UNIVERSIDADE FEDERAL RURAL DE PERNAMBUCO

PRÓ-REITORIA DE PESQUISA E PÓS-GRADUAÇÃO

PROGRAMA DE PÓS-GRADUAÇÃO EM RECURSOS PESQUEIROS E AQUICULTURA

Avaliação de impactos ambientais em um estuário neotropical do litoral de Pernambuco, Nordeste do Brasil.

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Tese apresentada ao Programa de Pós-Graduação em Recursos Pesqueiros e Aquicultura da Universidade Federal Rural de Pernambuco como exigência para o título de Doutor.

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"Todo homem deve viver e morrer como um guerreiro".

- Mário Ferreira dos Santos

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Resumo

O Complexo Estuarino de Itapessoca, pertencente ao Ecossistema Estuarino de Itamaracá, caracteriza-se por um histórico de intensas atividades econômicas que se desenvolvem às margens de seus rios tributários, muitas vezes exercidas sem qualquer controle ou planejamento. Para relacionar eventos naturais e antrópicos com a idade do sedimento foi realizada a geocronologia pela determinação do radionuclídeo de chumbo Pb-210 em excesso (fallout), pela técnica de Fluxo Proporcional Gasoso. A geocronologia foi aplicada para rastrear a contaminação por mercúrio no ecossistema estuarino. Dos resultados de Pb-210, as taxas de sedimentação confirmaram a contaminação por Mercúrio (Hg) em Itamaracá desde 1965. Os eventos de precipitação extrema e seca têm também sido relacionados com o padrão de distribuição das concentrações de Hg em sedimentos profundos. Para investigar possíveis perturbações nos recentes processos de sedimentação na área de estudo, foram coletadas 20 amostras de sedimento de superfície e 2 testemunhos para análise das concentrações dos elementos químicos Al, Ca, Fe, K, Mg, Mn, Ni, Pb, Si, Sr, Ti e Zn, determinadas pela técnica de Fluorescência de Raios-X por Dispersão de Energia - EDXRF. Por meio dos fatores de enriquecimento e razões entre alguns elementos associados a dados geocronológicos, foi possível identificar mudanças geoquímicas na sedimentação dos pontos amostrados, com aumento de minerais associados a frações finas e diminuição das proporções de elementos associados a frações grosseiras. A geocronologia revelou que o enriquecimento de Pb e o aumento acentuado dos fatores de enriquecimento de Ca e Sr estão fortemente associados à atividade antrópica da região (mineração e fabricação de cimento). As características da ictiofauna como a diversidade ou suas relações com as características abióticas foram estudadas na área. Um total de 76 espécies distribuídas em 33 famílias foi coletado. Aspectos como guildas funcionais e diversidade forma investigados e comparados entre as áreas de Catuama e Itapessoca. Embora muitas espécies de importância comercial na região estejam jovens, apenas uma espécie foi classificada como vulnerável (IUCN). Análise estatísticas mostraram que condutividade elétrica da água, Total de Sólidos Dissolvidos, salinidade e o metal zinco foram os fatores mais correlacionados com a composição especifica da ictiofauna embora nenhum padrão claro foi identificado. Este estudo revelou que a área de estudo possui relevância para a alimentação e abrigo para diversas espécies marinhas e que processos naturais parecem exercer maior influência sobre a composição da ictiofauna ocorrente.

Palavras-chaves: Estuário tropical; Mercúrio; Geocronologia; Pb-210; Guildas funcionais, diversidade.

Abstract

The Itapessoca Estuarine Complex, belonging to the Itamaracá Estuarine Ecosystem, is characterized by a history of intense economic activities that develop along the banks of its tributary rivers, often performed without any control or planning. In order to relate natural and anthropic events with the age of the sediment, a geochronology was carried out by the determination of Pb-210 in excess (fallout), by the Gas Proportional Flow technique. Firstly, geochronology was applied to trace mercury contamination in the estuarine ecosystem. Two sediment cores were sampled, stratified and analysed by the Gas Proportional Flow Counter technique for determination of Pb-210 activity, a radionuclide applied to geochronology. Mercury was quantified in sediment samples by Cold Vapor Atomic Absorption Spectrometry, ranging from 0.17 to 1.29 mg.kg-1 in deep sediments. From the Pb-210 results, sedimentation rates of 0.84 (±0.07) cm.year-1 and 1.03 (±0.22) cm.year-1 confirmed Hg contamination in Itamaracá since 1965. Extreme precipitation and drought events have also been related to the distribution pattern of Hg concentrations in deep sediments. To investigate possible disturbances in the recent sedimentation processes in the study area, 20 surface sediment samples and 2 cores were collected for analysis of chemical elements Al, Ca, Fe, K, Mg, Mn, Ni, Pb, Si, Sr, Ti and Zn concentrations, determined by Energy Dispersive X-Ray Fluorescence - EDXRF technique. Through the enrichment factors and ratios between some elements associated with geochronological data, it was possible to identify geochemical changes in the sedimentation of the sampled points, with an increase in minerals associated with fine fractions and a decrease in the proportions of elements associated with coarse fractions. The geochronology revealed that the enrichment of Pb and the marked increase in the enrichment factors of Ca and Sr are strongly associated with the anthropic activity of the region (mining and cement factory). A total of 76 species distributed in 33 families were collected. Aspects such as functional guilds and diversity were investigated and compared between Catuama and Itapessoca. Although many species of commercial importance in the region are young, only one species was classified as vulnerable (IUCN). Statistical analyses showed that electrical conductivity of the water, Total Dissolved Solids, salinity and the metal zinc were the factors most correlated with the fish assemblage variation although no clear pattern were found. This study revealed that the study area has relevance for feeding and shelter for several marine species and that natural processes seem to exert more influence on the composition of the occurring ichthyofauna.

Keywords: Tropical estuary; Mercury; Geochronology; Pb-210; Functional guilds, diversity.

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Introdução

A zona costeira é um ecossistema frágil e dinâmico, localizado na interface oceano-continente, cujos processos bióticos e abióticos funcionam de maneira complexa. A forma e sedimentação desses ambientes são controladas globalmente pelas oscilações do nível do mar e tectônica global, mas em níveis regionais, o balanço entre os processos meteorológicos, oceanográficos e sedimentares são responsáveis pelas alterações nestes ecossistemas (PERILLO, 1995; ELLIOTT e McLUSKY, 2002; KNIGHT e FITZGERALD, 2005). A zona costeira também abriga cerca de 70% da população mundial, fator determinante para a modificação dos padrões sedimentares e da morfologia da linha de costa (ZOURARAH et al., 2007). Dentre as diferentes feições da zona costeira, estuários se apresentam como áreas salobras formadas pela combinação de dois ecótonos – o rio salobra e o mar (ATTRIL e RUNDAN, 2002). As características peculiares dos estuários, marcadas por intensa variabilidade físico-química, determinam um menor número de espécies residentes em comparação às espécies migrantes marinhas, devido aos complexos mecanismos fisiológicos necessários para lidar com a vida em um ambiente com tantas variações (ALBARET et al. 2004; BLABER, 2000). A depender de nuances locais, o desenvolvimento de condições hiperhalinas ocasionado por variações hidrológicas pode aumentar as tensões sobre organismos eurialinos que vivem nestes sistemas (WHITFIELD et al., 2006). Todavia, as características peculiares dos estuários asseguram o sustento das comunidades de peixes, aspecto que lhes confere importância ecológica e econômica, uma vez que são áreas de alimentação e reprodução para inúmeras espécies marinhas que dependem desse ecossistema (PAIVA et al, 2008), inclusive, de importância pesqueira (BLABER, 2000). Estuários são tidos como berçários naturais por oferecerem alimento e abrigo para toda a sorte de organismos incidentes (COURRAT et al., 2009; VASCONSCELOS FILHO et al., 2003). Além de fornecer abrigo para espécies de importância comercial, gerando bens e serviços para comunidades locais, estuários transferem nutrientes e matéria orgânica para águas costeiras adjacentes (CLARK, 2001).

Além da importância econômica, bastante evidenciada pela pesca, estuários apresentam grande importância social, visto que o desenvolvimento da sociedade moderna está fortemente atrelado aos ambientes costeiros. Nesse sentido, os estuários ocupam lugar de destaque por serem favoráveis à ocupação humana, pois oferecem portos naturais e alimento, razão pela qual também acabam se tornando vulneráveis à destruição, sujeitos à diferentes escalas de impacto humano (HITCHCOCK E MITROVIC, 2019).

A capacidade de recuperação ecológica natural dos estuários – a autodepuração, embora não seja ainda bem compreendida, está relacionada aos processos que regem a hidrodinâmica do sistema – os processos estuarinos estão diretamente relacionados à interação de suas condições forçantes com a morfologia local (PAIVA et al, 2016). A autodepuração estuarina, no entanto, pode ser influenciada descargas antropogênicas (ACEVEDO-MERINO et al., 2005). Agentes estressores antropogênicos alteram o equilíbrio do ecossistema, que passa a se expressar de maneira anormal. Tal alteração pode ser exemplificada por incessantes descargas de efluentes domésticos e industriais em nossos principais corpos d'água, agravadas pela instalação de metade da população mundial, que habita num raio de até 100 km da costa (BARRAGÁN e ANDRÉS, 2015). Contudo, por conta das supracitadas e intensas variações ambientais, estuários muitas vezes proporcionam estresses naturais semelhantes aos estresses antrópicos e considerando a dependência excessiva das características estruturais dos ecossistemas nos indicadores de qualidade, tais como a diversidade, faz com que a detecção do estresse antrópico seja mais difícil (ELLIOTT e QUINTINO, 2007).

A intensificação do uso humano da zona costeira brasileira ocorreu historicamente pela urbanização e processos industriais desde 1630 (PONTUAL, 2001). Essa intensificação ocasiona alterações ambientais com a introdução de nutrientes, perturbação e destruição de habitats, alteração nos padrões de sedimentação, exploração dos recursos naturais, poluição industrial e doméstica, aterramento, interferências na linha de costa (ZOURARAH et al., 2007). Nesse contexto, o litoral norte do estado de Pernambuco também tem sido palco de exploração humana (CPRH, 2003). Embora sejam protegidas por lei, as áreas estuarinas do Litoral Norte têm sido agredidas por diferentes atividades antrópicas, em especial, pela ocupação urbana desordenada, implantação de infraestrutura de suporte ao turismo, pela pesca predatória, mineração clandestina, disposição de lixo e pelo avanço dos empreendimentos de carcinicultura (CPRH, 2003).

Em Goiana, município do litoral norte, a devastação crescente da cobertura florestal contribui para a intensificação de processos erosivos em morros e encostas (CPRH, 2003). A expansão urbana sobre os mangues e áreas alagáveis, também constitui grave problema ambiental. Guimarães *et al* (2010) demonstram que a carcinicultura é responsável por 9,6% do total da supressão de manguezal, contudo, alguns viveiros de camarão em atividade foram antigos viveiros de peixes, contrapondo a tese de que a carcinicultura seria o grande algoz dos manguezais no litoral norte de Pernambuco – embora um aumento da cobertura de manguezal tenha sido reportado por Pelage *et al*. (2019). Os diversos aportes de nutrientes e a elevada carga de poluentes industriais e urbanos no litoral norte de Pernambuco foram proficuamente identificados pela CPRH (2003), que sinaliza inclusive o comprometimento dos mananciais e a vulnerabilidade dos recursos hídricos subterrâneos.

A contaminação por mercúrio da água, sedimentos e tecidos de peixes e ostras do Canal de Santa Cruz foram identificados pela CETESB (1981; 1984) que apontou para uma indústria de soda-cloro como responsável pela liberação do contaminante. Elevados níveis de contaminação foram confirmados por Meyer (2017), entretanto, a baixa exportação de Hg para áreas costeiras sugere que muito do Hg remobilizado é ciclado no próprio sistema estuarino ou é liberado para a atmosfera, o que representa risco considerável para os organismos expostos ao mercúrio.

De acordo com Medeiros *et al* (2001) a poluição foi agravada pela descarga concomitante de cloro e ácidos residuais das usinas de açúcar, que aumentaram a dissolução do Hg, dificultando a sua remoção a partir da coluna de água, facilitando assim sua distribuição ao longo do ecossistema estuarino. Lins e Wanderley (1999) detectaram elevados teores de mercúrio em sedimentos do rio Botafogo, no distrito industrial do município de Igarassu, litoral norte da Região Metropolitana do Recife - RMR.

Efluentes terrestres são portas de entrada para grandes quantidades de metais-traços no ambiente estuarino (CLARK, 2001). Os metais pesados liberados no ambiente como o mercúrio, se acumulam nos organismos e seus níveis tendem a crescer com o crescimento e aumento do nível trófico, indicando sua posição na cadeia (LAVOIE et al., 2013). Nesse contexto, a contaminação por mercúrio pode ser considerada a mais emblemática devido a sua elevada toxicidade e históricos de contaminação em ambientes aquáticos (KASPER et al., 2007), sendo um poluente persistente (ARIYA et al, 2004) e extremamente tóxico para seres humanos (WHO, 1990). A concentração de mercúrio em peixes carnívoros, de nível trófico mais elevado é, em geral, maior do que nos não carnívoros e demais organismos (CASTILHOS et al., 2005). Considerando que muitas espécies de peixes utilizam os estuários tropicais como berçários, locais de alimentação e abrigo em diferentes estágios do seu ciclo de vida (BLABER, 2007), o mercúrio destaca-se quanto à perniciosidade à biota, uma vez que é o único metal que transpõe todos os níveis da cadeia trófica aquática mediante processos de bioacumulação e biomagnificação (LINDQVIST et al., 1991). O mercúrio pode acarretar, por exemplo, mudanças dos mecanismos fisiológicos vinculados à relação predador-presa (SLOMAN et al., 2005). Outros efeitos subletais adversos comumente reportados incluem alterações em aspectos reprodutivos, incluindo inibição do desenvolvimento gonadal (FARREL, 2011). Matta et al. (2001) observaram diminuição da habilidade reprodutiva da espécie de peixe *Fundulus heteroclitus* (Linnaeus, 1766), quando exposto ao metil mercúrio.

O sedimento constitui um dos principais reservatórios de nutrientes de um ecossistema aquático, atuando como acumulador de metais-traços no ciclo hidrológico, pois reflete a qualidade geral do sistema e o comportamento histórico de parâmetros hidrológicos e químicos (ROBBINS e

EDGIGTON, 1975; HEIM e SCHWARZBAUER, 2013; XUE et al, 2007). Os sedimentos conservam o registro de contaminações ocorridas ao longo do tempo, uma vez que áreas recentemente poluídas podem apresentar concentrações de metais mais elevadas nas camadas superficiais do que em camadas mais profundas, fornecendo registro de impactos ambientais, inclusive de fontes antropogênicas (SINEM ATGIN et al., 2000). Marx e Kamber (2014), constataram que os metais possuem grande afinidade com sedimentos finos, sendo estes controlados por processos que regem o transporte e deposição dos sedimentos. No caso do mercúrio, sua biodisponibilidade está atrelada a processos físico-químicos, por exemplo, a adsorção por argilas, sedimentação e complexação (quelação) pela matéria orgânica (ULLRICH *et al.*, 2001).

O quadro geral apresentado justifica a proposição da presente pesquisa e a importância de se aprofundar a avaliação da qualidade ambiental dos ecossistemas estuarinos do litoral norte e compreender os fatores envolvidos nos eventuais processos de degradação ambiental. Diante do exposto, o presente estudo busca disponibilizar informações acerca do atual cenário ambiental, com base em registros minerais do sedimento e estudo da composição de assembleias ícticas coletadas na área de estudo. O estudo está organizado em três capítulos: o primeiro capítulo fornece informações precisas sobre a evolução dos níveis de contaminação de mercúrio total no sedimento, mediante a datação de testemunhos coletados na área de estudo, por meio de técnicas de química nuclear e faz inferências sobre possíveis fontes de contaminação. O segundo capítulo traz inferências sobre a evolução da concentração de metais ao longo do tempo, presentes em testemunhos coletados no litoral norte, através de análises multi elementares e datação por Pb-210 e busca correlações de atividades antrópicas e naturais com eventuais padrões geoquímicos de sedimentação local. O terceiro capítulo é um levantamento da biodiversidade da ictiofauna local, com estudos sobre a composição de riqueza, abundância e biomassa, mediante abordagem de guildas funcionais, correlacionadas com variáveis ambientais de maior influência. A síntese das principais informações está disposta nas considerações finais.

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CAPÍTULO 1

Tracking Hg historical inputs by pb-210 geochronology for the Itapessoca Estuarine Complex, Pernambuco, Brazil

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Tracking Hg historical inputs by Pb-210 geochronology for the Itapessoca Estuarine Complex, Pernambuco, Brazil

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Abstract
The application of geochronology for tracking mercury contamination was remarkably demonstrated in the Itamaracá Estuarine Ecosystem, Pernambuco State, Brazil. Here, two sediment cores were sampled, layered and analyzed by the Gas Flow Proportional Counter technique for determining ^{210}Pb, radionuclide applied to geochronology. Mercury was quantified in sediment samples by Cold Vapor Atomic Absorption Spectrometry, varying from 0.17 to 1.29 mg kg^{-1} in deep sediments. From ^{210}Pb results, the sedimentation rates of 0.84 (0.07) cm year^{-1} and 1.03 (0.22) cm year^{-1} confirmed Hg contamination in Itamaracá since mid-1965. Events of extreme precipitation and drought have been also related to the distribution pattern for Hg concentrations in deep sediments.

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Introduction

Modern society is greatly affected by environmental hazards related to the increasing levels of trace elements generated by the chemical industry. Mercury (Hg) is one of the most relevant trace elements due to its toxicity and availability to organisms, mainly in its organic form, methylmercury. High levels of Hg biomagnification have already been noticed in diverse species, including humans [1]. Unfortunately, many estuarine areas are subjected to diverse anthropogenic pressures of this type [2]. There are few works dealing with the actual levels of mercury contamination in Brazilian estuaries [3].

One of the most relevant environmental problems for the Itamaracá Estuarine Ecosystem has been the release of 22–35 metric tons of mercury into the Botafogo River by a chlor- alkali factory between 1964 and 1987 [4, 5]. The impact of this accident was aggravated by the concomitant discharge of chlorine and acid wastes from sugarcane mills in the area, increasing the dissolution and thus facilitating Hg distribution throughout the Itamaracá estuarine ecosystem. In 1991, leakage of the precipitation basin, constructed to avoid further contamination, continued to enrich the Hg concentrations in sediments [5]. Moreover, there are other sources of mercury present in the area,

such as coal burning, production of non- ferrous metals and cement [1, 6]. High concentrations of mercury have been found in the area, contaminating seafood [4, 7] and marine fish [8] and, thereby, humans [9].

The Itapessoca Estuarine Complex is within the Itamaracá Estuarine Ecosystem, which is of utmost importance for the supply of potable water, biodiversity conservation, aquaculture, fishing and recreational activities in the State of Pernambuco, Brazil. Nevertheless, the tracking of Hg historical inputs in deep sediments from the Itamaracá Estuarine Ecosystems had not been yet carried out. In fact, many studies have employed 210Pb to date sediments for tracking the recent evolution of anthropogenic mercury in estuarine sediments [10–12].

Deep sediment geochronology is the base for studies in estuarine areas regarding environmental impact assessment, monitoring and environmental reconstruction. In terms of Brazilian environmental legislation, even though reference values could be obtained for ecological restoration of impacted areas, deep sediment chemical composition can be used for the determination of background values in the case of less disturbed estuaries.

Nuclear analytical techniques are especially apt for deter- mining radionuclides in deep sediment samples, mainly unsupported 210Pb (210Pb in excess compared to the same radionuclide originally present in the geological material), that is the activity concentration of atmospheric 210Pb incorporated into the sediments during the sedimentation. This dating technique allows evaluating events that have taken place in the latest 120 years, being very useful to register the recent Hg anthropogenic impacts in estuarine areas. This geochronologic technique can be applied to many estuarine ecosystems, although sediment dating may depend on environment dynamics that have affected the mixing of sediment layers [13].

Therefore, the objective of this work was to apply 210Pb geochronology for tracking the impact of Hg on the Itapessoca Complex Estuarine. For this, the Constant Initial Concentration model was used for the determination of sedimentation rates based on activity concentrations of unsupported (in excess) 210Pb. Total mercury in sediment profiles were determined by Cold Vapor Atomic Absorption Spectrometry—CVAAS.

Experimental

Studied area

The Itapessoca Complex Estuarine is one of the ecosystems that forms part of the Itamaracá Estuarine Ecosystem, in the State of Pernambuco, Brazil, with a total area of 842 km^2. The climate is tropical, hot and humid, that is, type Aws according to the Köppen-Geiger classification, with mean annual temperature of 26 °C and the annual precipitation of 1500–1700 mm [5]. Most of the freshwater comes from the Itapessoca, Arataca, Botafogo and Igarassu Rivers, with the last three being the major sources of freshwater (Fig. 1).

