The future of modern genomics*. Blackwell, London

- Book chapter

Brown B, Aaron M (2001) The politics of nature. In: Smith J (ed) *The rise of modern genomics*, 3rd edn. Wiley, New York, pp 230-257

- Online document

Cartwright J (2007) Big stars have weather too. IOP Publishing PhysicsWeb. <http://physicsweb.org/articles/news/11/6/16/1>. Accessed 26 June 2007

- Dissertation

Trent JW (1975) *Experimental acute renal failure*. Dissertation, University of California

Always use the standard abbreviation of a journal’s name according to the ISSN List of Title Word Abbreviations, see

- [ISSN LTWA](#)

If you are unsure, please use the full journal title.

For authors using EndNote, Springer provides an output style that supports the formatting of in-text citations and reference list.

- [EndNote style \(zip, 2 kB\)](#)

Tables

- - All tables are to be numbered using Arabic numerals.
- - Tables should always be cited in text in consecutive numerical order.
- - For each table, please supply a table caption (title) explaining the components of the table.
- - Identify any previously published material by giving the original source in the form of a reference at the end of the table caption.
- - Footnotes to tables should be indicated by superscript lower-case letters (or asterisks for significance values and other statistical data) and included beneath the table body.

Artwork and Illustrations Guidelines

Electronic Figure Submission

- Supply all figures electronically.
- Indicate what graphics program was used to create the artwork.
- For vector graphics, the preferred format is EPS; for halftones, please use TIFF format. MSOffice files are also acceptable.
- Vector graphics containing fonts must have the fonts embedded in the files.
- Name your figure files with "Fig" and the figure number, e.g., Fig1.eps.

Figure Lettering

- To add lettering, it is best to use Helvetica or Arial (sans serif fonts).
- Keep lettering consistently sized throughout your final-sized artwork, usually about 2–3 mm (8–12 pt).
- Variance of type size within an illustration should be minimal, e.g., do not use 8-pt type on an axis and 20-pt type for the axis label.
- Avoid effects such as shading, outline letters, etc.
- Do not include titles or captions within your illustrations.

Figure Numbering

- All figures are to be numbered using Arabic numerals.
- Figures should always be cited in text in consecutive numerical order.
- Figure parts should be denoted by lowercase letters (a, b, c, etc.).
- If an appendix appears in your article and it contains one or more figures, continue the consecutive numbering of the main text. Do not number the appendix figures, "A1, A2, A3, etc." Figures in online appendices (Electronic Supplementary Material) should, however, be numbered separately.

Figure Captions

- Each figure should have a concise caption describing accurately what the figure depicts. Include the captions in the text file of the manuscript, not in the figure file.
- Figure captions begin with the term Fig. in bold type, followed by the figure number, also in bold type.
- No punctuation is to be included after the number, nor is any punctuation to be placed at the end of the caption.
- Identify all elements found in the figure in the figure caption; and use boxes, circles, etc., as coordinate points in graphs.
- Identify previously published material by giving the original source in the form of a reference citation at the end of the figure caption.

Figure Placement and Size

- Figures should be submitted separately from the text, if possible.
- When preparing your figures, size figures to fit in the column width.
- For most journals the figures should be 39 mm, 84 mm, 129 mm, or 174 mm wide and not higher than 234 mm.
- For books and book-sized journals, the figures should be 80 mm or 122 mm wide and not higher than 198 mm.

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If you include figures that have already been published elsewhere, you must obtain permission from the copyright owner(s) for both the print and online format. Please be aware that some publishers do not grant electronic rights for free and that Springer will not be able to refund any costs that may have occurred to receive these permissions. In such cases, material from other sources should be used.

Accessibility

In order to give people of all abilities and disabilities access to the content of your figures, please make sure that

- All figures have descriptive captions (blind users could then use a text-to-speech software or a text-to-Braille hardware)
- Patterns are used instead of or in addition to colors for conveying information (colorblind users would then be able to distinguish the visual elements)
- Any figure lettering has a contrast ratio of at least 4.5:1

Electronic Supplementary Material

Springer accepts electronic multimedia files (animations, movies, audio, etc.) and other supplementary files to be published online along with an article or a book chapter. This feature can add dimension to the author's article, as certain information cannot be printed or is more convenient in electronic form.

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Submission

- Supply all supplementary material in standard file formats.
- Please include in each file the following information: article title, journal name, author names; affiliation and e-mail address of the corresponding author.
- To accommodate user downloads, please keep in mind that larger-sized files may require very long download times and that some users may experience other problems during downloading.