Hydrology varies according to the season. Salinity and total suspended sediments (TSS) tend to be lower during the rainy period. A large part of the TSS remains in the channel and tidal trapping promotes its homogeneous distribution throughout the dry season. During the rainy season, despite the large riverine input of suspended matter, retention by mangrove swamps and water exchange appears to remove TSS from the system. Advective transport dominates the net longitudinal salt flux and transport of TSS, independent of the season [5].
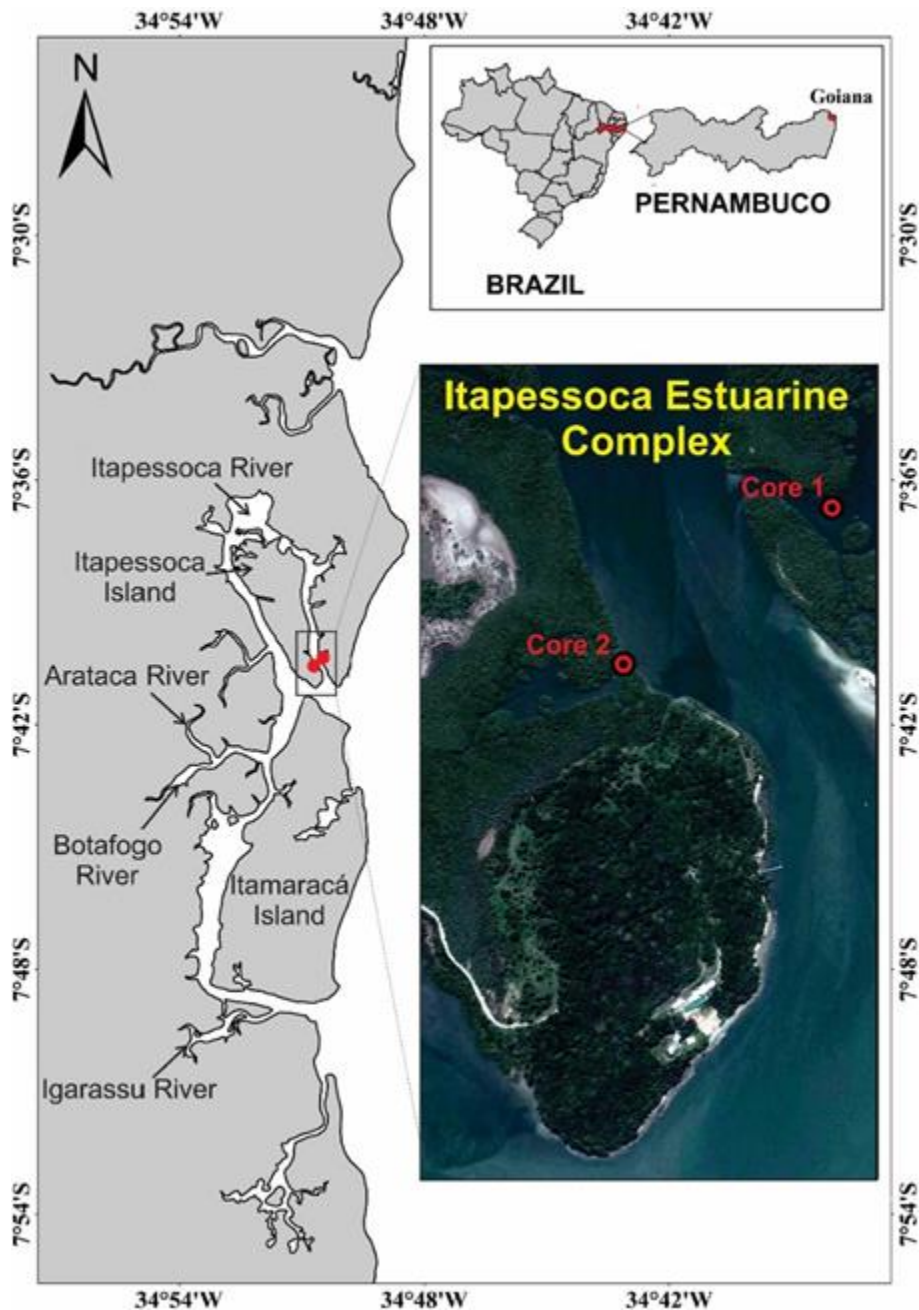
Fig. 1 Itapessoca Estuarine Complex within the Itamaracá Estuarine Ecosystem in the State of Pernambuco, Brazil. Cores 1 and 2 (in red) sampled in the estuary.

Sampling and sample preparation

The selection of the sampling units was based on the accessibility of the estuarine areas and the security of the people involved. Core 1—Catuama was sampled in the man- grove at the margins under influence of the Ponta de Pedras Municipality, while Core 2—Itapessoca was collected at the opposite margin, under the influence of Itapessoca Island (Fig. 1). This river is the main carrier of

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residues from chem- ical industries located in the Metropolitan Region of Recife, Pernambuco, Brazil.

Sediment profiles were collected using clean PVC (polyvinyl chloride) - corers of 150 cm which were thrust into the sediment during the lowest daily tides in April, 2017. The PVC corers were immediately covered to avoid losses of sediment and to enable their transportation in a vertical position to the Centro Regional de Ciências Nucleares do Nordeste—CRCN-NE for sample preparation. The sediment profiles were divided into layers of 1–2 cm, depending on the sediment texture (clay and organic matter allow thicker slicing). A total of 21 samples were obtained for each core. Samples of 50–100 g were oven-dried until constant weight (consecutive weighing difference of 0.1 mg) and comminuted in porcelain mortar until reaching a particle size of less than 80 µm. Porcelain mortar was used to avoid metallic contamination during the milling.

Radiometric analysis

The radiochemical procedure was adapted from Godoy et al. [14]. Test portions of 5 g of sediment samples were transferred to polyethylene flasks to which were added 1 g of hydroxylamine hydrochloride, 1 mL of Pb carrier (metallic lead + HNO_3 20 mg.mL^{-1}) and 100 mL of hydrobromic acid 0,5 M. Analytical blanks (n = 3) were also prepared with the samples using the chemical reagents only. The mixtures were vigorously shaken for 12 h, followed by filtration through a cellulose filter and transfer to clean polyethylene vials. The filtered sample solutions were poured to an ion-exchange column containing the resin Dowex® 1X8 chloride form, 50–100 mesh soaked in Milli-Q water. The lead retained in the resin was extracted using 100 mL of HNO_3 1 mol L−1. The solutions obtained were transferred to a 250 mL beaker, previously decontaminated with nitric acid and distilled water, and then the solutions were heated on a heater plate until dry. Ultrapure water (electric resistivity of 18.2 MΩ cm) was added to the remaining solution to complete it to 50 mL. A solution of NH_4CH_3COO 40% was used to adjust the pH to the range of 4.5–5.0, using methyl red [2-(*N*,*N*-dimethyl- 4-aminophenyl) azobenzenecarboxylic acid]. Then, the solutions were heated again to the boiling point and 2 mL of sodium chromate was added to precipitate the analyte as lead chromate. The precipitated material was cooled and filtered using a Millipore system with a 0.45 µm pore opening cellulose filter. The filters containing the precipitated material were oven-dried at 80 °C for 2 min, also allowing the gravimetric determination of the chemical yield.

The activity concentration of 210Pb was determined from its decay product, 210Bi, after a 2-week waiting time to reach secular equilibrium, using beta counting on the Canberra Gas Flow Proportional Counter, model Tennelec Series 5 XLB. In this case, only the beta activity of 210Bi was

meas- ured because the filter paper used to cover the sample filters hold back the low energy beta-particles of 210Pb and the alpha-particles of ingrown 210Pb [15]. The radioactivity of sample and blank filters was measured during 100 min after equipment settings for the alpha/beta plateau (a) and detection efficiency (b). For (a), the radioactivity of 241Am (580 α s−1; reference date: March 2007) and 90Sr/90Y (2020 β s−1; reference date: March 2007) sources were measured from 330 to 1620 V during 1 min for each step of 30 V [16]. For determining (b), the same radioactive sources that had been used before were measured for 15 min [17]. Typically, the alpha plateau, beta plateau, alpha efficiency and beta efficiency were 660 V, 1500 V, 48.8% ± 0.7% and 46.8% ± 0.7%, respectively. 210Pb determination analytical uncertainty was estimated from independent analysis of standards for true- ness (n = 5) and repeatability (n = 10). The individual uncertainties due to precision (analytical replicates) and trueness (deviation among the ratios between obtained and reference values) were combined according to the recommendation of the Eurachem/Citac Guide CG [18]. The expanded analytical uncertainty at 95% confidence level for the determination of Pb-210 in sediments samples by GFPC technique was estimated in 15%.

It was assumed that the proposed leaching method was able to recovery only 210Pb in sediment samples according to the Godoy et al. [14]. In that work, the IAEA 315 Marine Sediment was analyzed after the hydrobromic acid extraction, resulting in a mean activity concentration of 44.8 Bq.kg^{-1} ± 3.8 Bq.kg^{-1} for a reference value of 48 Bq.kg^{-1} (42.2–54.1 Bq.kg^{-1}).

For each core, background values (supported 210Pb) were calculated by averaging results of the deep sediments as recommended by Godoy et al. [14] because the leach- able method had been applied to the comminuted sediment samples (particle size smaller than 80 µm). When a constant value of 210Pb activity concentration with deep sediments had been achieved, this value was subtracted from the 210Pb activity concentration for each layer located above this depth. These corrected excess 210Pb activity concentrations were employed for the sedimentation rate evaluation per Godoy et al. [14].

Mercury analysis

All chemical reagents were of analytical grade as well as ultrapure water with a resistivity of 18.2 MΩ cm (Milli-Q system, Millipore) were used in all procedures. The glass- ware was new and entirely dedicated to Hg analysis to avoid interference. The Hg analysis consisted of acid chemical treatment, solution preparation for CVAAS analysis and the chemical analysis itself by Cold Vapor Atomic Absorption Spectrometry—CVAAS.

For the preparation of the sediment samples, the method was modified from Akagi and Nishimura [19]. Analytical portions (0.5 g) of sediments and of the Standard Reference Material® 2710 Montana Soil were transferred to 100 mL volumetric balloons to which were added 1 mL of sub boiled HNO_3 p.a., 1 mL of $HClO_4$ p.a., 5 mL of sub boiled H_2SO_4 and 1 mL of ultrapure water. The mixtures were heated at 90 °C for 30 min. For keeping the samples in constant reflux, quartz spheres were placed in the top neck of the volumetric balloons. After heating, solutions were left at room temperature (24 °C) to cool down. The volumes of samples, reference material and analytical blanks were completed to 50 mL with ultrapure water.

For CVAAS analysis, aliquots of 40 mL of sample, reference material and blank solutions were prepared adding 5 mL of hydroxylamine hydrochloride 30% (m/v) and 4.2 mL of HCl 12 mol L−1. A solution of 25% m/v $SnCl2$ in 12 mol L−1 HCl, used as a reducing agent, was prepared daily by dissolving 25 g of salt (Merck) in about 20 mL of concentrated hydrochloric acid, followed by heating for 10 min and diluting with up to 100 mL of ultra-pure water. Standard mercury solutions (10–50 µg L−1) were prepared by stepwise dilution from 1000 mg L−1 stock solution (Merck) with Milli-Q water [20].

All solutions were analyzed in the spectrometer Agilent model AA240FS with the Vapor Generation Accessory 77 (VGA 77). The analytical conditions were wavelength of 253.7 nm and slit width of 0.1 nm. The mercury vapor generated in VGA 77 was transported through a nitrogen (99.999%) flow into the Agilent 220 FS spectrometer for analysis [21].

All analytical results were calculated using Microsoft Excel®, including the estimate of the expanded analytical uncertainty at the 95% confidence level according to method proposed elsewhere [18]. The expanded analytical uncertainty for Hg analysis by CVAAS (k = 2) was estimated in 4.9%. Figure 2 shows the control chart for all analytical portions analyzed (from RM1 to RM10), in which all results were under control at the 99% confidence level ($- 1 < z < 1$).

Results and discussion

The results of 210Pb activity concentrations in sediments from cores 1—Itapessoca and 2—Catuama are presented in Fig. 3. By comparing the respective median values of 39 Bq.kg^{-1} and 32 Bq kg−1 for both profiles, all surface sediments (0–15 cm) presented higher activity concentrations of 210Pb. Moreover, the activity concentrations were quite low a lower depth (> 40 cm), allowing prediction of the sedimentation rates. However, the activity concentrations of 210Pb from Core 2 did not decrease steeply (from 37 to 28 Bq.kg^{-1}) compared to the other core (Fig. 3).
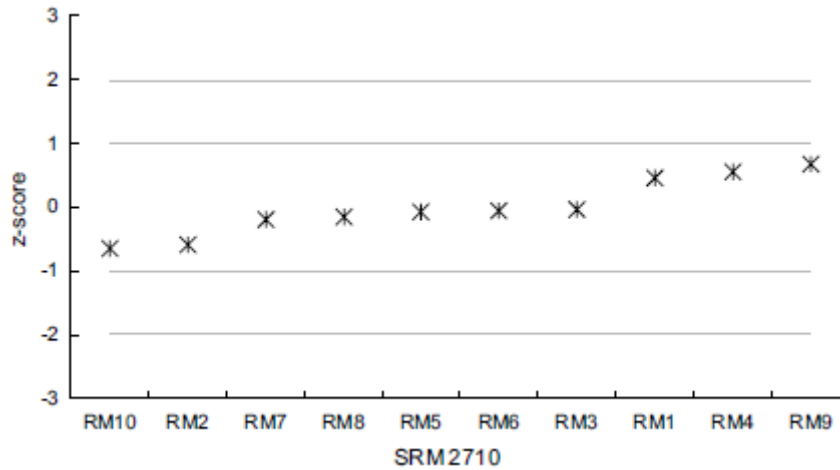
Fig. 2 z-Score (*value obtained – value reference / uncertainty reference*) for Hg measurements of SRM 2710 (RM) (n = 10)

Linear regression was applied to $\ln(210Pb_{exc})$ and depth (cm) at the 95% confidence level, according to the results from Table 1. The sedimentation rate was obtained by dividing the 210Pb decay constant by the adjusted linear regression coefficient, thereby supposing a constant unsupported 210Pb supply to the estuaries. Despite the complexity of geochronology in terms of model application and difference between models [13], the sedimentation rates of 0.84 ± 0.07 cm year−1 and 1.03 ± 0.22 cm year−1 were determined for Cores 1 and 2, respectively (Table 1).
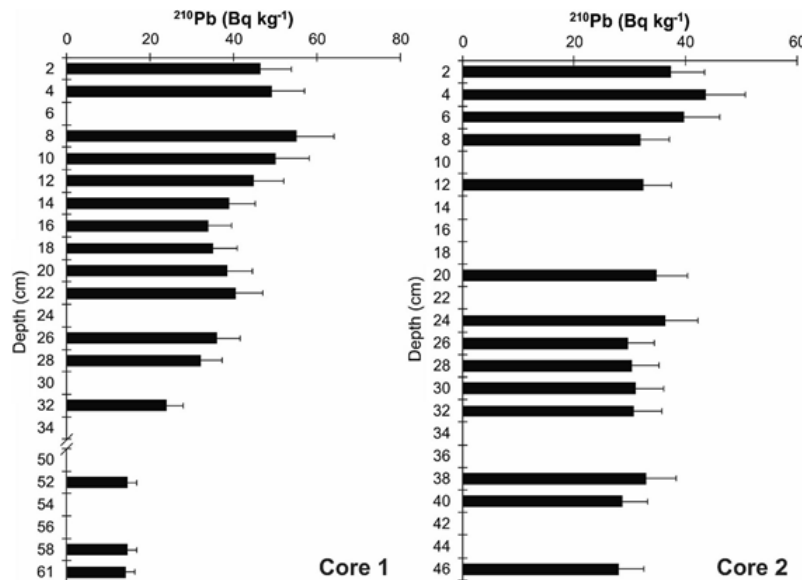
Fig. 3. Pb-210 concentration activity for Cores 1 and 2 employed for geochronology. Error bars refer to the expanded analytical uncertainty at the 95% confidence level.

Given that the expected sedimentation rate should have been closer to other estuaries (approximately 0.5 cm.year^{-1}) in the State of Pernambuco [22], higher sedimentation rates for Cores 1 and 2 were associated with an anthropogenic influence due to the erosion around the Itapessoca Island and other areas near the Catuama margin (to a lower degree, since the sedimentation rate has been 21% lower). It seems that the almost whole of Core 2 was subjected to mixing [13], resulting in lower adjusted-R^2 (0.59) in comparison with that obtained for Core 1 (0.92). The sedimentation could be different for each set of layers, indicating a possible variable sedimentation rate in Core 2 affected by the erosion of abandoned mining areas in the Itapessoca Island [6].

The main outcome of this research in the Itamaracá Estuarine Ecosystem was a reconstruction of the timeline to explain the Hg concentrations determined in the sediments. The analytical technique CVAAS was able to quantify the Hg concentrations higher than 0.04 mg kg−1 in sediments. The obtained Hg mean value of 32.6 mg kg−1 ± 1.8 mg kg−1 was equal to the reference value of 32.6 mg kg−1 ± 1.8 mg kg−1 present in the SRM 2710 certificate of analysis. Considering the high precision (2.3%) and trueness (0.1%), CVAAS was a good choice for determining total Hg in sediments [19].

According to the results from Fig. 4, a distribution pat- tern was observed for Hg concentrations from Core 1, in which concentrations were higher in the surface sediments (0–15 cm) than those from middle depth (15–40 cm). Not- withstanding, the deep sediments (> 40 cm) showed Hg concentrations below the minimum determinable concentration of 0.04 mg kg−1. Core 2 presented a totally different distribution pattern with Hg concentrations decreasing with depth. The maximum value of 1.29 mg kg−1 for the whole area was also determined in this core. It is essential to empha- size that most of the values ascertained were higher than the Interim marine and freshwater sediment quality guidelines— ISQGs of 0.13 mg kg−1 and 0.17 mg kg−1, respectively. Some maximum concentrations were also higher than the respective probable effect levels—PELs of 0.70 mg kg−1 and 0.486 mg kg−1 for marine and freshwater sediment guidelines [23].

Figure 4 also shows the core dating and the main anthropogenic and natural events that have contributed to the trace element contamination in the estuaries. The first increase in Hg concentration was confirmed in mid-1965 due to the undesirable release of Hg [5] according to the results of Core 1. Core 2 presented a higher sedimentation rate, resulting in layers dated only after 1967. In between, the extreme precipitation event in 1975 probably contributed to an increase in Hg concentrations in Core 1 because of the peak observed for Hg concentrations around 1980 (Fig. 4). Although the rainfall could have diluted the Hg concentration in the estuarine water, fine suspended sediments were mainly transported from the continent to the estuaries [24]. Under proper hydrodynamic conditions, the fine sediments, which are enriched in chemical substances, precipitate and enrich the deep sediments in

chemical elements. However, for Core 1, the increase in Hg concentrations could be noticed only after 1979, indicating different conditions for sedimentation patterns in the region. During the leakage event, another peak for Hg was identified in 1989 in Core 1 (Fig. 4), originating from the chlorine-soda industries located along the banks of the Botafogo River [6]. However, for Core 2, the leakage event had caused the Hg contamination until 1995 according to the results since the first drop in the Hg concentrations occurred in sediments from this year (Fig. 4). The next Hg concentration peak was noticed for all cores in 2001, when the annual precipitation reached 2300 mm referring to the influence of the La Niña climatologic event [25]. After, a depletion of Hg concentration occurred probably due to the drought season, in which mean precipitation has achieved only 1100 mm [6]. A similar behavior was found for the Puruzinho lake in Brazilian Amazon, in which, during the rainy season, the areas of higher Hg concentrations expanded compared to the dry period [26].

A decrease in Hg concentrations was only noticed for Core 2 (Fig. 4), probably related to a higher sedimentation rate due to the erosion of abandoned limestone mining areas. The Hg concentrations in sediments seem to have stabilized from 2007 to 2017 for the Catuama and Itapessoca Cores (1 and 2). Given the state of the economy, more and more areas, previously used for limestone mining, were abandoned [10]. As well, the calcareous rocks from the Gramame geological formation presented very low Hg concentration ($0.5 \ \mu g.kg^{-1}$) [26]. By plotting the linear regressions between the Hg concentrations determined in sediments and the sediment deposition year (from 1930 to 2017) in Fig. 5, the behavior of Hg in the sampled cores was confirmed to be totally different.

Table 1 Linear regression results for ln(210Pbexc) and depth (cm) and geochronology results for Core 1-Catuama and 2-Itapessoca.

Core	Coefficient		SE	*P* value	Geochronology	
					Sedimentation rate	Estimated error
1	Intercept	4.012	0.081	<0.0001	0.84	0.77
	Angular	-0.037	0.003	<0.0001		
2	Intercept	2.659	0.176	<0.0001	1.03	0.22
	Angular	-0.030	0.007	0.0006		

For Core 1, a significant positive relation was observed at the 95% confidence level (adjust–R^2 = 0.62), corroborating a constant contamination in the estuary during the release and leakage of Hg. After 1995, the concentrations have stabilized at 0.35 mg kg^{-1}, in which no correlation could be assumed, until starting to increase at 0.55 mg.kg^{-1} once more after the extreme precipitation event in 2001. After this year, Hg concentrations achieved 0.63 mg kg^{-1} with stabilization, after drought in 2010, at 0.52 mg kg^{-1} (Fig. 5).
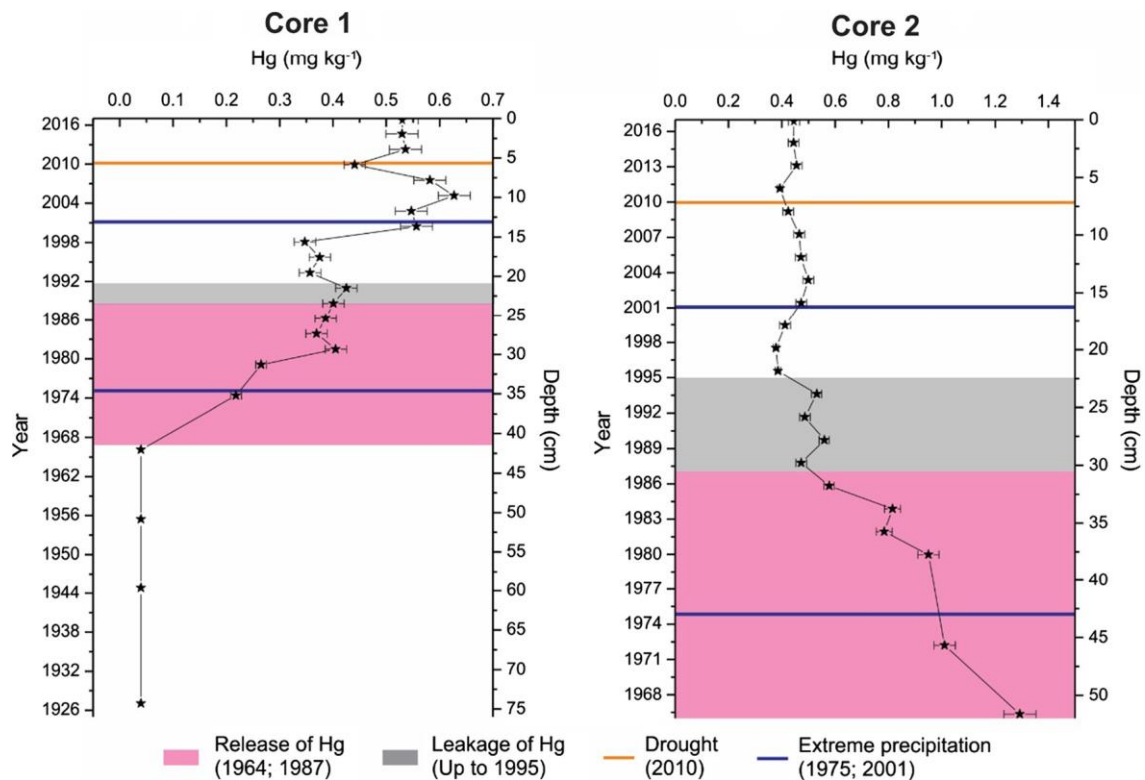
Fig. 4 Core dating, total Hg concentrations obtained in sediment layers and the main assumed natural and anthropogenic events.
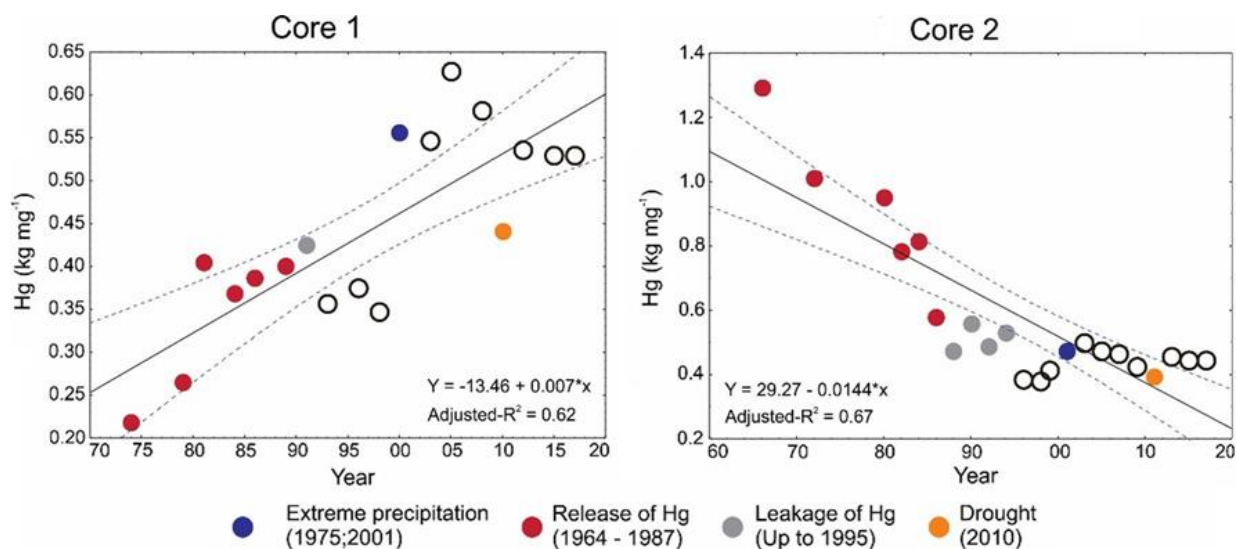
Fig. 5. Linear regression and regression bands at the 95% confidence level (hashed lines) between Hg concentrations and year (from 1920 to 2017 for Core 1 and from 1960 to 2017 for Core 2) of sediment layer deposition.

For Core 2, the relation was significantly negative at the 95% confidence level (Fig. 5), mainly considering the sediments dated until 1995. Since 1967, Hg concentrations have diminished even though the release of Hg was still occurring in the Itamaracá Complex Ecosystem. This phenomenon was associated with the decrease of operation of mining activities in the Itapessoca Island [6] as mentioned before, in which suspended sediments and organic matter from mining residues should have acted as main adsorption medium for Hg [27]. Unfortunately, both plots indicated another contamination event of Hg after the extreme precipitation in 2001, probably resulted from anthropogenic activities nearby the Itapessoca Estuarine Complex.

Conclusions

The application of 210Pb geochronology was especially demonstrated in this work for tracking Hg contamination in Itapessoca Estuarine Complex. Despite the analytical difficulties and the limited bar robust dataset, this work was the first to combine Hg determination and geochronology to aware of this environmental problem in Pernambuco State, Brazil. The estimated sedimentation rates by the radiometric analyses confirmed Hg contamination in the Itamaracá region since mid-1965. It is possible to conclude that the decrease of the Hg concentrations was probably caused by the sedimentation of non-enriched geological material between 1967 and 1995 from degraded areas

in the Itapessoca Island. This phenomenon could be also have been occurring in other areas of this estuary at a less intense level. Events of extreme precipitation or absence of rain have been also related to the increase or decrease of Hg concentrations in sediments. An intensive monitoring should be carried out in the Itamaracá Estuarine Ecosystems aiming to clarify the anthropogenic influence on Hg distribution in sediments and define the actual extension of Hg contamination.

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CAPÍTULO 2

Anthropogenic influences on sedimentary geochemistry of

Itapessoca Estuarine Complex, Pernambuco, Brazil

(Submetido ao periódico *Environmental Monitoring and Assessment*)

Anthropogenic Influences on Sedimentary Geochemistry of Itapessoca Estuarine Complex, Pernambuco, Brazil

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Abstract

The Itapessoca Estuarine Complex is characterized by a history of intense economic activities developed on the banks of its tributary rivers, often exercised without any control or planning. In order to relate natural and/or anthropic events to the sediment age, geochronology was performed by determining excess Pb-210 in the sediment using the Proportional Gas Flow technique. To investigate possible disturbances in recent sedimentation processes in studied area, 20 surfaces sediment samples and 2 sediment cores were collected for analysis of concentrations of the chemical elements. Al, Ca, Fe, K, Mg, Mn, Ni, Pb, Si, Sr, Ti and Zn concentrations were determined by the Energy Dispersion X-Ray Fluorescence - EDXRF technique. Through the enrichment factors and ratios among some elements associated with geochronological data, it was possible identify geochemical changes in sedimentation of sampled points, with increase of minerals associated with fine fractions and decrease of the proportions of elements associated with coarse fractions. Geochronology reveals that Pb enrichment and the exacerbated increase of Ca and Sr enrichment factors are strongly related to the anthropic activity in the region.

Keywords: Estuary, Geochronology, Enrichment Factor, Sediment Pollution, Environmental Impact

Introduction

Estuaries are recognized for their biological richness and as important sources of nutrients and shelter for different animal and plant species (Whitfield and Elliot 2011). These environments are under constant anthropogenic threat: half the world's population living in cities with more than 100,000 inhabitants is located within a radius of up to 100 km from a coast (Barragán and Andrés 2015). In Brazil, 26.6% of the population live in coastal zone cities as a result of historical factors relating to the way the territory was occupied, causing impacts on the marine biome and survival of its species (IBGE 2011). The estuaries are subject to anthropic disturbances such as mining and pollution (Davis et al. 2000). Due their intense natural physical-chemical variability, however, anthropic alterations are difficult to detect in these environments and they can be confused with natural stress (Elliot and Quintino 2007).

The Itapessoca Estuarine Complex is part of Itamaracá Estuarine Ecosystem, one of most important ecosystems of the Pernambuco State coast, an ecological unit of environmental and socioeconomic

significance due to its considerable biodiversity and the activities developed in region (Medeiros et al. 2001). However, the occupation and soil use caused by anthropic activities have produced significant changes in the environment (Oliveira 2017). Tourism, fishing, sugarcane culture, shrimp farming, sand mining and limestone mining are the main local economic activities (CPRH 2003; Barreto et al. 2011). Artisanal fishing has played an important role in the survival of several traditional fishing communities in region, with a predominance of estuarine fishing over marine fishing, since the northern coast concentrates most of the estuarine areas of Pernambuco state (CPRH 2003). Although sugarcane monoculture has advanced toward the mangrove environment, shrimp farming and mining are among the most damaging activities, due to the suppression of native vegetation coverage on large scale (Oliveira 2017). Open pit sand mining has created large craters where shrimp farms have been implemented to reuse the mined areas (Oliveira 2017). Unfortunately, this mining reclamation method has caused major environmental impacts such as deforestation and chemical pollution (Oliveira 2017). Besides deforestation, urban and industrial development have altered the chemical properties in the water column, sedimentation patterns and caused metal contamination (Lacerda et al. 2006).

A set of analytical techniques can help in understanding the environment status. Sediment core geochronology has been used to understand environmental evolution in coastal areas, providing natural or anthropic records of sedimentation patterns (Joshi and Ku 1979). The Dispersive Energy X-Ray Fluorescence (EDXRF) is an effective technique for the determination of chemical elements in different environmental matrices (Fernandéz et al. 2017), without needing sample digestion (Marguí et al. 2005). Multielemental chemical analysis by EDXRF has been employed to investigate metal concentrations in estuarine sediments (Olsen and Simpson 1978; Barcellos et al. 2017). The variation in concentrations of chemical elements in a sediment profile can be related to both natural and anthropogenic factors. The geochemical normalization technique using aa conservative element enables the detection of anomalies in the concentration of these elements, facilitating the identification of anthropogenic contamination (Loring 1991). Different conservative chemical elements have been used as normalizers, usually Al (Loring 1991) and Fe (Blomqvist et al. 1992). The ratios between chemical elements quantified by different techniques can be used for several purposes, including acting as indicators of ecological processes (Lopez et al. 2006).

Although there are many studies of anthropic impact on the region, this present work has not been preceded by other studies that diagnosing the behavior of chemical elements (metals and metalloids)

over time in the Estuarine Ecosystem of Itamaracá. The objective of this study was to investigate the distribution and evolution of metal concentrations at a number of sampling points in the Itapessoca Estuarine Complex as well as the eventual implications of these on the geochemistry of the local sedimentation.

Materials and methods

Study Area

The Itapessoca Estuarine Complex (7°40'S/34°50'W) is located on the northern coast of the state of Pernambuco, in Brazil, about 70 km from the capital, Recife, and approximately 10 km from the border of the state of Paraíba. The study area is under the influence of the As climate (Köppen-Geiger classification), or tropical Atlantic, with winter rains, and annual precipitation average of 1800 mm. The average temperatures of the area oscillate between 24 ℃ in July and August, 27 ℃ in February, with low annual thermal amplitude (CPRH 2003).

Five geological units make up the northern coast of Pernambuco state: Barreiras Formation, Beberibe Formation, Gramame Formation, Marinha Farinha Formation and Itamaracá Formation, belonging to Paraíba Sedimentary Basin (Barbosa et al. 2003; CPRH 2003). The Gramame and Maria Farinha deposits have been intensively exploited by the cement industry for limestone to use as raw material (CPRH 2003). Solid waste from mining and limestone processing is commonly disposed in landfills or dumped directly onto the land without any process or treatment (IPEA 2011).

The Gramame Formation is the first carbonatic unit in the marine domain, and occurs on the Itamaracá Formation (Oliveira 1940). This unit dates back to the Maastrichtian period (Beurlen 1967), is fossiliferous and has alternating deposits of limestones and marls on a shallow carbonate platform (Barbosa et al. 2007) that directly reflect the environmental changes associated with the marine phase (Westphal 2006). The Maria Farinha Formation is composed of marine limestones and thick strips of marl in its lower portion, with dolomitic fossiliferous limestones in its upper portion (Beurlen 1967). This formation displays sedimentary deposits characteristic of a regressive phase, from the cretaceous-tertiary age, related to the evolutionary process of the Paraíba Basin and the expansion of the South Atlantic Ocean (Mabesoone 1967).
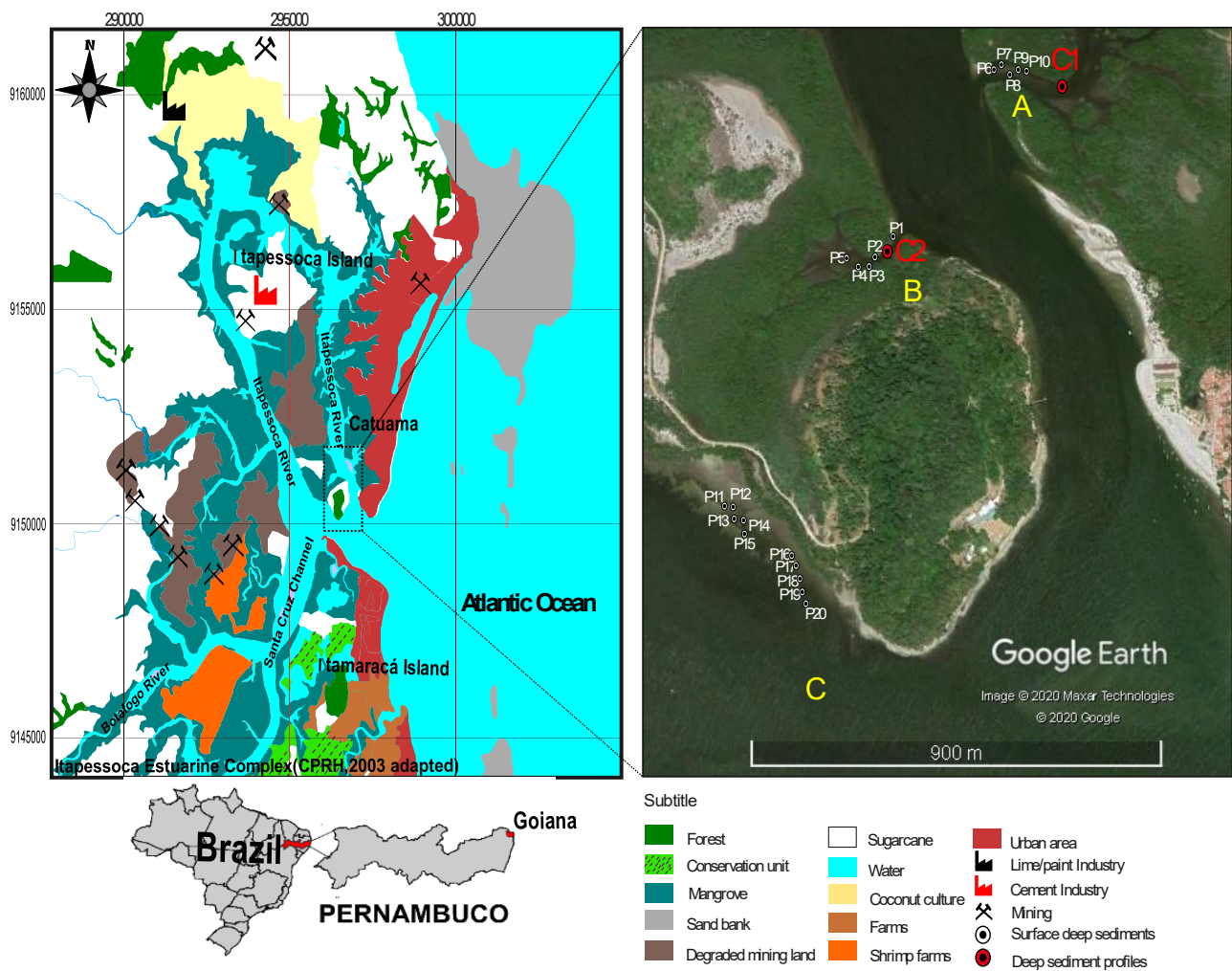
Fig. 1. Estuarine Complex of Itapessoca, Pernambuco, Brazil, with details on land use and occupancy. White points indicate surface sampling points (P1 to P20). Red points indicate sediment core sampling points (C1 and C2), in A, B and C sectors (in yellow letters).

Sampling

Initially, a bathymetric survey of the area was done, where sediment samples were collected from the surface down to 20 cm deep, at different points distributed in the estuary, using a Van-Veen grab sampler. Sediment core samples were collected at 2 points in the study area (Fig. 1) using the *pushcore* method. The accessibility of the estuarine areas and the feasibility of penetrating the tubes were the criteria used to choose sample points. The abrupt increase in depth made it impossible to sample sediment core at some points. This is due to the fact that the region is located in geological faults areas, with grabens or tectonic pits, and the estuarine system of Itapessoca is considered a ria estuary, of tectonic origin (Silva et al. 2011; Topan and Lima Filho 2017).

The collection points of superficial samples and sediment cores were executed in intertidal banks, divided in sectors: Sector A - situated on the Catuama margins, where the superficial samples were collected from P6 to P10 and C1 sediment core; Sector B - opposite margin, on the Itapessoca Island, where the superficial samples were collected from P1 to P5 and C2 sediment core; and Sector C - situated on the Itapessoca Island, its banks bathed by the Santa Cruz Channel, where the points P11 to P20 of the superficial samples were collected. 76 cm were recovered for C1 and 52 cm for C2. The deposits were transported and conditioned at the Environmental Monitoring Service of the Regional Center for Nuclear Sciences of the Northeast - SEAMB/CRCN-NE. Subsequently, they were thawed, visually described and sectioned into 1-2 cm layers, depending on the texture and sedimentary structures (clay layers allowed thicker cuts), totalling 56 samples. The samples were dried at 40 ºC until they reached aa constant weight and then they were crushed to a particle size of less than 80 µm.

As a differentiation and classification factor of surface and subsurface sediments, a visual description of the collected samples in terms of texture (sandy/coarse and mud/fine), sedimentary structures and concentration of marine biogenic indicators (biodetritic carbonate - CaCO3) was made before the maceration of the sampled material.

Analytical procedures

Samples of 1 g sediment and reference materials were transferred to polyethylene tubes and sealed with specific polypropylene films for analysis of X-Ray Fluorescence by Dispersive Energy - EDXRF. Measurements were performed on Shimadzu ED-720 instrument, previously calibrated, with specific Setting Up Samples - SUS and A750 calibration standards.

For the quality assessment of the analytical procedure, two reference materials were used: IAEA-SL-1 "Trace and Minor Elements in Lake Sediments" and SRM1646a - "Estuarine Sediment", produced by the National Institute of Standards and Technology - NIST. The samples and reference materials were subjected to an atmospheric vacuum less than 30 Pa to measure the induced radioactivity for 300 s, with a maximum *Dead Time* of 36%.

The elements As, Cu, Fe, Ga, Mn, Pb, Zn, Sr and Ti were analyzed with a Mo filter and voltage adjusted to 50 kV. The Al, Ca, K, Mg and Si elements were measured with an Al filter and 15 kV

tension. Ba, Ni, Va elements were measured with Ti filter at 50 kV. The concentrations were expressed in *parts per million* - ppm. Details on the method can be found in Fernandéz et al. (2017).

Zinc and lead concentration values were compared with the Canadian Council of Ministers of the Environment (2001) guidelines for marine and freshwater sediments. Threshold Effect Levels (TEL's) and Probable Effect Levels (PEL's) guidelines choice is justified by information on degree of sediment contamination based on toxicological studies. TEL and PEL values are used to relate chemical concentrations of a given element to its biological effects: a) concentration values below the TEL suggest minimal effect range, with rare occurrence of adverse effects; b) the range of values between TEL and PEL indicates possible adverse effects and C) values above the PEL indicate likely occurrence of frequent adverse effects.

Geochronology

The geochronology had been previously performed by the unsupported (excess) Pb-210 activity method, adapted from Godoy et al. (1998), with the Pb-210 radionuclide being used as a geochronological marker for determining sedimentation rates of coastal environment (Wanderley et al. 2014). Radionuclides were determined by the Proportional Gas Flow technique. Sedimentation rates of 0.84 ± 0.07 cm.yr^{-1} and 1.03 ± 0.22 cm.yr^{-1} were determined for sediment cores 1 and 2, respectively, and reported by Albuquerque et al. (2019), where further details on geochronology can be found.

Geochemical normalization and ratios between chemical elements

The Enrichment Factor - FE was used for the geochemical normalization of metals (and the metalloid Si) analyzed in the sediment cores, based on the concentration of a chemical tracer element. The tracer element can be from the sediment core itself, from background values of the planet Earth or from reference values (Barbieri 2016; Barcellos et al. 2017). For the present study, Fe was used as a normalizing element, based on the enrichment factor (EF), being: EF = (C/Fe) $_{Sample}$ / (C/Fe) $_{Reference\ Value}$, where C $_{sample}$ is the concentration value obtained from the analyte, Fe $_{Sample}$ is the concentration value of Fe as a tracer element, C $_{Reference\ Value}$ is the reference value or background and Fe $_{Reference\ Value}$ is the reference value for Fe. Enrichment Factors values < 1 indicate no enrichment, < 3 little or poor enrichment, 3-5 moderate enrichment, 5-10 severe enrichment, 25-50 very severe and > 50 indicate

extremely severe enrichment (Szefer et al. 1998). For the calculation of the Enrichment Factor, the reference values proposed by Turekian and Wedepohl (1961) were used. Enrichment Factors up to 1.5 suggest that certain elements originate from natural sources, raw materials or natural weathering processes; EFs above 1.5, however indicate that a significant proportion of these elements originated from anthropogenic processes (Garcia-Ordiales et al. 2014).

The following are the ratios determined for Mg/Ca, Mn/Sr, Al/Fe, Ti/Fe, Si/Fe, Mn/Fe and Fe/Ca determined in the samples of the sediment cores. The Mg/Ca ratio was used to distinguish sediments originating in limestone taken from the different formations of the Paraiba basin, as proposed by Nascimento-Silva et al. (2011). The Mn/Sr ratio was used to distinguish sediments from carbonates of different degrees of diagenetic alteration (Nagarajan et al. 2008), on the assumption that the proportions between both reflect the carbonate characteristics of the source area where Mn/Sr <2 ratios did not indicate diagenetic alteration, the sediments would have originated from predominantly detritus carbonates. Mn/Sr>2 ratios confirm diagenetic change (Jacobsen and Kaufman 1999). For surface sediments, only the Mg/Ca and Mn/Sr ratios were used.

Some minerals are associated with sediments with different granulometries. Aluminium and Iron, for example, are associated with fine particles of sediment (Biscaye 1965; Araújo et al. 2002). Fe and Al have also been used as river proxies for sediment transport (Nizou et al. 2010). In this regard, the Ti/Fe ratio consists of an indicator of sediment provenance (Konfirst et al. 2011), since Iron (Fe) and Titanium (Ti) represent chemical proxies of the contribution of terrestrial material as they are associated with essentially clay minerals and siliceous components, respectively (Arz et al. 1998). Si is used as a proxy for the contribution of terrestrial sediments (Blanchet et al. 2007; Kleiven et al. 2007) and in studies of provenance (Frenz et al. 2009). The Mn/Fe ratio is used as an indirect measure of the redox potential of sediment, since Mn can be mobilised under suboxic conditions, separating from Fe during diagenesis (Marsh et al. 2007). Constant Mn/Fe ratios indicate oxic conditions and Mn/Fe peaks occur during suboxic diagenesis (Thomson et al. 1993). The Fe/Ca ratio was used as a proxy for sediment provenance, considering that these two elements reflect marine production and terrestrial input, respectively (Nizou et al. 2010).

Statistical analysis

The sediment dataset consists of 11 variables in 20 surface samples and 56 samples of C1 (32 samples) and C2 (24 samples) cores. Descriptive statistics for the surface samples and the control samples were developed, as well as multivariate analysis with the STATISTICA (v.10) software support. Factorial analysis was used to reduce the dimensions of the data and to identify concentration patterns of measured elements in superficial sediment samples. The factors were calculated by the Principal Factor method and rotated by Varimax method (Kaiser 1958) in order to maximize the loadings of some variables of different factors for the production of simple structures more easily interpreted. The Kaiser (1960) rule was used for the choice of factors - the factors with eigenvalues greater than 1 being chosen. The communalities measure the percentage of variance in a particular variable explained by all factors together and can be used as a reliability index. Communalities were estimated by sum of the squared loadings for the corresponding variables. Simple linear regressions between the concentrations of the chemical normalizing element candidate metals (Al and Fe) and other metals were adjusted, where the highest adjusted R^2 values were used to choose of the normalizing element. All graphics were made with STATISTICA (v.10), Origin (v.8.0) and Inkscape software.

Results and discussion

Figure 2 shows the validation of the analytical procedure with E_n number values for the analytical portions of the SRM-1646a and IAEA-SL-1 certificates. Fe, K, Mn, Ni, Pb, Sr, Ti and Zn values are at the 95% significance level (-1 < z < 1) of both certificates, while Al, Ca, Mg and Si are not certified for IAEA-SL1. The elements As, Cu, Ga and V are below the Minimum Detectable Concentration - MDC.
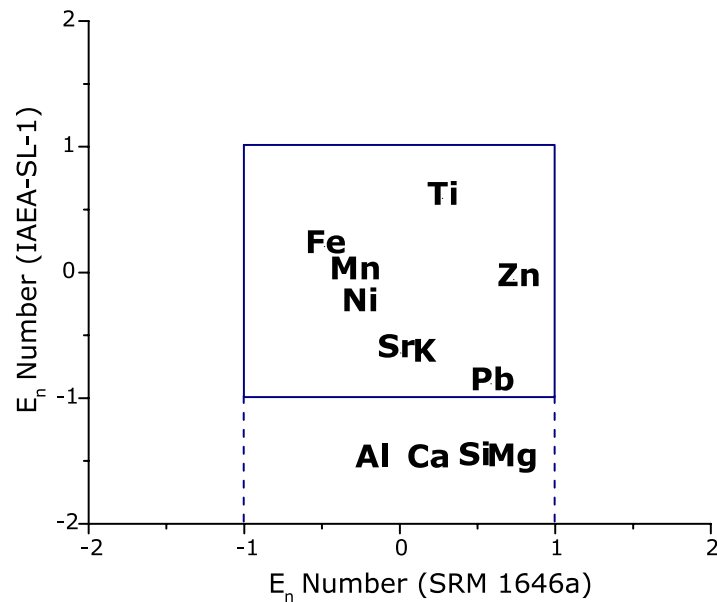
Fig.2. Quality control of the analytical procedure for SRM-1646a and IAEA-SL1 certificates. Surface sediment

According to Table 1, the average of the concentrations of the elements in Sector B (Itapessoca Island) is close to an arithmetic mean between the concentrations of sediments collected in sectors A and C. Despite this, the sampling system does not allow to us state that sector B is a mixing zone of marine and terrestrial materials. The average concentrations of zinc and lead found in all surface sediment samples are below the TEL values (124 mg.kg^{-1} and 30.2 mg.kg^{-1} respectively), although the Pb concentrations (24 ppm) in the sectors B and C are close to the TEL in some points. Considering only the maximum values, the surface sediments reveal that sector A had the lowest concentrations of the elements. Sector B showed the highest maximum concentration of elements commonly associated with fine particles, such as Al, Fe, Mn and trace metals Ni, Zn, Pb (Kouassi et al. 2018). In contrast, sector C showed higher maximum concentration for Ti and Si elements, commonly associated with coarse sediment fractions, together with Ca, Sr, K, Mg associated with marine sediment.

Table 1. Descriptive statistics for the surface sediment samples collected in sectors A, B and C in ppm (Dm=Descriptive Measure; Min=Minimum; Max=Maximum; Med=Median; AM=Arithmetic Mean).

Sector	DM	Mn	Fe	Ni	Zn	Pb	Sr	Ti	Mg	Al	Si	K	Ca
A	Min	94	7800	3	11	11	251	3157	4868	16652	219400	7710	48960
(P6-P10)	Max	144	16000	14	36	20	578	3873	7564	49810	331500	11560	75300
	Med	122	11000	5	20	16	481	3373	6786	41420	256000	10500	55540
	AM	119	11440	7	21	16	454	3452	6335	37115	260920	10082	60760
B	Min	113	9100	6	20	14	475	3015	6174	27749	196500	9090	61880
(P1-P5)	Max	164	19600	19	46	24	942	4190	8247	78254	264400	12000	90930
	Med	134	15000	11	25	18	757	3609	7439	59442	225700	10750	78980
	AM	137	14420	12	31	19	749	3636	7339	53240	229200	10704	78892
C	Min	129	7000	1	2	8	562	3357	1135	11369	219800	9030	69260
(P11-P20)	Max	161	9800	9	22	24	1090	5163	11014	43254	2629200	14450	131260
	Med	138	8500	5	16	11	733	3828	6952	26905	252400	12725	104940
	AM	141	8500	5	14	12	770	3966	7272	25992	493370	12217	101011

Factor analysis supported the identification of intercorrelation patterns between the variables, allowing a geochemical characterization of the sediment samples. Three factors were extracted, explaining 82.1% of the variance. The results of the factorial analysis for the three factors solution can be seen in Table 2. Projection of factorial loadings on a three-dimensional plot can be seen in figure 3.

Table 2. Factorial analysis results for surface sediment and individual explained variance for each factor. The estimation of communalities is given by SMC - squared multiple correlation.

Chemical Element	Factor1 Fine Sediments	Factor2 Marine Sediments	Factor3 Coarse Sediments	Communality (SMC)
Mn	0.023	0.22	0.79	0.69
Fe	0.99	-0.06	-0.09	0.99
Zn	0.91	-0.13	0.26	0.93
Sr	0.09	0.68	0.54	0.83
Ti	-0.08	-0.02	0.73	0.58
Mg	0.18	0.77	-0.02	0.79
Al	0.89	0.22	-0.31	0.97
Si	-0.81	-0.51	-0.02	0.98
K	0.10	0.97	0.2	0.94
Ca	-0.15	0.90	0.2	0.89
Explained Variance%	39.3	28.9	13.9	-

The factor 1, denominated "fine sediments", presents high positive load for Al (0.89), Fe (0.99) and Zn (0.91) and high negative load for Si (-0.81), denoting the presence of two groups: Al, K, Fe, Mn, Mg, Zn, usually associated with fine sediment particles and Si, associated with coarse particles (quartz). Negative correlations between Fe-Si and Al-Si were also reported by Delgado et al. (2010). The negative correlation of Ti (-0.08) also suggests a difference in the composition of sediments associated with coarser fractions, in a smaller proportion. Factorial loads represent higher proportions of fine sediments in sector B (Itapessoca) at points P1, P2, P3 and P4, as seen in Figure 4. In sectors A and C, the fine fractions tend to be proportionally smaller, contrasting with an increase in the detritus fractions of Si, especially in Sector C, located in an area under the influence of the Rio Botafogo and the ocean.
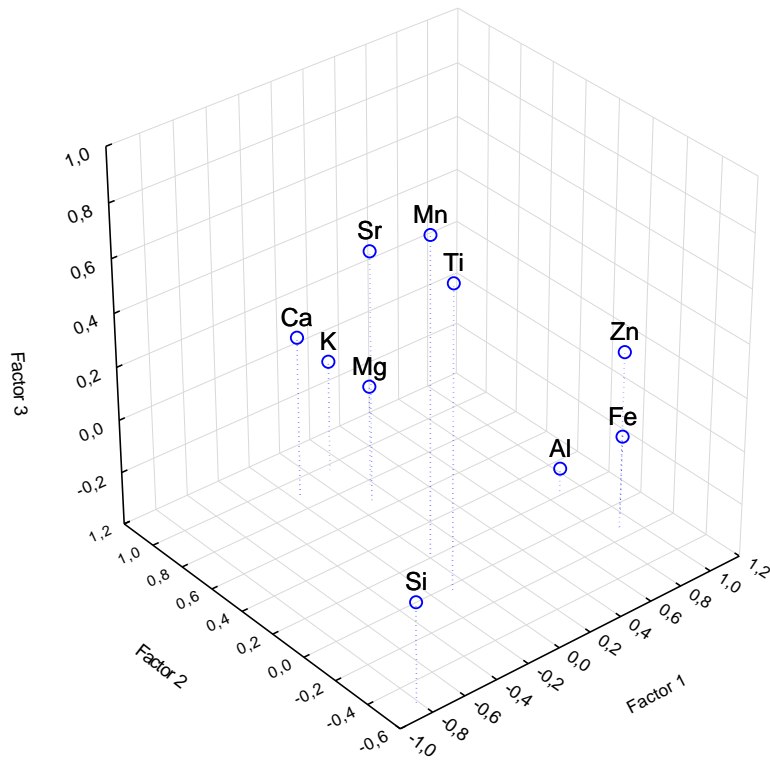
Fig.3. Projection of factorial loadings on a three-dimensional plot for three factors extracted by Principal Factor, rotated by the normalized Varimax method.
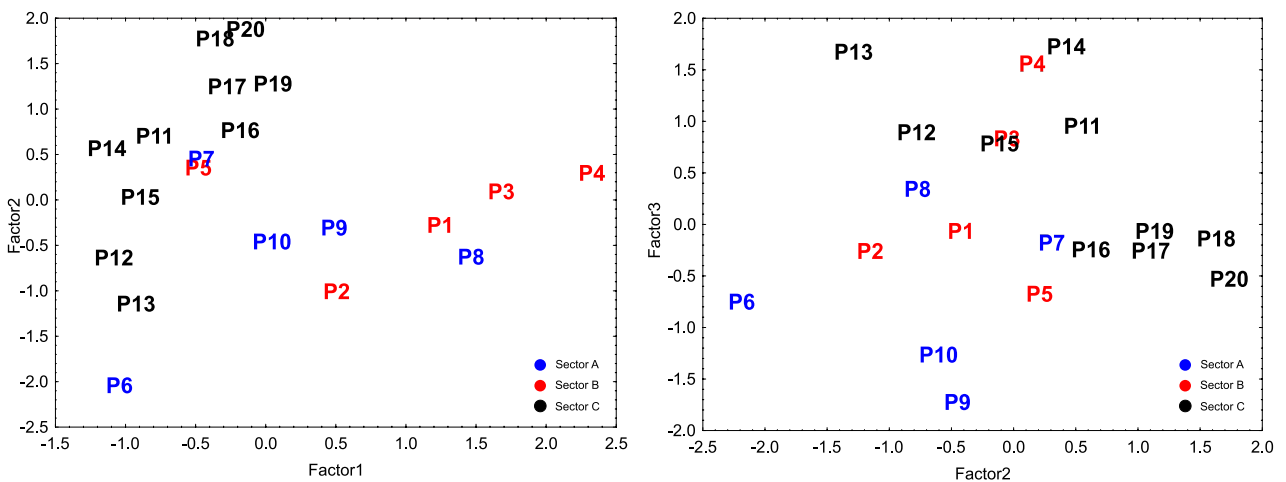
Fig. 4. Scatter plots of factor loads values obtained in factor analysis for the three factors.

Factor 2 distinguishes sediments based on the contraposition between quartz (Si) and carbonates (Ca), two chemically distinct groups, exhibiting negative correlation for metalloid Si (-0.51), high positive

factorial load for Ca (0.90) associated with carbonates, and high load for K (0.97). This is because the distributions of K and Ca are commonly related to drainage basin lithology, which explains a higher percentage of K associated mainly with sedimentary feldspar (Araújo et al. 1998). The increasing tendency of Ca at estuary points flowing into the sea is a result of the sediment mixing with materials originating from the adjacent marine platform, including biogenic material. Oliveira et al. (2017) observed an import of marine biogenic sandy gravel sediments, which are brought by the high tide to the lower Itapessoca estuary, through the discharge of the system (Barra de Catuama), at each tidal cycle. However, factor values suggest that higher factorial loads associated with sector B (P1 to P5) may be justified by the limestone deposits, abundant in the region (Beurlen 1967) and outcropping in the areas immediately adjacent to the sediment core C2 and sampling stations B. Thus, factor 2 has been called "Marine Sediments", whose elements are associated with both shallow marine detritus and the carbonate depositional system, also of marine origin.

Factor 3, named "Coarse sediments", explains the distribution of higher granulation particles of the surface sediment, considering the higher load values for Ti, usually associated with heavier mineral particles (Araujo et al. 2002). Agreeing with this, factor 3 presents a factor load with a minor negative correlation of Si (-0.02) among the three factors, indicating higher concentrations of Si, also associated with thicker fractions of sediment. The higher factor loads of Ti in samples collected in sector C, more specifically at points P11 to P15 indicate a greater marine influence concerning the composition of this sediment, directly related to the closer proximity to the system outflow (Barra de Catuama) in relation to the collection stations of A and B. For the other points, the factor 3 values reflect a mobilization of heavy minerals, with a tendency to accumulate non-resuspended materials at points less influenced by the estuarine hydrodynamics. The higher loads for the Mn element, on the other hand, suggest that this sediment is related to the limestone from the Gramame formation, whose carbonates have high levels of Mn, besides Fe (Nascimento-Silva et al. 2011).

Sediment Core - geochemical normalization, concentrations and ratios between chemical elements

Geochemical normalization

Through linear regression adjustments, when compared to Al, Fe was chosen as the normalizing chemical element for the calculation of the Enrichment Factor because it presented higher adjusted coefficients of correlation for most of the elements. Aluminium had better adjusted correlation

coefficients only for Ni, Pb and Si (Table 3). Although Al is routinely used for normalizing elements analysed by EDXRF, its proximity to the spectrometer detection limits may restrict its use.

Table 3: Adjusted coefficients of determination (R^2) values between Fe and Al and the other elements (95% confidence interval).

Dependent variable	Fe		Al	
	Adjusted R^2	p	Adjusted R^2	p
Ca	0.291	<0.0001	0.005	0.2334
K	0.708	<0.0001	0.468	<0.0001
Mg	0.411	<0.0001	0.165	0.0001
Mn	0.719	<0.0001	0.534	<0.0001
Ni	-0.027	0.7714	0.139	0.0239
Pb	0.186	0.0369	0.208	0.0281
Si	0.294	<0.0001	0.435	<0.0001
Sr	0.719	<0.0001	0.028	0.0697
Ti	0.874	<0.0001	0.624	<0.0001
Zn	0.792	<0.0001	0.754	<0.0001

The chemical elements concentrations in the profiles and Enrichment Factor

The results of the elements Al, Ca, Fe, K, Mg, Mn, Ni, Pb, Si, Sr, Ti, and Zn concentrations in analytes of the two cores are summarized in Table 4. Higher concentrations for the conservative elements, such as Fe, Al and Si, and lower concentrations for Mn, Pb, Zn and Ni are observed. It is noted that, in general, the C2 core presents higher concentrations for Mn, Fe, Ni, Pb, Al, Sr and Ca, considering the maximum values, which denotes greater relationship with limestone, given the proximity with outcrops of local carbonate source rocks. Differently, the C1 sediment core presents higher maximum values of Si, which denotes its greater association with siliceous terrigenous sediments. Thin to thick silica sand palimpsests are the main components of the unconsolidated sediments that make up the coastal plains, beaches and estuarine-lagunar channels of Pernambuco state (Manso et al. 2018).

Table 4: Descriptive statistics with results of analyte concentrations from the sediment cores (D.M=Descriptive Measurements; Med=median; Max=Maximum; Min=minimum; n=n sample).

Core	D.M	Mn	Fe	Ni	Zn	Pb	Sr	Ti	Mg	Al	Si	K	Ca
C1	Med	123	15600	13	30	28	373	3552	6775	48566	235647	11504	54503
	Max	150	18696	15	47	30	813	4203	8967	61675	276094	12312	84311
	Min	101	13116	12	20	24	126	2956	5261	33812	210210	10142	10098
	n	32	32	8	32	5	32	32	32	32	32	32	32
C2	Med	137	17133	13	34	30	812	3363	7062	59941	218884	10864	78412
	Max	175	22524	19	38	40	1015	4196	8940	82983	235017	11615	97300
	Min	120	15057	12	26	24	512	3138	5713	46736	188591	10036	49705
	n	24	24	16	15	8	24	24	24	24	24	24	24

The Enrichment Factor ranges for the metals and metalloids analysed in C1 were as follows: Mn 0.29-0.49 (mean 0.39), Ni 0.37-0.52 (mean 0.88), Zn 0.65-1.15 (mean 0.85), Pb 0.96-2. 80 (mean 1.67), Sr 0.75-5.12 (mean 1.67), Ti 1.91-2.98 (mean 2.35), Mg 0.77-1.41 (mean 1.01), Al 0.89-1.41 (mean 1.19), Si 1.15-2.02 (mean 1.53), K 0.65-0.98 (mean 0.8), Ca 0.69-6.22 (mean 2.52). For C2: Mn 0.32-0.45 (mean 0.39), Ni 0.56-1.43 (mean 0.98), Zn 0.76-1.08 (mean 0.92), Pb 0.96-3.14 (mean 1.68), Sr 2.05-5.49 (mean 3.76), Ti 1.89-2. 29 (mean 2.05), Mg 0.66-1.38 (mean 0.93), Al 1.03-1.51 (mean 1.32), Si 0.99-1.54 (mean 1.22), K 0.55-0.84 (mean 0.67), Ca 2.32-6.32 (mean 4.24). K, Mn and Zn metals are unenriched in both C1 and C2 - the zinc concentrations between 20-55 ppm in both controls imply little enrichment, with values below TEL values (124 mg.kg-1). Mg and Ni reveals poor enrichment (Figs. 5 and 6), not anthropogenic. For the sediment cores, there is a difference in the distribution table between elements associated with fine and coarse sediment fractions: in general, the C1 core has more Si enrichment and less Al enrichment compared to the C2 core.
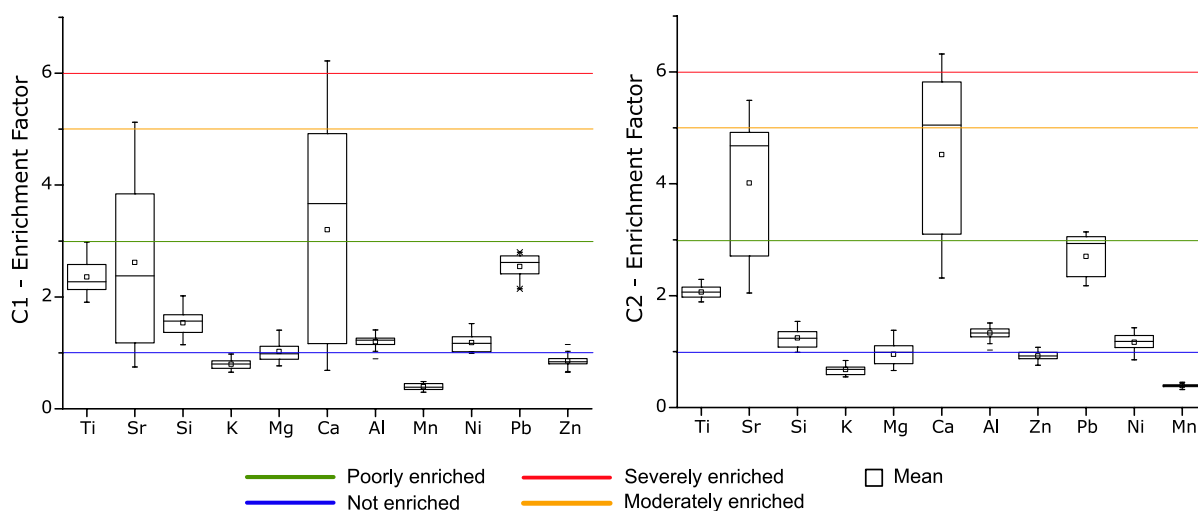
Fig. 5. Box plots of Enrichment Factors for metals and metalloids in C1 and C2 cores.

Although the poor enrichment (<1.5) of the aluminium element in C1 and C2 cores indicates origin in natural processes, the highest peaks occur in the 1960s: 1963 (EF 1.41) in C1 and 1969 (1.49) in C2 (Fig. 6). In general, Ti and Si present little enrichment and a slight tendency towards impoverishment, with little variation along the profiles, although there were some oscillations. In C1, the most prominent peak of Ti occurred in 1963 (EF 2.98) and in C2, in 2009 (EF 2.29). For Si, there was a peak from 1952 (EF 2) in C1. In C1, enrichment peaks for Ca, Mg, Mn and Si elements are noticeable in 1934. After 1934, there was a decrease in the enrichment factors, with subsequent enrichment of the elements Al, Ca, K, Mg, Mn, Si and Sr in 1952. In C2, there was an increase in the enrichment factors of the elements Al, Ca, Mg, Sr, Ti, Zn in 1969. After that, the enrichment of the other elements did not accompany the enrichment of Ca and Sr - the Ca, that presented low enrichment until 1982, started to present severe enrichment in 1994. The Sr, in turn, was little enriched until 1986, starting to be severely enriched from 2005.

The Ca and Sr concentrations were the most enriched in both cores (Fig. 5 and 6). In C1, the Ca enrichment occurs from 1966 (EF 1.15), with peaks in 1979 (EF 5.35), 1984 (EF 6.22) and 1996 (6.10). Since then, there has been a retreat and the severe enrichment has been moderate. In C2, Ca has shown little enrichment since 1966 (EF 2.32), but moderate enrichment in 1982 (EF 3.15). From 1994, the enrichment has been severe (EF 5.06), with highest peaks in 1996 (EF 6.32) and 2005 (EF 6.07). Unlike C1, the behaviour of Ca in C2 does not show significant attenuation and the enrichment remains severe up to the most recent layers. The behaviour of the Sr element follows the behaviour of the Ca element in both cores. The persistence of the severe enrichment of Ca and Sr in C2 may

justify the higher rate of sedimentation of this core, collected in a place strongly influenced by limestone mining for Portland cement manufacture, whose industrial plant is installed in the Itapessoca island, officially in operation since 1951 (BRAZIL 2019), fact that justifies the behaviour of some elements around 1950.
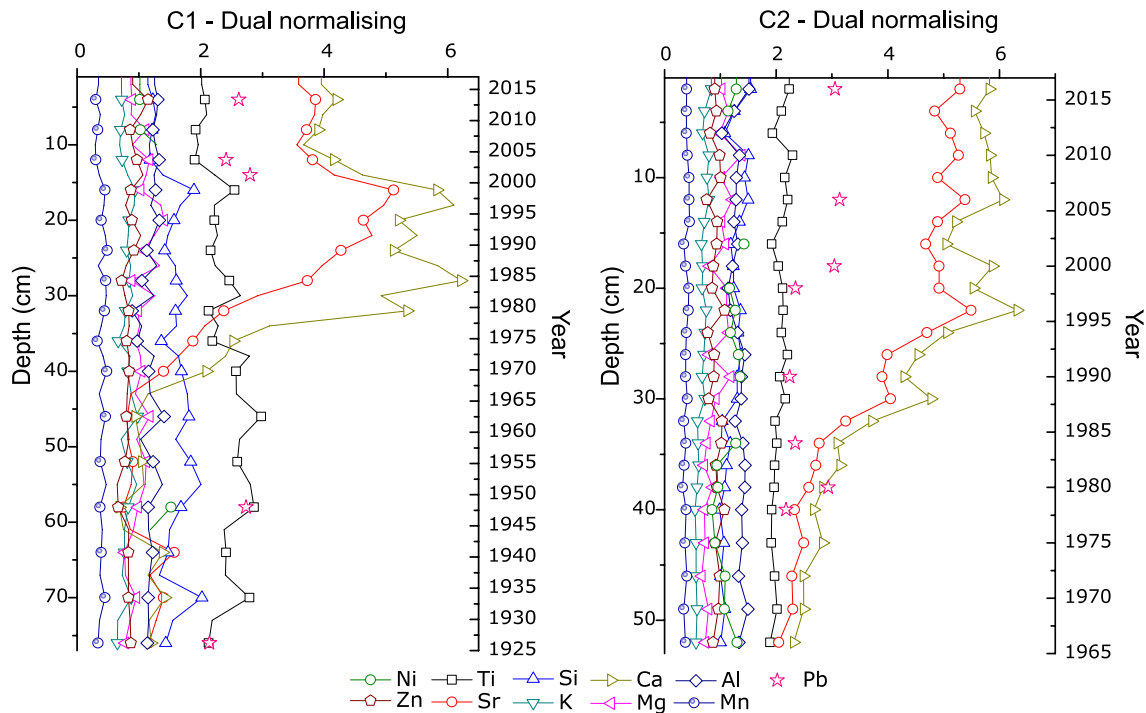
Fig. 6. Vertical distribution of the enrichment factors of the Al, Ca, Mg, Mn, Ni, K, Pb, Si, Sr and Ti elements for C1 and C2 cores.

For toxic metal Pb, some samples showed concentrations below the detection limit of the method, however, the remaining samples (5 samples in C1 and 9 samples in C2) were sufficient to identify enrichment in both cores. In C1, all layers analysed showed poor Pb enrichment, with higher values in recent layers and all concentrations below TEL values. Barcellos et al. (2017) found Pb concentrations with similar enrichment (EF<3) in deposits collected from the Capibaribe River estuary, which is about 45 km from Itapessoca Island and attributed the geogenic origin to Pb enrichment. In C2, in the 12 cm deep layer, which corresponds to the year 1999 (Albuquerque et al. 2019), the concentration of Pb exceeds the TEL reference value (30.2 mg.kg-1), reaching 40 ppm of Pb. The layer at 18 cm C2 (1990) (Albuquerque et al. 2019), also presents values above the TEL limits, with 33 ppm Pb. The moderate enrichment of Pb in C2 since 1978 could be related to sugarcane cultivation, because the application of fertilizers and pesticides contributes to the increase of toxic metals in the soil and sediments, such as Cr, Zn and Pb (Yadav et al. 2009). It should be noted,

however: 1) the sugarcane monoculture in the region has been going on since the 16th century (Schwartz 2005); 2) curiously, it is observed that Pb in C1 has been enriched since 1927. In these circumstances, it cannot be safely said that sugarcane monoculture is responsible for the enrichment of Pb, because the import and use of organosynthetic pesticides in Brazil took place around 1950 (Moragas and Schneider 2003). The region also has old calcination furnaces - vestiges of lime production for civil construction, built by Portuguese and Dutch colonialists in the 17th century (Santos and Oliveira 2015), however, this fact does not justify the enrichment of Pb in the 1920s, being more likely that enrichment in this period is associated with the urban development of the Recife Metropolitan Region - RMR. In C2, it was only possible to identify Pb enrichment from 1978 onwards. Albuquerque et al. (2019) reported a peak Hg increase in sediment core collected on the Itapessoca island around 1980. Although there is some relationship between Pb and Hg enrichment in the environment due to the proximity of events, geochronological evidence indicates a higher relationship between Pb enrichment and the cement industry. One proof of this is that in C1, it was possible to identify an increase in Pb enrichment from 20 ppm in 1927, to 27 ppm in 1948, a bit before the official start of operation of industry-scale limestone mining and cement manufacturing. The cement industry can contaminate the soil through emissions of particulate matter released by calcination furnaces, with the emission of toxic metals originating from the burning of raw materials and mainly fuels used in the clinker production process (Freitas and Nóbrega 2014). Part of the Pb retained and accumulated in old diagenetic processes, associated with local sources, for example, the carbonate sediments themselves (Barcellos et al. 2017), may have been made available through burning. Cement dust released by industry may contain toxic metals such as lead, chromium, nickel and mercury (Baby et al. 2008). Holban et al. (2015) report that the air pollutants generated by the cement industry produce significant pollution: they found a concentration of 41.9 ppm of Pb in a soil sample near a cement plant. A similar value has found in the present work, of 40 ppm in C2 (Itapessoca Island).

The concentration of the analysed elements is subject to local hydrology, because salinity and Total Suspended Solids (TSS) tend to be lower during the rainy season (Albuquerque et al. 2019). Despite the higher contribution of fine sediment and higher dilution of the elements, in the rainy season, under appropriate hydrodynamic conditions, the fine sediments are enriched and, precipitated, enriching the deep sediments (Xavier et al. 2016). It's conceivable that the concentration of many elements is associated with the cycles and scales of limestone/cement production. In this context, Albuquerque et al. (2019) noted that the decrease in mercury (Hg) concentration along with the release of this

element into the environment was associated with a decrease in the operation of mining activities on Itapessoca Island, where suspended sediments and residual organic matter from mining would act as the adsorption medium for Hg.

Ratios between chemical elements

The superficial sediments had low Mg/Ca ratios (0.008 to 0.13). This means that the relations between Ca and Mg are more compatible with the ratios present in carbonates from the Gramame Formation (0.02 to 0.09), indicating that it is more exploited in the region than the carbonates from the Itamaracá Formation (around 0.5), for example (Nascimento-Silva et al. 2011). The cores also gave Mg/Ca ratios within the range for the Gramame formation: in C1 0.062 to 0.63 (mean 0.22) and in C2, 0.06 to 0.14 (mean 0.09). The increase in the Mg/Ca ratio found in C1 reveals a sharp peak in 1948, reinforcing the possibility that limestone mining on the island of Itapessoca began before the concession for cement production in the 1950s, also corroborated by the more enriched contents of Pb. This is possible considering the existence of the installation phase before the operation and marketing stages of the limestone/cement production chain. The decline of the Mg/Ca ratio from the 1960s in C1 and C2 cores seems to be related to the enrichment of Ca and Sr caused by limestone mining. The results of Mn/Sr ratios indicated that all samples in the C1 and C2 cores had Mn/Sr <2 ratios, not indicating diagenetic alteration, as mentioned by Jacobsen and Kaufman (1999). The Mg/Ca and Mn/Sr ratios are shown in Fig.7. The Mn/Sr and Mg/Ca ratios indirectly point to a decrease in Fe (most visible in C1), considering that Ca is a typical anti-correlate of Fe and other earth elements (MacLeod et al. 2001).
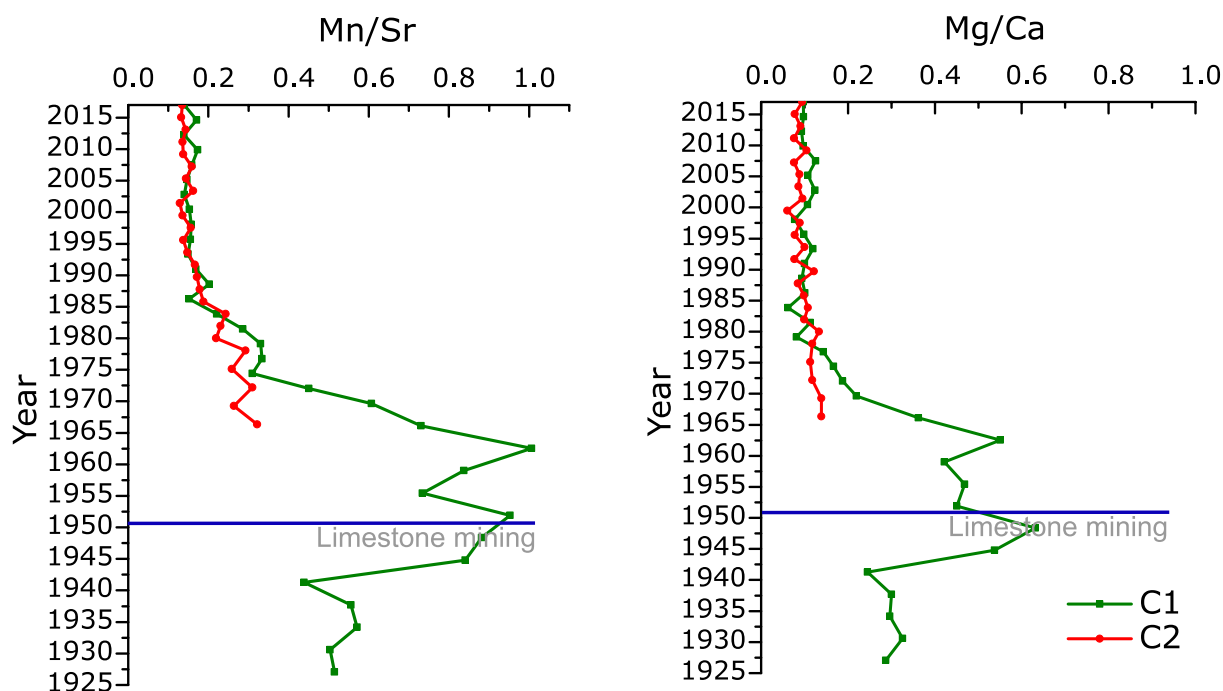
Fig. 7. Mg/Ca and Mn/Sr ratios in C1 and C2 cores.

The higher concentration of Fe in C2 denotes terrestrial origin associated with mining (Fig. 8). The Al/Fe ratio increases slightly in the C1core in mid-1950. In C2, the Al/Fe ratio increases quite sharply, with a more evident increase in the 1980s. The Si/Fe ratio in C1 shows many oscillations, but with slight depletion over the years in C1, with an increase in the Al/Fe ratio. In summary, the Ti/Fe, Si/Fe ratios indicate an increase in the Ti and Si ratios in C2 and a slight depletion in C1. The Al/Fe ratio indicates an increase in the proportion of aluminium in both ratios, although there is a more marked increase in C2 from 1965 onwards, when there is also an increase in the Si/Fe ratio in C2. Considering the above, it can be concluded that there is a decrease in the proportion of denser elements associated with thicker sediment, an increase in the proportion of elements associated with finer fractions of sediment and a lower proportion of quartz sand in C1. In C2, the availability of silica components from mining and limestone processing waste on the island of Itapessoca may explain the increased proportion of Al, Ti and Si in C2. Clays are one of the largest impurities in carbonated rock; alumina, silica and iron oxides in the form of clay minerals are the most common (Sampaio and Almeida, 2005). This also includes the leaching of exhausted mines. One should also consider the proximity of outcrops of the carbonate source rock and the resulting natural contribution of limestone sediments from the Gramame Formation to C2. The terrestrial material and marine carbonates reason expressed by Fe/Ca indicates an increase in the proportion of Ca in the two cores, however, there is a sharp drop in the Fe/Ca ratio in C1, from a peak in 1952. The Mn/Fe ratio shows an almost stationary behaviour

along the C1 and C2 profiles, with peaks revealing   suboxic conditions; however, the diagenetic formation of carbonates still depends on available metabolizable organic matter (Coleman et al. 1993) and on concentrations of dissolved oxygen and sulphate ions in the interstitial water of the pores (Curtis 1987). The concentrations of Fe (in mg.kg-1) and the Fe/Ca, Al/Fe, Mn/Fe, Si/Fe, Ti/Fe ratios over time can be seen in Figure 8.
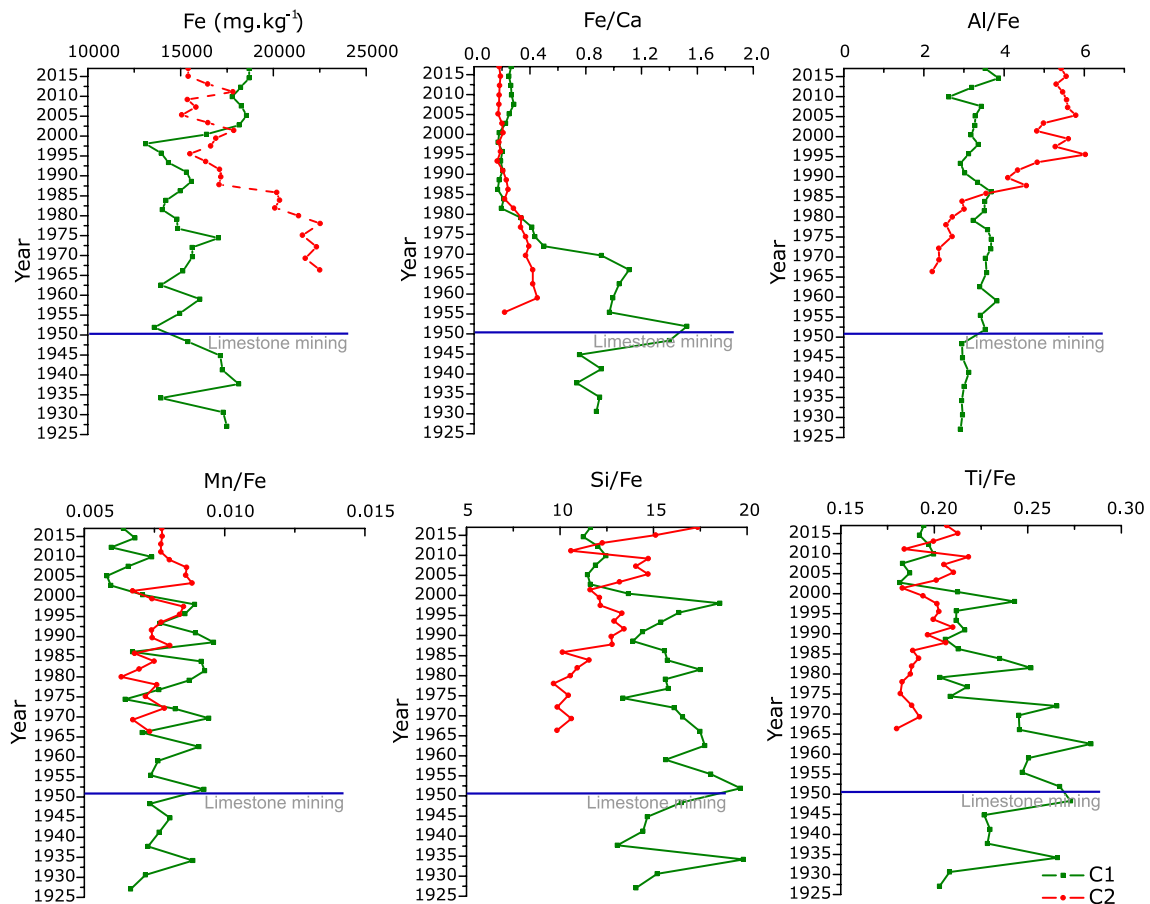
Fig. 8. Fe concentration for both cores. Al/Fe, Fe/Ca, Mg/Ca, Mn/Fe, Mn/Sr, Si/Fe and Ti/Fe ratios in C1 and C2 cores.

As mentioned, the Mn/Sr, Mg/Ca and Fe/Ca ratios indicate an increase in the proportion of these elements in the two cores, again suggesting the influence of mining on local sedimentation through the greater contribution especially of Ca and Sr. The availability of these and other elements through the loading of Suspended Particulate Material (MPS), Total Suspended Solids (TSS) and consequent accumulation of sediment in the study area seems to have favoured, for example, the advancement of the mangrove swamp, generating positive feedback on account of the mangrove's own nutrient retaining nature (Tam and Wong 1993). Pelage et al. (2019) found general growth in the mangrove

system attributed to increased salinity in the Santa Cruz Channel. The high rates of sedimentation observed in both cores (C1: 0.84 ± 0.07 cm.yr^{-1} and C2: 1.03 ± 0.22 cm.yr^{-1}) when compared, for example, with the rate of the mid and low Capibaribe estuaries 70 km south, 0.55 cm.yr^{-1} and 0.44 cm.yr^{-1}, respectively (Barcellos et al. 2017; Xavier et al. 2016), corroborate these geochemical indications, which may be related to the high mobility and morphosedimentary dynamics of intertidal banks, associated with the expansion of the fringe of mangroves adjacent to C1 and C2 cores.

Conclusion

The analysis of superficial sediments and sediment cores suggests the influence of both natural and anthropic components in the sedimentation process. The geochemical composition of the superficial sediments enabled the identification of three factors related to finer terrestrial material, coarser sediments and calcareous/carbonate sediments of marine origin. The variations in the distributions of elements such as Al, Fe and Si seem to reflect different granulometric fractions, since Si is the main constituent of coarse particles (quartz), while Al and Fe compose the enrichment of clay minerals. The multi elementary approach also allowed the identification of the variations in the concentrations of the elements for the two deposits, signalling geochemical changes in the sedimentation of the points sampled in the Itapessoca Estuarine Complex. This assertion is supported by geochronology, which identified a higher sedimentation rate in C2, a strong indication of the influence of cement industry and limestone mining, officially in operation since the 1950s. The quantitative analysis of the elements in the sediment cores in association with geochronology enabled the identification of a change in the element ratios associated with fine fractions and greater sediment granulation, with an increase in elements associated with fine fractions and associated with carbonates from mining.

These ratios between the chemical elements which reinforce the results of the Enrichment Factors assist in the understanding of two important issues involving the geochemistry of local sedimentation: 1) recent sediments have their origin mostly in the region's own carbonate system, especially the Gramame formation; 2) there is a clear increase in the proportion of elements associated with carbonates in periods very close to the official start of the operational phase of limestone mining and cement manufacturing. From the evidence, it can be concluded that man-made activities related to mining and cement manufacturing have disturbed local sedimentation, leading to increased concentrations of the toxic metal lead in the region.

Acknowledgements

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CAPÍTULO 3

Comparing diversity of fish assemblages and relationship

with environmental variables in a tropical estuary

(A ser submetido ao periódico *Scientia Marina*)

Comparing diversity of fish assemblages and relationship with environmental variables in a tropical estuary

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Abstract: The fish fauna was captured in the Itapessoca Estuarine Complex in 2017. A total of 76 species from 33 families were recorded. The multivariate analyses employed did not identify any clear pattern, although there was a predominance of zoobentivores species. A difference in terms of species diversity index were identified between Itapessoca's Island and Catuama inlet. PCA analysis suggest difference between abiotic factors in the different areas, but NMDS ordination suggest which of some sorted objects seems to have been influenced by abiotic factors governed by natural processes. The Bioenv routine confirms NMDS ordination and showed Electrical conductivity of the water, Total Dissolved Solids a Salinity which the factors most correlated with community distribution, however, the Zinc element is commonly associated with human factors. These factors may be responsible for the biological diversity and fish fauna composition in the study area.

Keywords: Environment, Biodiversity, Fish fauna

Introduction

Estuaries are a major focus of anthropogenic activities and are subject to high levels of disturbance caused by multiple stressors. Chemical contaminants from urban and industrial activities are released into estuaries and accumulate in benthic sediments (Birch, 2008), which are resuspended by physical disturbances from fishing, dredging, and storms (Eggleton and Thomas, 2004). Other impacts such as landscape alteration (e.g. urbanization, deforestation of mangroves, dams) and overfishing affect

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the composition of ichthyofauna (Araújo et al., 2009; Lima et al. 2018; Lopez-Angarita et al. 2016; Viana and Frédou, 2014).

The high concentration of nutrients in estuaries causes a high primary production (Correl, 1978) and, consequently, these environments can be colonized by mangroves, which form highly productive ecosystems capable of exporting energy and materials to adjacent areas, sustaining a diverse heterotrophic food chain, which includes fish (Barletta et al. 2003; Blaber, 2000; Deegan, 1993; Hogarth, 2007). Because of their high productivity, estuaries favour occupation by fish at all stages of their life cycle, especially in the early stages, where they find food and protection from predators (Barbieri et al., 2014). The estuarine fish fauna worldwide is dominated by species that accumulate biomass and subsequently move offshore after reaching adulthood, exporting nutrients and energy (Yanez-Arancíbia, 1985), considering the displacement between adjacent coastal environments (Potter et al, 2011).

Taxonomic inventories are the most elementary data in biogeography, macroecology and conservation biology and play key roles in constructing patterns of species richness, delineating species ranges, quantifying extinction risk and prioritizing conservation efforts in impacted areas (Mora et al., 2008). However, for the description of estuarine fish assemblage structures, not only the classical, taxonomic approach has been used, but also the application of functional groups (Elliot et al. 2007) to simplify the structure and dynamics of ecosystems and facilitate understanding of complex factors (Blondel, 2003). Ecological guild is defined as a set of species that subsist on the same resource, whose exploitation occurs in a similar manner (Blondel, 2003). In this type of approach, fish species are grouped according to different dimensions of niche, generally trophic level, reproductive strategy and use of the estuary, reflecting a better characterization of use and occupation of the environment, considering the ecological patterns of the ichthyofauna and the behavior of fish during their stay in the estuary (Elliott et al., 2007).

Quantifying and assessing changes in biological diversity has been a central theme in many ecological studies, but the methods used to estimate biological diversity from sampling data have been unclear, as diversity estimates - including species richness, vary as a function of sample size and sampling effort (Chao et al., 2014). To avoid the data discarding occasioned by the traditional (rarefaction) approach, Colwell et al. (2012) proposed the use of a sample size-based rarefaction and extrapolation sampling curve for species richness that can be rarefied to smaller sample sizes or extrapolated to a

larger sample size. Chao and Jost (2012) refined the method and showed that the rarefaction and extrapolation sampling curve for a given degree of sample completeness is better able to judge the magnitude of differences in richness between communities, classifying communities more efficiently. Studies have pointed to fish diversity associated with environmental variables (Kouamélan et al. 2003; Hossain et al. 2012). The spatial and temporal distribution of fishes in estuarine environment is intrinsically associated with the wide variation of its natural environmental characteristics (Elliott and Hemingway, 2002), however, the habitats and the configuration of fish assemblages can be affected by anthropic changes, which can influence, also, the food resources (Molina et al. 2020) - the structure and taxonomic composition of meiofauna assemblages, food for many fish species, can be influenced by sediment concentrations of trace metals (Schratzberger et al., 2000). McKinley et al. (2000) also found a correlation between the concentration of heavy metals found in sediment and the distribution of fish. The Itapessoca Estuarine Complex integrates the Estuarine Complex of the Santa Cruz Channel and constitutes an important local ecosystem; however, it has been the target of urban expansion, mining, tourism and other anthropic activities (CPRH, 2003) - some extremely harmful, which cause the accumulation of heavy metals in the sediment compartment (Albuquerque et al. 2019). Besides the main water quality parameters (salinity, temperature, turbidity, pH and dissolved oxygen) affect the distribution of fish in the estuary (Blaber and Blaber, 1980), it is known that the sediment characteristics also influence the distribution of fish by the availability of prey (Marchand, 1993).

Many studies developed in the study area were based only on classical taxonomy of fishes, however, some more recent studies conducted in the northern coast of Pernambuco include the use of functional variables, such as those developed by Favero et al. (2019); Ferreira et al. (2019); Silva-Júnior et al. (2017), but none of these studies seek to investigate direct relationships with environmental variables in the sediment compartment.

Fishing activities in estuarine environments have clear impacts on the structure and functioning of the estuarine ecosystem (Blaber, 2000), however, other non-fishing activities that cause environmental changes - such as industry, imply the removal or alteration of these environments and reinforce the need for an integrated approach to coastal zone management, where some form of resource-based action plan can provide relevant information for specific management (Blaber 2000). In this context, the characterization of the functional structure of fish assemblages can be useful for the assessment of the quality of the tropical estuarine environment, because the functional

characteristics of organisms affect the ecosystem processes (Diaz and Cabido, 2001), entailing relevant information about the functioning of the environment, when compared only to the classical taxonomic diversity. Considering the ecological importance of the estuarine environment and its socio-economic relevance, this present study on the ecology and biodiversity of the ichthyofauna is a tool for a better understanding of the biogeography and ecology of species, adding strategic information, essential for conservation measures and management of fisheries resources, with the main objective of investigating possible differences in the composition and diversity of fish assemblages based on taxonomic and functional variables, considering possible differences in sediment composition between the sampled areas and possible relationships with environmental variables.

Material and methods

Study area

The Itapessoca Estuarine Complex, located in the northern coast of the State of Pernambuco, Brazil, is characterized by the Itapessoca River basin, with an estuarine area of 3.998 hectares (FIDEM 1987) and the presence of Itapessoca Island (Fig. 1). This estuarine complex involves only the Catuama Bar, the northern mouth of the Santa Cruz Channel - the main channel of Itamaracá Estuarine Ecosystem, with 20 km long and variable depth between 1 and 17 m (Vasconscelos Filho et al. 1998). The Catuama Bar is 1.5 km wide, with variable bathymetry and abrupt increase in depth at some points present in geological faults (Topan and Lima Filho, 2017).

The Estuarine Complex is part of the Tropical Hot and Humid climate, according to the Köppen-Geiger climate classification (Köppen, 1936), type Aws, with an average annual air temperature of 26ºC with a maximum of 34º C and a minimum of 18º C (Medeiros et al, 2001). The rainy season occurs between the months of February and August, with average monthly precipitation of 180-212 mm. As the average monthly precipitation decreases, between 40 and 51 mm, evaporation begins to exceed precipitation, characterizing the dry season, which occurs between the months of September and January (Medeiros et al, 2001). The discharge from rivers, streams and rainfall shows significant seasonal differences, with total average flow varying between 55.9 m³s⁻¹ at the peak of the rainy season and 0.8 m³s-l at the height of the dry season (Medeiros and Kjerve, 1993). Associated with climatological factors, water temperature presents seasonal variation (Medeiros and Kjerve, 1993).

The Itapessoca Estuarine Complex is part of the Itamaracá Estuarine, one of the most important ecosystems of the Pernambuco State coast, with great socioeconomic importance (Medeiros et al. 2001). The region also presents a variety of connecting habitats that favors the development of ichthyofauna (Vasconcelos Filho et al. 2009). Because it is considered highly productive (Macedo et al. 2000), the region favors fishing activity, one of the main local economic activities, which exerts great influence on the dynamics of traditional communities (CPRH 2003).

Data collection

Specimens were collected during the dry (September/December) and rainy (March/July) seasons of 2017 in the Itapessoca Estuarine Complex. A "mangote" net (seine net) was used for the capture. All fisheries were carried out at low tide. Each sampling campaign comprised three sets of approximately 30 minutes duration. Each seine net deployment took place at the shores of Catuama and at the shores of Ilha de Itapessoca (Itapessoca's Island) - herein named CAT and ITA areas. The seine net was 129 meters long, with a mesh size of 10 mm between knots, 9 meters body height and 3.5 meters on the sides. Specimens were properly preserved on ice for later identification in the laboratory, according to the taxonomic classification of Nelson et al (2016). Before each haul, environmental information on water quality was collected, the parameters: temperature (ºC), total dissolved solids - tds (ppt), salinity (ppm), pH, electrical conductivity (µS∕cm), dissolved oxygen (mg/L and %), using a Hanna multiparameter probe.

Twenty surface sediment samples of up to 20 cm depth were collected with the aid of a Van-Veen bottom grab: points 1 to 5 were collected in the Catuama sector (CAT) and points 6 to 10, in the Itapessoca sector (ITA). After drying and comminution, 1 g samples of sediment and reference materials were used for Energy Dispersive X-Ray Fluorescence - EDXRF analysis. The measurements were performed in Shimadzu ED-720 equipment, calibrated with the specific Setting Up Samples - SUS and A750 calibration standards. For the evaluation of the quality of the analytical procedure, two reference materials were used: IAEA-SL-1 "Trace and Minor Elements in Lake Sediments" and SRM1646a - "Estuarine Sediment", from the National Institute of Standards and Technology - NIST. The elements were analysed: Al, Ca, Fe, Mg, Mn, Ni, K, Pb, Si, Sr, Ti, Zn.
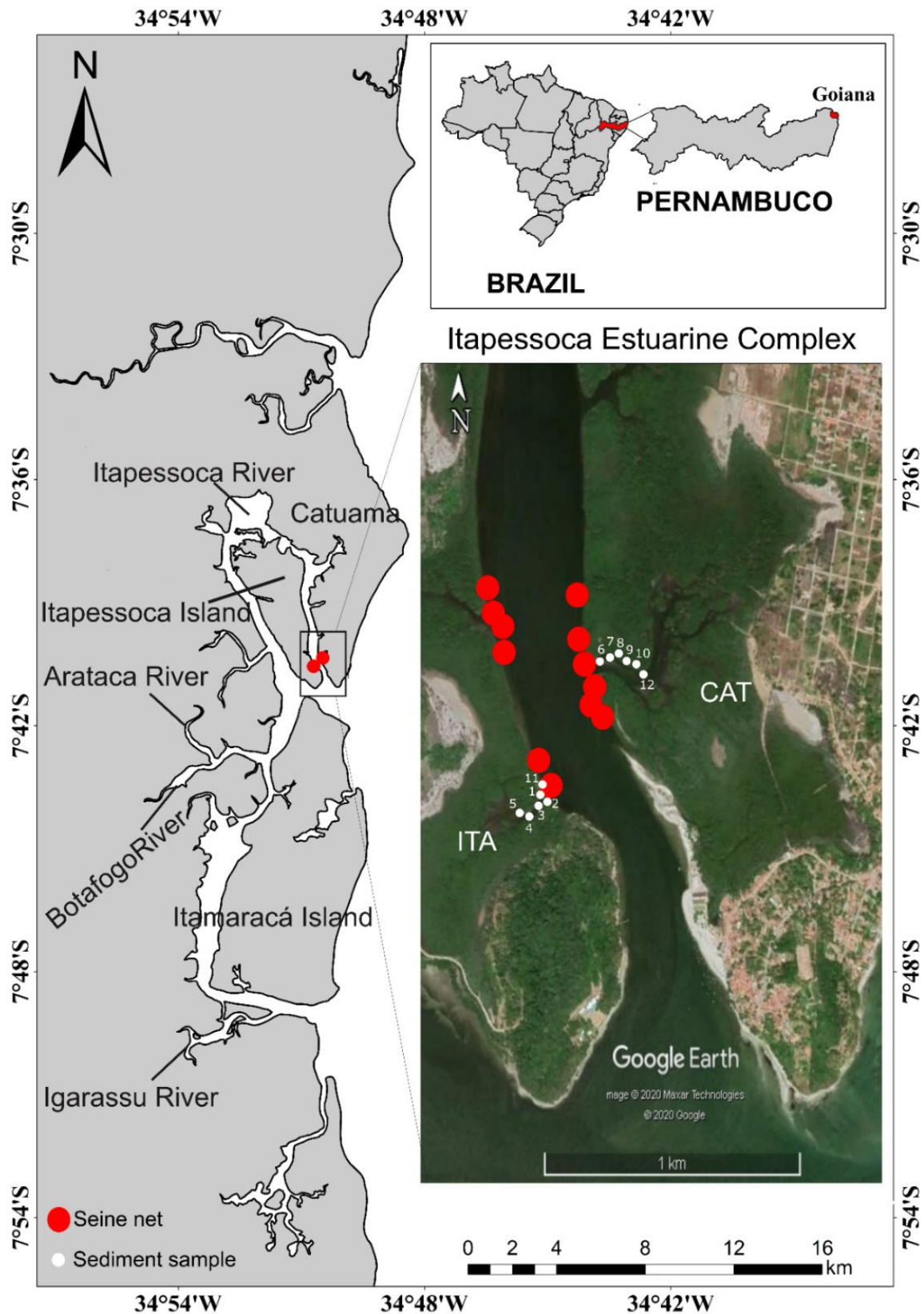
Fig.1. Study area of the Itapessoca Estuarine Complex, Pernambuco State, Brazil and areas location:
Ita (Itapessoca Island) e Cat (Catuama Inlet).

Biodiversity

Biodiversity was assessed based on three diversity indexes (Magurran, 2004): species richness (N_0; q = 0); the exponential Shannon diversity (N_1; q=1); and Simpson concentration (N_2; q=3). For that, we used a generalization function of q order, the Hill's numbers (N_q) measured as 'effective number of species', which integrate species richness and species relative abundance to propose a more intuitive and statistically rigorous alternative to calculate diversity measures (Chao et al., 2014). We compared diversity using: (1) the construction of the sample-size-based rarefaction and extrapolation sampling curves (Hsieh et al. 2016) to test for differences between area; (2) the construction of a sample completeness curve to link sample-size- and coverage-based sampling curves; (3) Comparing coverage-based sampling curves up to a ''base coverage''. For any fixed sample size or completeness in the comparison range, if the 95% confidence intervals do not overlap, then significant differences at a level of 5% among the expected diversities (whether interpolated or extrapolated) are guaranteed. In addition, N_0, N_1, N_2 were estimated by extrapolation (Chao et al. 2014). Evenness was assessed using the Hill's ratio (Shannon evenness is $E_1 = N_1/N_0$, and Simpson evenness is $E_2 = N_2/N_0$). All diversity analyses were implemented in the R package iNEXT (Hsieh et al. 2016).

Species were assigned a conservation status according to the categories based in the International Union for Conservation of Nature - IUCN (IUCN 2021) Red List criteria of threatened species, categorized at regional level (ICMbio 2018) in 10 categories: extinct (EX), regionally extinct (RE), extinct in the wild (EW), critically endangered (CR), endangered (EN), vulnerable (VU), near threatened (NT), least concern (LC), data deficient (DD) and not evaluated (NE).

In order to detect differences in fish communities across areas, sites were observed using unconstrained ordination methods (NMDS, Bray–Curtis distance). Stress values < 0.15 indicate a good fit (Clarke and Warwick 2001), representing good relationship among samples in the multidimensional space. The analyses were performed with metaMDS within R vegan, using a Wisconsin double standardization. To visualize relationships between fish communities and environmental parameters, the NMDS biplot was interpreted using a post-hoc correlation with significant soil/environmental parameters (function envfit) (Oksanen et al. 2020) projected into the NMDS biplot.

Albuquerque et al (2019) performed the dating of sediment cores in the Itapessoca Estuarine Complex to evaluate the concentrations of mercury over time, in sediments collected in the Catuama community and Itapessoca Island. Considering that the two cores showed different concentrations of Hg-Total (Albuquerque et al. 2019), it is expected that the distribution of concentrations of other chemical elements may lead to a difference in the sediment geochemistry of the different areas, causing a difference in the composition of local biocenoses to be revealed mainly by the discrepancy in the composition of functional guilds between the areas of Itapessoca's Island and Catuama.

Fish community and abiotic variables relationships

Principal Component Analysis was used to interpret the abiotic data (water quality parameters and metal concentration in sediment) and your interactions. To test whether any structure pattern in the fish community was significantly correlated with this in any combination of abiotic variables (and if so, which was the best sub-set), the biota and environment matching routine [BIOENV; Clarke and Ainsworth (1993)] were used. In all of these analyses, Bray-Curtis matrices constructed from the pre-treated fish data were used as the response matrix, while the water-quality data comprised the predictor matrix. For BIOENV, the Spearman rank correlation coefficient (ρ) was used as the matching coefficient and Euclidean distance was used to define sample resemblances for the abiotic data. A mantel test was then applied to test the significancy of the correlation (p<0.05).

All statistical analyses were performed using the vegan (Oksanen et al. 2020), and ggplot2 (Wickham, 2016) packages from R Core Team (2020).

Results

A total of 3,269 individuals distributed along 33 families (31 Actinopterygii e 2 Elasmobranchii) 76 species were sampled (table 1). Only 2 families of elasmobranchs have been identified: Narcinidae and Rhinobatidae. The Paralichtydae family was dominant in richness in the sampled points of the estuary, with 8 species, followed by the families Carangidae (7 species) and Gerreidae, Engraulidae, Lutjanidae and Tetraondontidae, with 6 species each. Gerreidae (1142; 34.9%), Clupeidae (780; 23.9%), Haemulidae (610; 18.7%), Tetraondotidae (130; 4%) were the most abundant families in the estuary, with the species *Eucinostomus sp.* (577; 17.65%), *Haemulopsis corvinaeformis* (571; 17.47%), *Opisthonema oglinum* (501; 15.33%), *Eucinostomus argenteus* (271; 8.29%) were the most abundant.

Regarding biomass, the families Haemulidae (15412.3g; 28.5%), Gerreidae (7971.22g; 14.7%), Trichiuridae (7334g; 13.6%), Clupeidae (6330.6g; 11.7%) and Tetraodontidae (2895.84g; 5.4%) were the most representative. *Haemulopsis corvinaeformis* represented the largest biomass caught (15087.98; 27.15%), followed by *Trichiurus lepturus* (7334; 13.2%), *Eucinostomus sp.* (6534.87; 11.76%), *Opisthonema oglinum* (5325.62; 9.58%). Further details can be glimpsed in Table 1.

Table 1: Composition of the Species observed in the area in biomass and number. Env.use = Estuarine Use Functional Group. MS = marine stragglers, MM = marine migrants, ES = estuarine or FS = freshwater species. Troph = Feeding Mode Functional Group: DV = Detritivore, HV = herbivore, ZP = zooplanktivore, ZB + zoobenthivore, OV = omnivore, PV = piscivore and OP = opportunist. IUCN = Categories based in the International Union for Conservation of Nature Red List criteria of threatened species: EX = extinct, RE = regionally extinct, EW = extinct in the wild; CR = critically endangered; EN = endangered; VU = vulnerable, NT = near threatened, LC = least concern; DD = data deficient and NE = not evaluated. N = abundance. b = biomass.

Family (32)	Specie	Env.use	Troph	IUCN	N	b	%b	%N
Achiridae	*Achirus achirus* (Linnaeus,1758)	ES	ZB	LC	5	64.2	0.12	0.15
	Achirus lineatus (Linnaeus,1758)	ES	ZB	LC	57	1113.23	2	1.74
Ariidae	*Sciades couma* (Valenciennes, 1840)	ES	ZB		1	522.41	0.94	0.03
Atherinopsidae	*Atherinella blackburni* (Schultz, 1949)	ES	OV	LC	6	32.1	0.06	0.18
	Atherinella brasiliensis (Quoy & Gaimard, 1825)	ES	OV	LC	1	6.7	0.01	0.03
Carangidae	*Caranx latus* (Agassiz, 1831)	MS	ZB	LC	1	13.3	0.02	0.03
	Caranx sp.	MS	ZB		1	2.9	0.01	0.03
	Oligoplites palometa (Cuvier,1832)	MM	PV	LC	7	29.81	0.05	0.21
	Oligoplites saurus (Bloch & Schneider, 1801)	MM	PV	LC	2	3	0.01	0.06
	Selene vômer (Linnaeus, 1758)	MS	PV	LC	9	347.69	0.63	0.28
Centropomidae	*Centropomus mexicanus* (Bocourt, 1868)	MM	PV	LC	3	33.3	0.06	0.09
	Centropomus parallelus (Poey, 1860)	MM	PV	LC	14	645.96	1.16	0.43
	Centropomus undecimalis (Bloch, 1792)	MM	PV	LC	8	708.07	1.27	0.24
Clupeidae	*Anchovia clupeoides* (Swainson 1839)	MM	ZP	LC	130	825.23	1.49	3.98
	Chirocentrodon bleekerianu (Poey, 1867)	MS	ZP	LC	1	3.66	0.01	0.03
	Harengula clupeola (Cuvier, 1829)	MS	ZP	LC	84	717.29	1.29	2.57
	Lile piquitinga (Schreiner & Miranda Ribeiro, 1903)	ES	ZP	LC	64	267.61	0.48	1.96
	Opisthonema oglinum (Lesueur, 1818)	MS	ZP	LC	501	5325.62	9.58	15.33
Cynoglossidae	*Symphurus tessellatus (Quoy & Gaimard,1824)*	MM	ZB	LC	3	64.43	0.12	0.09
Dactylopteridae	*Dactylopterus volitans* (Linnaeus, 1758)	MM	PV	LC	24	114.21	0.21	0.73
Diodontidae	Chilomycterus spinosus spinosus (Linnaeus, 1758)	MS	ZB	LC	34	1171.71	2.11	1.04
Engraulidae	*Anchoa spinifer (Valenciennes, 1848)*	MM	ZB	LC	1	2.6	0	0.03

Family	Species				N	Weight	%	%
	Cetengraulis edentulus (Cuvier, 1829)	MM	ZP	LC	6	44	0.08	0.18
	Cetengraulis sp.				8	16.9	0.03	0.24
	Engraulidade spp.				45	75.4	0.14	1.38
	Lycengraulis grossidens (Spix & Agassiz, 1829)	ES	PV	LC	39	674.13	1.21	1.19
	Lycengraulis spp.	ES	PV		12	100.6	0.18	0.37
Ephippidae	*Chaetodipterus faber* (Broussonet, 1782)	MM	OV	LC	31	612.39	1.1	0.95
Fistulariidae	*Fistularia tabacaria* (Linnaeus, 1758)	MM	ZP	LC	3	122.7	0.22	0.09
Gerreidae	*Diapterus auratus* (Ranzani, 1842)	MM	ZP	LC	10	22.3	0.04	0.31
	Diapterus rhombeus (Cuvier, 1829)	MM	ZP	LC	157	992.64	1.79	4.8
	Diapterus sp.				12	139.2	0.25	0.37
	Eucinostomus argenteus (Baird e Girard, 1855)	MM	ZB	LC	271	607.42	1.09	8.29
	Eucinostomus gula (Quoy & Gaimard, 1824)	MM	ZB	LC	98	249.89	0.45	3
	Eucinostomus lefroyi (Goode, 1874)	MM	ZB	LC	11	53.4	0.1	0.34
	Eucinostomus melanopterus (Bleeker 1863)	MM	ZB	LC	6	26.5	0.05	0.18
	Eucinostomus sp.				577	6534.87	11.76	17.65
Gobiidae	*Bathygobius* sp.				1	11	0.02	0.03
Haemulidae	*Haemulon parra* (Desmarest, 1823)	MS	ZB	LC	29	256.53	0.46	0.89
	Haemulon steindachneri (Jordan & Gilbert, 1882)	MS	ZB	LC	5	50.61	0.09	0.15
	Haemulopsis corvinaeformis (Steindachner, 1868)	MS	ZB	LC	571	15087.98	27.15	17.47
	Orthopristis ruber (Cuvier, 1830)	MS	ZB		5	17.19	0.03	0.15
Hemiramphidae	*Hemiramphus brasiliensis* (Linnaeus, 1758)	MS	HV	LC	1	1.35	0	0.03
Lutjanidae	*Lutjanus alexandrei* (Moura & Lindeman, 2007)	MS	ZB	LC	1	27.3	0.05	0.03
	Lutjanus analis (Cuvier, 1828)	MS	ZB	NT	6	82.69	0.15	0.18
	Lutjanus cyanopterus (Cuvier, 1828)	MM	ZP	VU	1	28.2	0.05	0.03
	Lutjanus griseus (Linnaeus, 1758)	MS	PV	LC	2	32.8	0.06	0.06
	Lutjanus jocu (Block &. Shneider, 1908)	MS	ZB	NT	15	578.44	1.04	0.46
	Lutjanus synagris (Linnaeus, 1758)	MS	ZB	NT	80	1153.08	2.08	2.45
Narcinidae	*Narcine bancroft* (Henle, 1834)	MS	ZB		2	29.4	0.05	0.06
Paralichthyidae	*Citharichthys macrops* (Dresel, 1885)	MS	ZB	LC	7	123.58	0.22	0.21
	Citharichthys spilopterus (Günther, 1862)	MM	ZB	LC	2	18.1	0.03	0.06
	Cyclopsetta chittendeni (Bean, 1895)	MS	ZB		3	51.15	0.09	0.09
	Cyclopsetta fimbriata Goode & Bean, 1885)	MS	ZB		1	19.1	0.03	0.03
	Etropus crossotus (Jordan & Gilbert, 1882)	MM	ZB	LC	9	194.22	0.35	0.28
	Paralichtys sp.				4	212.39	0.38	0.12
	Paralichtys brasiliensis (Ranzani, 1842)	MS	ZB	LC	1	394.55	0.71	0.03
	Syacium micrurum (Ranzani, 1842)	MS	ZB	LC	2	102.95	0.19	0.06
	Syacium papillosum (Linnaeus, 1758)	MS	ZB		2	155.3	0.28	0.06
Polynemidae	*Polydactylus virginicus* (Linnaeus, 1758)	MM	ZB	LC	3	218.08	0.39	0.09
Rhinobatidae	*Rhinobatus parcellens* (Walbaum, 1972)	MM	ZB		2	593.52	1.07	0.06
Scaridae	*Sparisoma* sp.				37	297.04	0.53	1.13
Sciaenidae	*Cynoscion microlepidotus* (Cuvier, 1830)	ES	ZB		3	1292.3	2.33	0.09
	Menticirrhus americanus (Linnaeus, 1758)	MM	ZB	DD	4	306.79	0.55	0.12
Scombridae	*Scomberomorus brasiliensis* (Collette, Russo e Zavala-Camin, 1978)	MS	PV	LC	1	15.6	0.03	0.03

	Scomberomorus cavala (Cuvier, 1829)	MS	PV		1	61.5	0.11	0.03
Scorpaenidae	*Scorpaena plumieri* (Bloch, 1789)	MM	PV	LC	1	180.6	0.33	0.03
Serranidae	*Rypticus saponaceus* (Bloch & Schneider, 1801)	MM	ZP	LC	4	113.8	0.2	0.12
Sparidae	*Archosargus rhomboidalis* (Linnaeus,1758)	MS	ZB	LC	10	59.58	0.11	0.31
	Calamus penna (Valenciennes, 1830)	MS	ZB	LC	1	6.2	0.01	0.03
Sphyraenidae	*Sphyraena barracuda* (Walbaum, 1792)	MM	PV	LC	3	389.41	0.7	0.09
	Sphyraena guachancho (Cuvier, 1829)	MS	PV	LC	2	40.8	0.07	0.06
Synodontidae	*Synodus foetens* (Linnaeus, 1766)	MS	PV	LC	5	157.5	0.29	0.15
Tetraodontidae	*Colomessus psittacus* (Bloch & Schneider, 1801)	MM	ZB	LC	1	256.7	0.46	0.03
	Lagocephalus laevigatus (Linnaeus, 1766)	MM	ZB	LC	4	511.05	0.92	0.12
	Sphoeroides greeleyi (Gilbert, 1900)	ES	ZB	LC	87	984.52	1.77	2.66
	Sphoeroides spengleri (Bloch, 1785)	MS	ZB	LC	1	8.8	0.02	0.03
	Sphoeroides testudineus (Linnaeus, 1758)	ES	ZB	DD	37	1134.77	2.04	1.13
	Tetraodontidae sp.				10	88.74	0.16	0.31
Trichiuridae	*Trichiurus lepturus* (Linnaeus,1758)	MS	PV	LC	21	7334	13.2	0.64
Triglidae	*Prionotus punctatus* (Bloch, 1793)	MS	ZB	LC	28	569.19	1.02	0.86
Teleostei	Teleostei sp.				5	9.1	0.02	0.15

Considering the trophic functional guilds, zoobentivore species were dominant in abundance (1425; 43.6%), followed by zooplanktivore species (951; 29.1%) and piscivore species (154; 4.7%). However, there is a higher proportion of zooplankton species in Catuama in July and in Itapessoca in December. In relation to the captured biomass, zoobentivores were dominant, (28410.35g; 52%), followed by piscivorous (10868.98g; 20%) and zooplanktivores (7631.95g; 14%) species.

Marine Stragglers (1451; 44.4%), Marine Migrants (828; 25.5%), Estuarine Species (348; 10.6%) were the most abundant estuarine use guilds - 19.5% were not classified. In March (rainy season), an increase in the proportion of estuarine species in both areas, being slightly higher in Itapessoca. In general, all the estuarine use guilds were more abundant in Itapessoca (MS=49.3%; MM=27.8%; ES=10.4%). Marine stragglers showed the highest biomass (30080.9; 60.5%), followed by marine migrants (8398.67; 15.4%) and ES (6578.17; 12%).

According to the sampling carried out, species in a lower state of concern (LC) are more abundant (93.8%), followed by non-threatened species (3.9%). Data Deficient represent only 2.2% of the total captured. By area, the proportions follow the same trend in ITA, with LC = 60.6%, NT=2.7% and DD=0.8%. In CAT, there is LT with 33.2%, NT=1.2% and DD= 1.5%. Only 1 (0.4%) species is considered vulnerable - *Lutjanus cyanopterus*, caught in September (dry season), in Catuama area.

The species ratios classified according to the IUCN criteria, proportion of estuarine and trophic use functional guilds are more detailed and can be better understanding through figures 2,3 and 4, respectively.
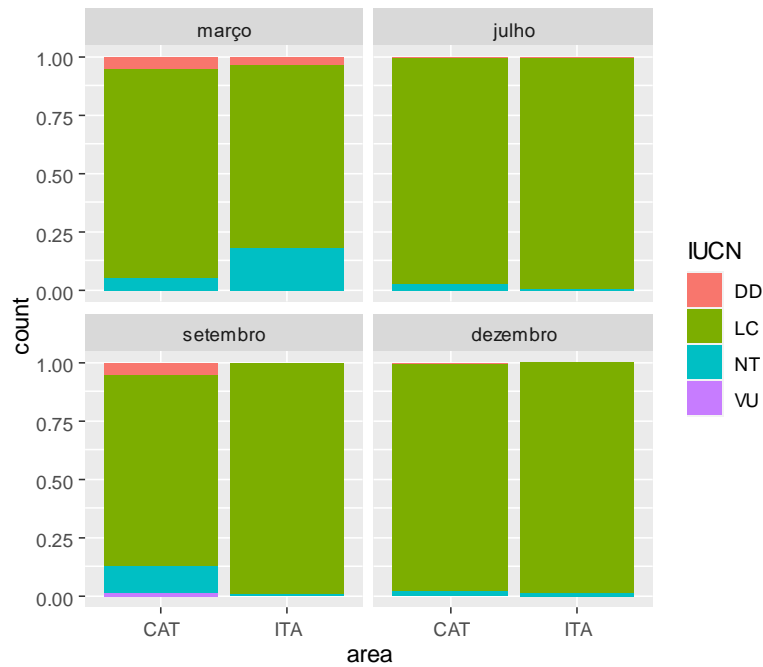
Fig.2. Involvement of groups based in the International Union for Conservation of Nature – IUCN Red List criteria of threatened species (VU = vulnerable, NT = near threatened, LC = least concern; DD = data deficient) in the four campaigns (March, July, September, December).
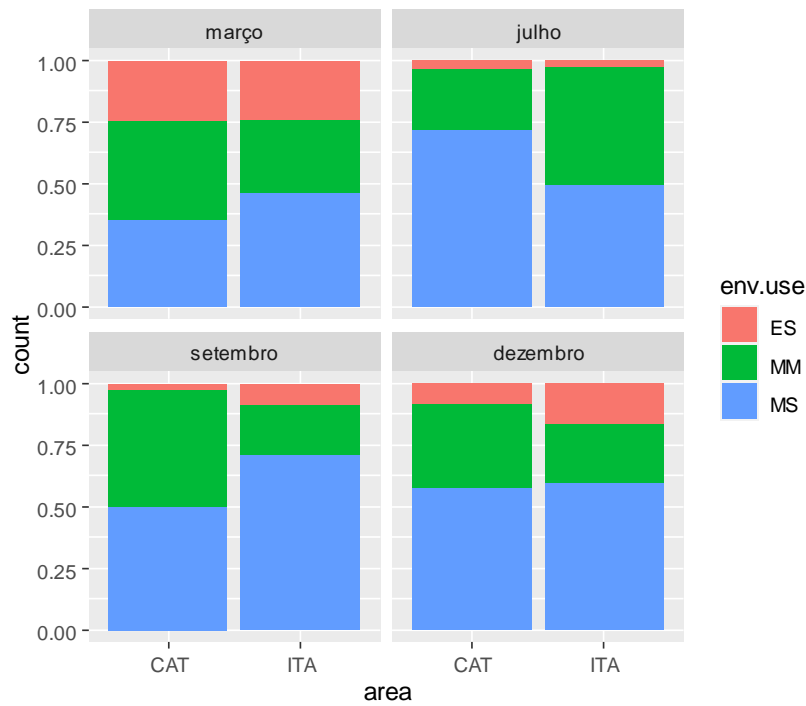
Fig.3. Estuarine use guilds participation (ES: estuarine species; MM: marine migrant; MS: marine straggler) in the four campaigns (March, July, September, December).

Fig.4. Trophic guilds participation (HV: herbivorous; OV: omnivorous; PV: piscivorous; ZB: zoobentivorous; ZP: zooplankton) by area (CAT: Catuama; ITA: Itapessoca), in the Itapessoca Estuarine Complex, during four campaigns (March, July, September, December).

Biodiversity

The Catuama and Itapessoca areas were different in terms of diversity. The reference sampling size was extrapolated up to size 6506 for the total are, size 2744 for Catuama and size 3768 for Itapessoca. In each plot, except for initial, small sample sizes, none of the con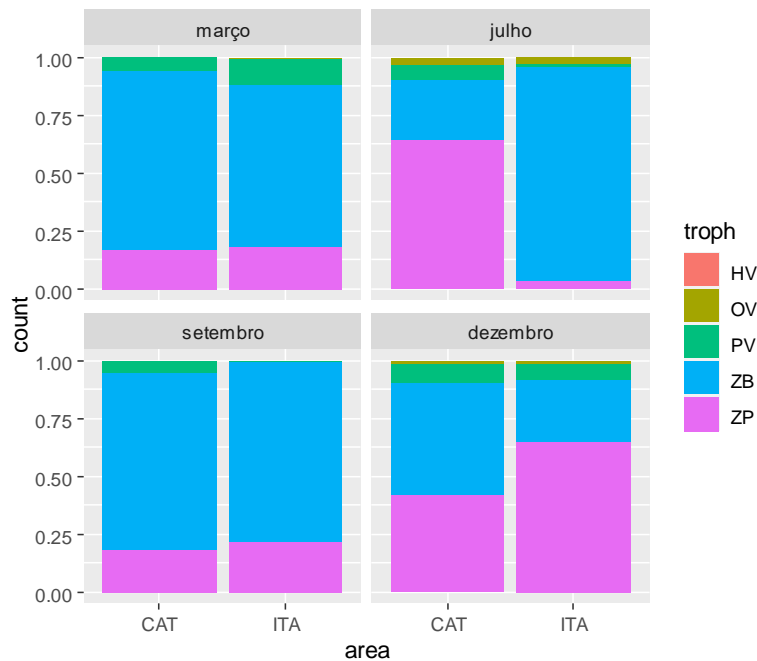fidence intervals for the three curves intersect (Fig.5) meaning they were significantly different ($p<0.05$). The sample coverage reached 99,5% for the entire area and when split 98,5% for the Catuama area and 99,2% for Itapessoca. The observed Species Richness (q =0) was 79 sp for all area, 66 sp in Catuama and 58 in Itapessoca (Fig. 6). The estimations of the species richness N_0, diversity indices (N_1 and N_2) and evenness (E_1, E_2) for the entire area (SC) as well as for the subareas (Catuama and Itapessoca) were calculated (table 2).

Table 2: Observed and estimated diversity indices (Hill's Number in number of equivalent species). SC = Entire area; CAT = Catuama area; ITA = Itapessoca area. s.e.: bootstrap standard error, LCL: lower confidence limit, UCL: upper confidence limit.

| Site	Diversity	Observed	Estimator	s.e.	LCL	UCL
SC	N_0 - Species richness	79	99.2	12.7	85.5	141.8
SC	N_1 - Shannon diversity	17.4	17.7	0.4	17.4	18.6
SC	N_2 - Simpson diversity	9.8	9.9	0.3	9.8	10.4
SC	E_1 - Shannon evenness	0.22	0.18	0.04	0.20	0.13
SC	E_2 - Simpson evenness	0.12	0.10	0.02	0.12	0.07
CAT	N_0 - Species richness	66	90.5	14.3	74.5	136.9
CAT	N_1 - Shannon diversity	13.1	13.6	0.6	13.1	14.8
CAT	N_2 - Simpson diversity	6.3	6.3	0.3	6.3	6.8
CAT	E_1 - Shannon evenness	0.20	0.15	0.04	0.18	0.11
CAT	E_2 - Simpson evenness	0.10	0.07	0.02	0.08	0.05
ITA	N_0 - Species richness	58	76.7	13.1	63.5	122.4
ITA	N_1 - Shannon diversity	16.3	16.6	0.5	16.3	17.6
ITA	N_2 - Simpson diversity	9.4	9.4	0.3	9.4	10
ITA	Shannon evenness	0.28	0.22	0.04	0.26	0.14
ITA	Simpson evenness	0.16	0.12	0.03	0.15	0.08
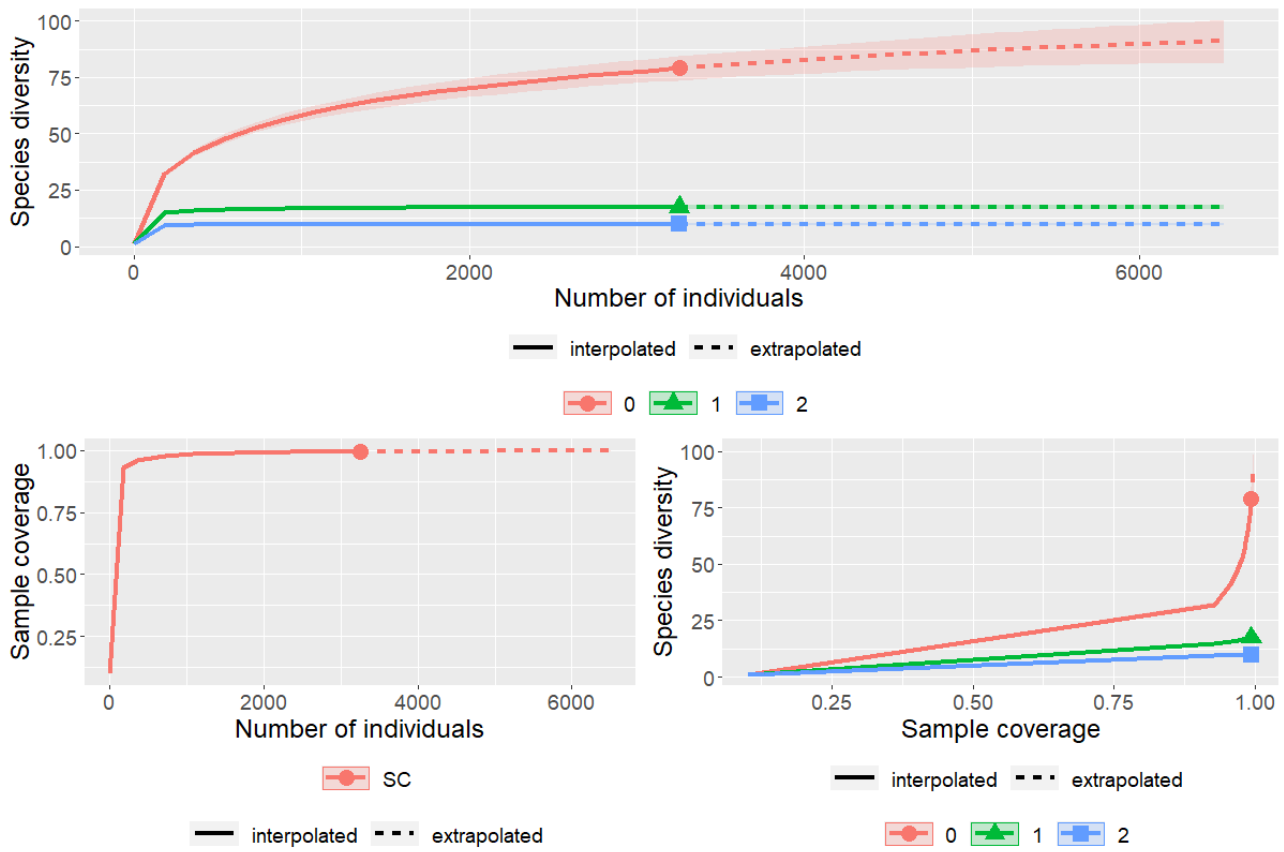
Fig. 5. (Upper) Sample-size-based diversity accumulation curve of fish species based in the Hill numbers (q0, q1, q2). Comparison of sample-size-based rarefaction (solid lines) and extrapolation (dashed curves). (Lower left) Sample completeness curves for richness. (Lower right) Coverage-based diversity accumulation curve, which plots the expected diversity.
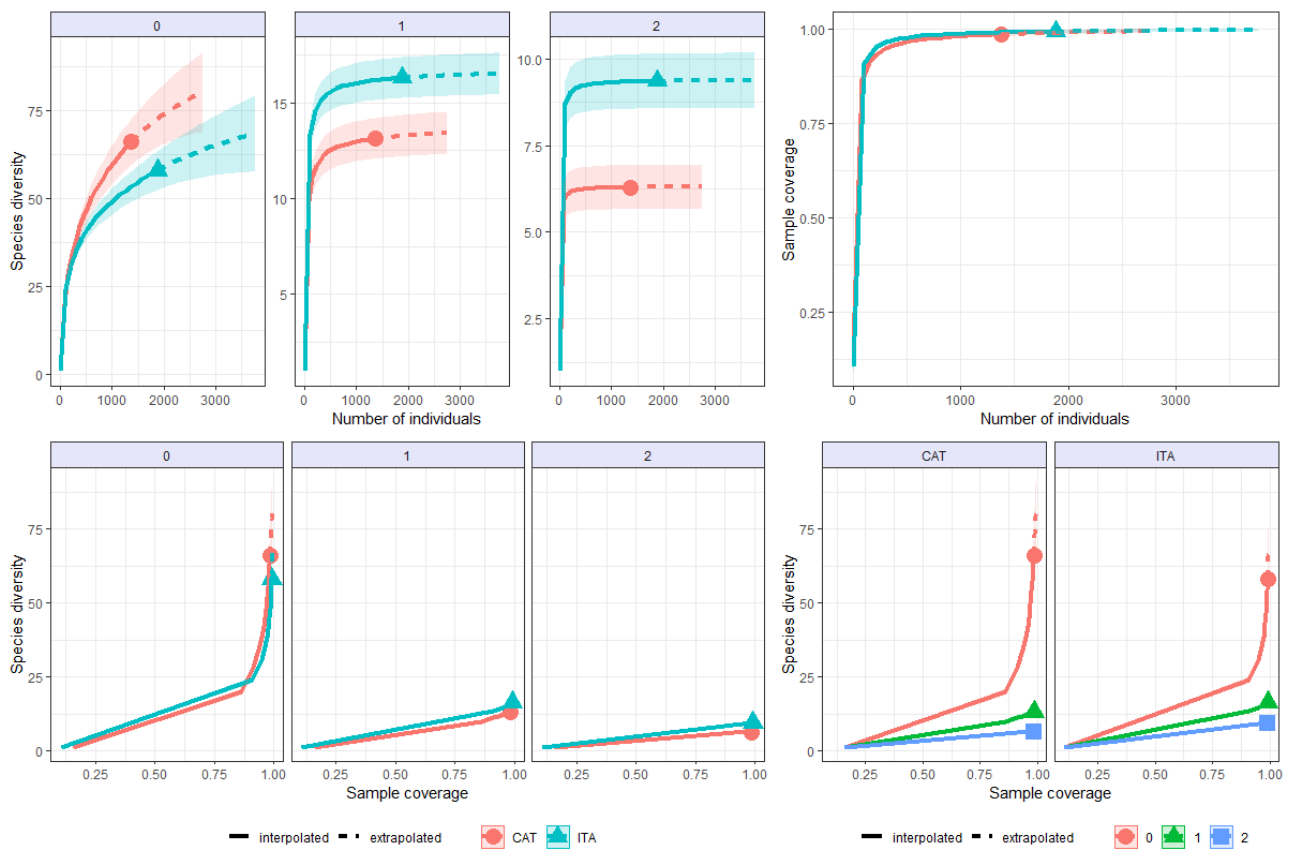
Fig. 6. Sample-size-based (Upper left) and coverage-based (lower left) rarefaction (solid line segment) and extrapolation (dotted line segments) sampling curves with 95% confidence intervals (shaded areas) for the fish data of two treatments (areas), separately by diversity order: q = 0 (species richness, left panel), q = 1 (Shannon diversity, middle panel) and q = 2 (Simpson diversity, right panel). The solid dots/triangles represent the reference samples. (upper right) Sample completeness curves linking curves are on the bottom.

Environmental factors and relationship with fish communities

The descriptive statistics of the physico-chemical parameters of water quality and chemical elements analyzed in the superficial sediment are present in tables 3 and 4. According to table 3, the mean values of the water parameters: temperature, electrical conductivity and salinity increase, while tds, pH and DO levels decrease. Regarding the sectors, only pH and electrical conductivity were higher in CAT. Other parameters were appreciably higher in ITA.

Table 3. Water quality parameters. ITA = Itapessoca; CAT = Catuama; Rain = Rainy season; Dry = Dry season; T = temperature (ºC); Cond = Conductivity(μS∕cm); Tds = total dissolved solids (ppm); Salt = Salinity (ppt); OD = dissolved oxygen.

	ITA				CAT				Rain (Mar/Jul)				Dry(Set/Dec)			
	Av	Min	Max	Sd	Av	Min	Max	Sd	Av	Min	Max	Sd	Av	Min	Max	Sd
T	27,7	25,7	30,6	2,3	27,3	25,5	30,	2,0	25,8	25,5	26,2	0,2	29,3	27,4	30,6	1,5
Cond	48,3	30,1	67,8	18,6	51,1	31,4	67,9	13,9	35,4	30,1	43,9	6,1	64,0	60,0	67,9	4,0
Tds	43,6	30,0	58,6	12,9	32,7	21,2	59,0	13,8	44,3	21,2	59,0	18,3	32,0	30,0	34,0	2,0
Salt	38,8	23,3	46,0	8,2	37,0	27,3	46,1	7,6	32,6	23,3	39,2	7,2	43,2	40,2	46,1	2,9
OD(mg/L)	7,0	0,9	31,8	12,2	1,9	0,9	3,7	1,0	7,7	1,9	31,8	11,8	1,9	0,9	1,8	0,3
OD%	38,8	6,4	76,3	29,1	30,2	14,9	63,9	18,4	40,1	6,4	73	24,5	29	14,9	76,3	23,69
pH	7,5	7,1	7,9	0,3	7,7	7,3	7,8	0,2	7,8	7,5	7,9	0,1	7,4	7,1	7,8	0,2

Regarding the multielemental analysis of the surface sediment, the ITA area showed higher averages for all elements except Si, which were higher in CAT. Maximum concentration values of elements associated with fine particles such as Al, Fe, Mn and trace metals Ni, Zn, Pb (Kouassi et al. 2018) were higher in ITA (tab.4). Higher averages of Mg (7.338 ppm), Ca (78.892 ppm) and Sr (749 ppm), probably associated with the transition between oceanic and continental influence of carbonatic system of the region – Gramame formation (Albuquerque et al. 2020 submitted) were found in Itapessoca.

Table 4. Descriptive statistics for the surface samples collected in the ITA and CAT sectors, in ppm. (Min = Minimun; Max = Maximum; Av = Average; Sd = Standard deviation).

	ITA				CAT			
	Av	Min	Max	Sd	Av	Min	Max	Sd
Mn	137	112,8	164,3	18,7	118,9	94	143,5	18,9
Fe	14420	9100	19600	4095,36	11440	7800	16000	3285,2
Ni	11,6	6,1	19,4	5	6,9	3,3	14,1	4,3
Zn	30,8	19,9	46,3	10,9	21,2	11,4	35,6	8,8
Pb	18,7	14	24,1	3,9	16,1	10,7	19,6	3,3
Sr	749,4	474,9	941,5	172	453,7	251,3	578,2	121,7
Ti	3635,5	3014,6	4189,6	486,7	3452	3157	3872,9	298,4
Mg	7338,8	6173,7	8247,2	812,6	6334,8	4867,5	7563,6	1199,1
Al	53239,7	27748,5	78254,4	19774,2	37114,9	16652,4	49810,3	12542,9
Si	229200	196500	264400	28713,7	260920	219400	331500	43715,2
K	10704	9090	12000	1062,5	10082	7710	11560	1443
Ca	78892	61880	90930	11660,3	60760	48960	75300	11391,7

The principal component analysis identified correlation patterns among the variables, whose results can be seen in table 5. PCA extract eleven factors. According to Kaiser's rule (Kaiser, 1960), only 4 factors presented eigenvalues greater than 1 (7.51, 4.55, 2.52 and 1.56, respectively), however, only the first two factors were used for discussion. The first two factors account for 63.5% of the variance. The distribution of factorial loadings can be visualized in figure 7. According to the first component, pH, total dissolved solids and the metalloid Si showed positive correlation (0.4; 0.3 and 0.9, respectively) - these, have negative correlation with the other metals and water quality parameters. The second component expresses negative correlation - almost diametrically opposite of pH (0.8) with temperature (-0.9), and shows negative correlations of elements commonly associated with fine particles (Kouassi et al. 2018) (e.g. Al, Fe, Mn, Ni) with K, Ca and Sr, associated with most of the points collected in Itapessoca area. According to Factor 1, it is also possible to see that the highest factor loading for the metalloid Si (0.93) is associated with the Catuama Sector, being diametrically opposite to the factorial loading for Al (-0.93), for the same factor. Negative correlations between Al and Si were also reported by Delgado et al. (2010).
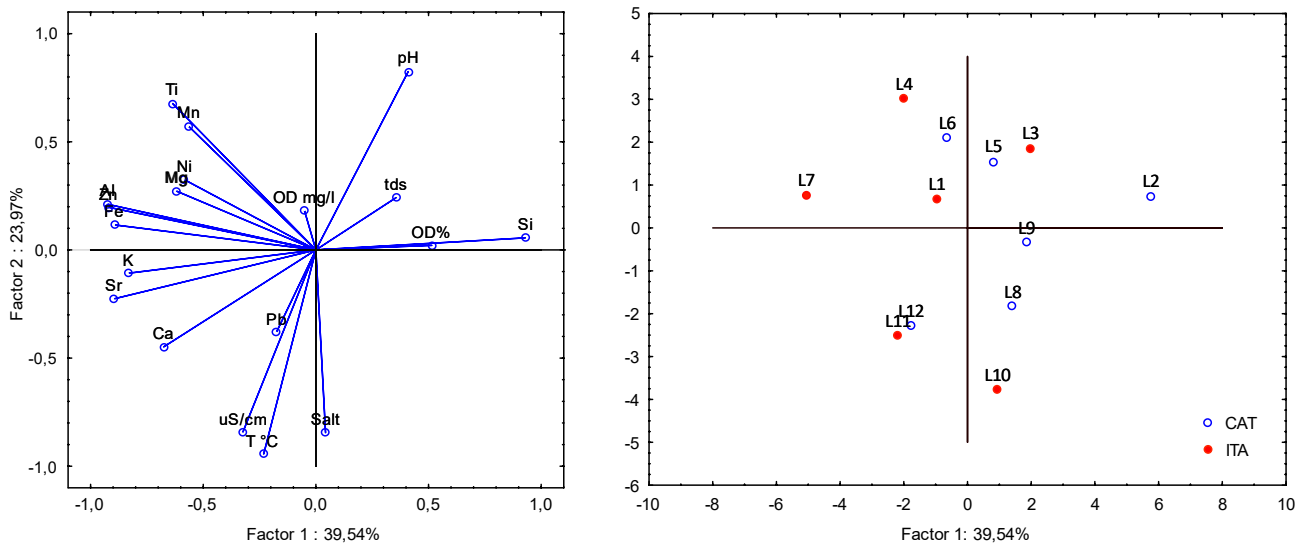
Fig.7. Projection of factor loadings of the variables and experimental units in the flat sector for two components.

Table 5. Principal components analysis results and correlations between factors and variables (loadings), based on correlations for two factors (63.5% of explanation power).

Var.	Factor 1	Factor 2
T °C	-0.23	-0.94
µS/cm	-0.32	-0.84
tds	0.36	0.24
Salt	0.04	-0.84
OD %	0.51	0.02
OD mg/l	-0.05	0.18
pH	0.41	0.82
Mn	-0.56	0.57
Fe	-0.89	0.12
Ni	-0.58	0.33
Zn	-0.92	0.20
Pb	-0.17	-0.38
Sr	-0.90	-0.23
Ti	-0.64	0.68
Mg	-0.62	0.27
Al	-0.93	0.21
Si	0.93	0.06
K	-0.83	-0.11
Ca	-0.67	-0.45
P.Expl.(%)	39.5	24

The NMDS ordination based on the abundance data of the collected species did not show the formation of groups among the areas and the sampled periods (Fig. 8). However, the proximity of some sorted objects suggests greater similarity and correlation related to the collection period.
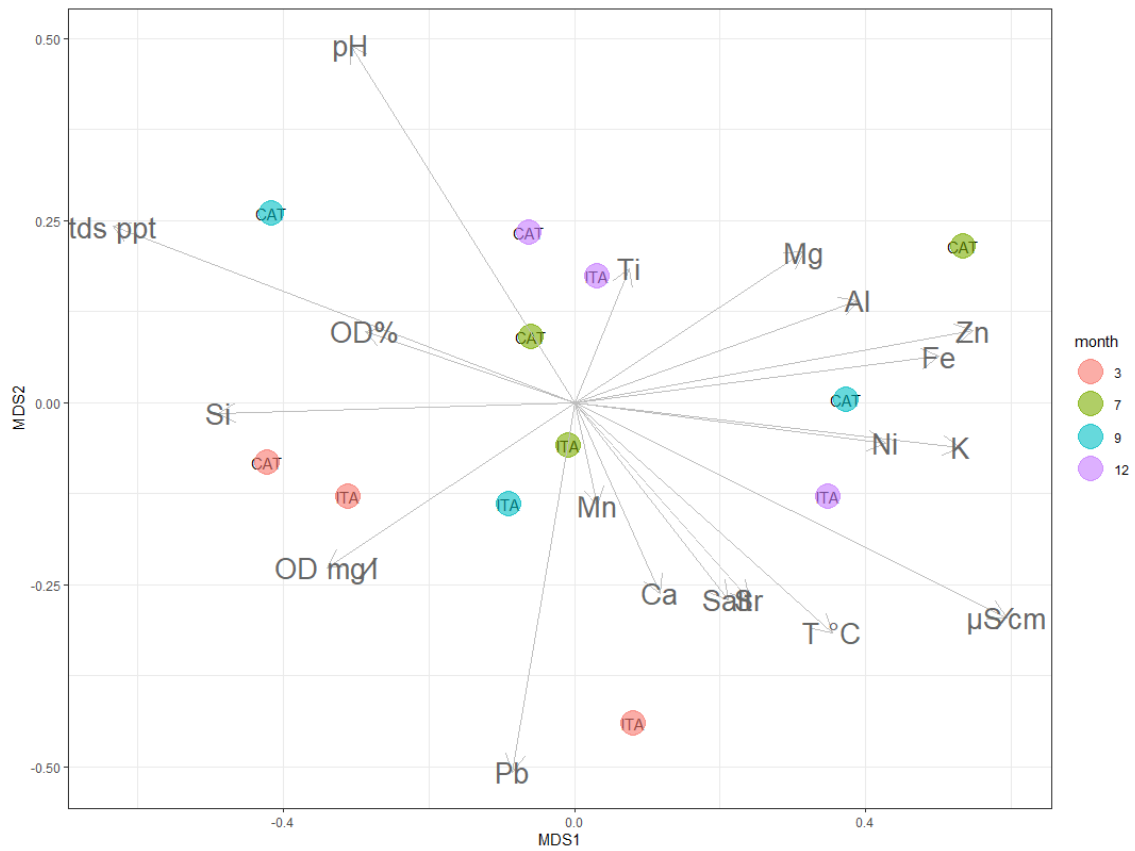

Fig. 8. NMDS based on the transformed fish data collected in the study area (Stress = 0.14). Arrows represent environmental variables. Month (in coloured circles) = 3 (March), 7 (July), 9 (September), 12 (December).

Bioenv results

The analyses performed by the BIOENV routine (Clarke and Ainsworth, 1993) showed that the trends of the fish fauna in each zone were significantly correlated with the best subsets of the abiotic variables obtained four variables: conductivity (µS∕cm), tds (ppt), salinity, Zn, but the extent of these relationships was small, according to Spearman's correlation coefficient ($\rho = 0.39$). The second best combination as a likely determinant of species distribution and composition is added element Sr ($\rho = 0.38$). The other correlations consist of the afore mentioned elements plus Mg, or subtracted from other elements, as can be seen in Table 6.

Table 6. First four results of the BEST-BIOENV test ($\rho = 0.39$; p=0.002) for environmental variables correlated to the distribution of captured ichthyofauna.

Nº.Vars	P	Selections
4	0.3979	Conductivity, tds, salinity, Zn
5	0.38	Conductivity, tds, salinity, Zn, Sr
6	0.35	Conductivity, tds, salinity, Zn, Sr, Mg

Discussion

The species composition in the estuary was similar to that found in other tropical estuaries, according to results of some studies developed in Northeast Brazil (Favero et al. 2019; Ferreira et al. 2019; Paiva et al. 2008; Vasconscelos-Filho and Oliveira, 1999), with the Gerreids being the most abundant family in the the Itapessoca estuarine complex (Northern coast) - a similar result was found by Favero et al. (2019), in the Southern coast of Pernambuco. Haemulidae shower greater biomass.

Differences were identified between the areas in terms of diversity. According to Magurran and McGill (2011) sampling can affect catch composition in terms of diversity, which did not occur due to standardization of fishing/catching effort. Species richness values were slightly higher in Catuama than in Itapessoca although Shannon and Simpson diversity indices denote greater diversity in Itapessoca. Albuquerque et al. (submitted), reported the influence of pollution caused by the cement industry located on the island of Itapessoca on the sediment geochemistry of the region. The greater diversity index in Itapessoca may be a reflection of moderate pollution, which can eliminate dominant

species, contributing to a greater evenness in terms of abundance and biomass, with a temporary increase in diversity through the flux of species more adapted to the environment (Elliot and Quintino 2007). Such situation was also reported by Favero et al. (2019).

The species that presented the highest biomass - *Haemulopsis corvinaeformis* (Haemulidae), *Eucinostomus sp.* (Gerreidae), *Opisthonema oglinum* (Clupeidae) are also commercially important species in Santa Cruz Channel, mostly marine stragglers, as pointed out by Vasconscelos Filho and Oliveira (1999). The species presented the highest biomass in March and July, except for *Eunicostomus sp.* as their catches were higher in September and December (dry period), which may be related to the higher availability of food to the species in the same period. Although many species of commercial importance in the region are young (Vasconscelos Filho and Oliveira, 1999), only one species classified as vunerable (IUCN) - *Lutjanus cyanopterus* (Cuvier, 1828) was captured in the Catuama area, which involves habitat selection, since young specimens commonly inhabit mangrove areas (Allen, 1985).

Estuarine use guilds revealed no differences in assemblage composition between areas. Overall, marine laggard species were dominant in richness, abundance and biomass, different from what was reported by Ferreira et al. (2019) – stenohaline species commonly live associated with coastal marine waters, as highlighted by Elliot et al. (2007).

It was possible to observe the predominance of zoobentivore species over other trophic guilds, which denotes a relationship with the substrate/sediment compartment. The dominance of zoobentivores in Itapessoca Estuarine Complex is linked to the benthic fauna of the region. The fauna associated with marine sediments, in great part, is composed of polychaetae annelids, crustaceans and molluscs (Molina and Vargas 1994). Benthic macrofauna constitutes an important food resource for epibenthic fishes (Herman et al. 1999) and is subject to the influence of abiotic factors such as salinity, temperature and sediment texture (Paiva et al. 2005). Laranjeira et al. (2018) identified relationship of vegetation cover with the presence of benthic macrofauna, in Catuama. Zooplanktivores constituted the second most representative group. According to Melo Júnior (2006), the Santa Cruz Channel is a source of decapoda larvae for coastal areas, which develop in the portion near the Catuama area, which evidently attracts zooplanktivorous predators, including the presence of *Mnemiopsis leidyi* and *Beroe ovata*, voracious predators of eggs and larvae of fish and crustaceans, commonly associated with human impacts (Campelo et al. 2019).

Usually, estuaries have high availability of detritus and organic matter, which contrasts with the absence of detritivorous specimens in this study. However, analyzing the sediment of Catuama, Oliveira et al. (2017), reported low levels of organic matter, suggesting that they may be related to the greater marine and hydrodynamic influence that the region is subjected. Considering the relationship of detritivorous species with the supply of organic matter and detritus (Vasconcelos Filho et al. 2009), it is possible to state that the low organic matter contents in the region do not favor the presence of species of this trophic guild. The substrate poverty in the Itapessoca estuarine complex (Oliveira et al. 2017) does not explain the dominance of zoobentivore species, however, it can be justified by the connectivity between estuarine and coastal environments, reported by Ferreira et al. (2019).

The abiotic factors were important in structuring the fish assemblages in the estuary. The temporal alteration of the chemical factors is evidenced in the changes of seasons, with a sensible decrease in pH, dissolved oxygen levels and increase in temperature in the dry season, with an increase in salinity and electrical conductivity, related to the decrease or absence of precipitation in the dry period. As already pointed out, estuaries exhibit a wide range of human impacts that can compromise their ecological integrity (Kennish et al. 2002). Greig et al. (2010), found that the strongest physicochemical predictors of fish diversity, density and biomass were the concentrations of dissolved metals (Fe, Al, Zn, Mn and Ni), rather than pH, in a New Zealand lake - the low pH and high concentrations of these elements were associated with acid drainage related to coal mining.

Associations between environmental parameters and species abundance are displayed, where four variables - conductivity, tds, salinity and Zn were best correlated with species distribution in the estuary. Similarly, the abiotic variables most contributing to spatial distinction in Minho Estuary (Iberian Peninsula) were water conductivity and the percentage of fine sand (Costa-Dias et al., 2010). The NMDS analysis did not show clear formation and distinction of groups, under reasonable stress values (stress = 0.14), however, it shows an approximation of groups associated to abiotic factors that seem to be controlled by natural processes. The pH, for instance, remained practically neutral in both areas and slightly more acidic in March and July (rainy season), therefore the influence of pH is more associated with seasonality, explained by PCA, and may exert influence on aspects related to habitat selection by species sensitive to pH ranges, which is almost diametrically opposite to electrical conductivity and salinity (both have positive correlation), which was expected, since TDS, salinity and conductivity are closely related (Sousa et al., 2008). Furthermore, the sediment characteristics

are different: Catuama presents more Si and Itapessoca presents higher concentrations of minerals associated with the fine fractions of the sediment, which may justify the higher abundance and biomass of fish caught in Itapessoca. PCA revealed an antagonistic correlation between Si and Al, associated with coarse and fine sediment fraction, respectively, with a higher association of minerals associated with fine particles with the Itapessoca area. More productive areas may be associated with fine sediment and food availability (Pombo et al. 2005). This fact may be related to the greater abundance, diversity, and evenness index in the Itapessoca area. As mentioned, the main abiotic factor responsible for the distribution of the communities was conductivity (which is correlated with salinity), considered one of the most important factors affecting estuarine communities worldwide, according to numerous studies (Costa-Dias et al., 2010). Although the sediment granulometry was not carried out, Zn is a element commonly associated with fine particles, such as Al, Fe, Mn, Ni and Pb (Kouassi et al. 2018) and may reflect the distribution of the epibenthic fauna, as identified by Costa-Dias (2010).

Although there is no evidence that Zn has anthropogenic origin (Albuquerque et al. submitted), it may be associated with the presence and dominance of certain functional groups - zoobentivorous species, considering that the sediment composition influences the community composition (Mannino and Montagna, 1997). Polychaetes, for example, tend to dominate low energy regions, composed of finer sediments, and molluscs occupy intermediate sediments (Dexter, 1983) - both macrobenthic species, the main feeding component of zoobenthic fishes. The decrease in the diversity of macrobenthic species - such as chironomids, for example, could be significantly correlated with heavy metals and other chemical elements present in the sediment (Cao et al. 2016), evidencing the combined impact of nutrients and toxic metals originating from anthropogenic activities.

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CONSIDERAÇÕES FINAIS

Apesar das dificuldades técnicas, este trabalho foi o primeiro a combinar determinação de mercúrio com a geocronologia para avaliação da problemática ambiental do Estado de Pernambuco, Brasil. As taxas de sedimentação estimadas por análises radiométricas confirmaram contaminação por Hg na região de Itamaracá desde meados de 1965. A diminuição da concentração de mercúrio total foi provavelmente causada pela sedimentação de material geológico não enriquecido entre 1967 e 1995 de áreas degradadas pela mineração no município da Ilha de Itapessoca. Fenômenos de precipitação ou a ausência de chuvas estão relacionados ao aumento ou diminuição das concentrações deste metal tóxico. A contaminação provavelmente não está restrita ao Ecossistema Estuarino de Itamaracá, devido à alta reatividade do mercúrio. Nesse sentido, um monitoramento intensivo deve ser realizado nos ecossistemas estuarinos do litoral norte de Pernambuco com o objetivo de esclarecer a influência antropogênica na distribuição de Hg nos sedimentos e definir a extensão real da contaminação por Hg. No capítulo 2, a análise dos sedimentos superficiais e testemunhos possibilitou a percepção da influência de componentes tanto naturais quanto antrópicos no processo de sedimentação. A composição geoquímica dos sedimentos superficiais permitiu a identificação de três fatores relacionados a material terrígeno mais fino, sedimentos mais grosseiros e sedimentos calcários de origem marinha. Apesar de não ter sido realizada a análise granulométrica, as variações nas distribuições dos conjuntos de alguns elementos refletem as diferentes frações granulométricas (ex. Si é o principal constituinte de partículas grossas/quartzo, enquanto Al e Fe compõem o enriquecimento de argilominerais). As análises multi-elementares permitiram a identificação das variações das concentrações dos elementos para os dois testemunhos, sinalizando mudanças geoquímicas na sedimentação dos pontos amostrados no Complexo Estuarino de Itapessoca. A geocronologia identificou maior taxa de sedimentação na Ilha de Itapessoca, caracterizando uma maior influência da indústria cimenteira e mineração de calcário, em operação desde a década de 1950. A análise multi-elementar dos testemunhos corrobora a análise de sedimento superficial – em associação com a datação radiométrica, identificou-se uma mudança na relação e proporção de elementos associados a frações finas e de maior granulação do sedimento, com aumento de elementos associados a frações finas e associados à carbonatos oriundos da mineração. Conforme salientado, as razões entre os elementos químicos reforçam os resultados dos Fatores de Enriquecimento, auxiliando na compreensão de duas questões importantes que envolvem a geoquímica da sedimentação local:

1) Os sedimentos recentes possuem origem majoritariamente no próprio sistema carbonático da região, especialmente da formação Gramame;

2) Há um evidente aumento da proporção de elementos associados aos carbonatos em períodos muito próximos ao início oficial da fase operacional da mineração de calcário e fabricação de cimento.

E a partir das evidências, pode-se concluir que as atividades antrópicas relacionadas às atividades de mineração e fabricação de cimento perturbaram a sedimentação local, inclusive, acarretando o aumento das concentrações do metal tóxico chumbo na região. Considerando o histórico de perturbação antrópica na região e recentes eventos de derramamentos de petróleo no litoral do nordeste, um monitoramento periódico deve ser implementado.

A composição da ictiofauna não mostrou nenhum padrão claro em relação aos impactos potenciais encontrados na área e apenas uma única espécie amostrada foi classificada como vulnerável, de acordo com a IUCN Red List. Quatro variáveis ambientais se mostraram importantes na estruturação das assembleias de peixes no estuário - a condutividade elétrica, total de sólidos dissolvidos, salinidade e o metal zinco se apresentaram como variáveis mais bem correlacionadas com a distribuição das comunidades de peixes no estuário – destas, a maioria é zoobentívora (43.6%) e retardatárias marinhas (44.4%). Das quatro variáveis eleitas, três variáveis são regidas principalmente por eventos naturais sazonais e apenas uma – a concentração de zinco no sedimento está mais relacionada à eventos antrópicos. A condutividade elétrica da água, por exemplo, cuja variação está evidentemente atrelada ao regime de chuvas da região – seu aumento está associado ao aumento da salinidade e relacionada à ausência/diminuição das precipitações no período seco. De acordo com a rotina BIOENV, os parâmetros de qualidade da água - evidentemente controlados por processos naturais, exercem maior influência sobre a distribuição dos peixes do que a composição mineral do sedimento. Complementando, a diferença entre as médias ou valores máximos para cada variável de qualidade de água tende a ser maior entre as estações climáticas do que entre as áreas. Embora a maioria dos parâmetros de qualidade de água e a concentração de elementos químicos do sedimento estejam maiores em Itapessoca, a condutividade elétrica, por exemplo, manteve-se com uma pequena diferença entre as áreas de Itapessoca (48,3 μS∕cm) e Catuama (51,1 μS∕cm), mas quase dobrou, considerando o período de coleta (mar-jul: 35% e set-dez 64%).

Diante do exposto, é possível dizer que o Complexo Estuarino de Itapessoca está impactado por atividades antrópicas, contudo, considerando o aspecto visivelmente íntegro da região, tais impactos não são evidentes, uma vez que o ambiente aparentemente está se recuperando de um longo processo de degradação ambiental ocasionado pela indústria cimenteira e fábricas no entorno, por conta do aumento da vegetação de manguezal. As análises químicas sensíveis revelam que o grau de contaminação de mercúrio excede os limites legais preconizados por órgãos e entidades ambientais. No presente estudo não foi possível alegar impacto ambiental sobre a comunidade de peixes, com base nas variáveis ambientais analisadas, contudo, considerando o impacto na atividade pesqueira e a contaminação a nível tecidual ocasionada pelo mercúrio, é muito provável que os impactos ecológicos sejam muito maiores do que se pode imaginar. Recomenda-se que os níveis de mercúrio e chumbo sejam mensurados em tecidos de peixes e em habitantes de comunidades tradicionais. Estudos paleontológicos associados com a geocronologia devem ser realizados para investigar a mudança da fauna bentônica ao longo do tempo na região.