UNIVERSIDADE FEDERAL DE PERNAMBUCO
CENTRO DE TECNOLOGIA E GEOCIÊNCIAS
DEPARTAMENTO DE OCEANOGRAFIA
PROGRAMA DE PÓS-GRADUAÇÃO EM OCEANOGRAFIA

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ORIGEM E DISTRIBUIÇÃO DE HIDROCARBONETOS NO ESTUÁRIO DE SUAPE - PE

RECIFE
2013

Catalogação na fonte
Bibliotecária Margareth Malta, CRB-4 / 1198

L557o Lemos, Rafael Thompson de Oliveira.
Origem e distribuição de hidrocarbonetos no estuário de Suape - PE / Rafael Thompson de Oliveira Lemos. - Recife: O Autor, 2013.
72 folhas, il., gráfs., tabs.

Orientadora: Profa. Dra. Eliete Zanardi-Lamardo.
Dissertação (Mestrado) – Universidade Federal de Pernambuco. CTG. Programa de Pós-Graduação em Oceanografia, 2013.
Inclui Referências.

1. Oceanografia. 2. Estuário. 3. Petróleo. 4. Contaminação. 5. UV-Fluorescência. 6. GC-MS. I. Zanardi-Lamardo, Eliete. (Orientadora). II. Título.

UFPE

551.46 CDD (22. ed.) BCTG/2013-147

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Dissertação apresentada ao Programa de Pós-Graduação em Oceanografia da Universidade Federal de Pernambuco, como parte dos requisitos para obtenção do título de Mestre em Oceanografia.

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Aprovada em: 25 de Março de 2013.

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A minha mãe Glaucia Sandra de Oliveira Lemos,
pela educação e exemplo de vida.

AGRADECIMENTOS

Agradeço primeiramente a minha família, principalmente minha mãe Glaucia e meu irmão Gabriel pelo apoio durante toda esta jornada de dois anos. Muito obrigado a minha mãe pela compreensão e incentivo no momento em que fiz a escolha de mudar de cidade para fazer este mestrado, e com clareza entendeu que isto seria melhor para a minha vida profissional.

Obrigado a minha namorada, esposa, companheira e amiga Cristiane Bezerra pela companhia durante estes dois anos em Recife. Fico muito feliz por juntos termos aprendido e vivido novas experiências nesta cidade e neste curso.

Agradeço a minha orientadora Eliete Zanardi-Lamardo pelos ensinamentos e motivação dados durante este mestrado. Agradeço a cada um da equipe OrganoMar, Dani Maciel, Dani Miranda, Bruno, Jéssica, Daidson, Nicole, Nykon, Gilvan pela participação direta e/ou indireta na realização deste trabalho bem como pela convivência alegre dentro do laboratório.

Agradeço ao Conselho Nacional de Pesquisa (CNPq) pela concessão da bolsa de pesquisa e pelo financiamento do projeto (Proc n°478589/2010-7) do qual as análises desta dissertação de mestrado fazem parte.

Agradeço a equipe do LabQOM da Usp pela disponibilização do laboratório para a realização das análises de hidrocarbonetos no sedimento contidas nesta dissertação. Muito obrigado ao Sr. Lorival e a Dr. Satie Taniguchi que tiveram bastante paciência para me ensinar todo o procedimento de tratamento e análise das amostras durante o pouco tempo em que passei em São Paulo.

Não posso deixar de agradecer ao professor Roberto Barcellos pela gentileza em disponibilizar seu laboratório e dar suporte com seus conhecimentos para a realização das análises granulométricas desta dissertação. Agradeço também a técnica Luciana pela ajuda durante estas análises.

Agradeço também a todas as pessoas que fizeram ou fazem parte da minha vida e de alguma forma contribuíram para esta minha vitória hoje.

RESUMO

O Estuário de Suape está localizado no litoral sul de Pernambuco, Brasil, cerca de 40 km da capital Recife. Este estuário está presenciando um rápido desenvolvimento industrial e portuário nas últimas décadas, com a implantação do Complexo Industrial Portuário de Suape (CIPS). Várias empresas instaladas na região operam cargas com derivados de petróleo, representando uma potencial fonte de hidrocarbonetos para o estuário. Amostras de água e sedimento foram coletadas com o objetivo principal de avaliar a presença de hidrocarbonetos no Estuário de Suape, identificando suas fontes e concentrações, em duas estações do ano (chuvosa e seca). As concentrações de hidrocarbonetos de petróleo dissolvidos e/ou dispersos na água foram determinadas usando a técnica de UV-Fluorescência. Os resultados variaram entre 0,05 e 4,59 µg L^{-1} equivalentes em óleo Carmópolis e entre 0,01 e 1,39 µg L^{-1} equivalentes em criseno, sugerindo que a região ainda pode ser classificada como não poluída. Algumas concentrações relativamente altas (>1 µg L^{-1}) estão possivelmente associadas a resíduos originados nas atividades portuárias e do estaleiro, bem como a eventuais descargas industriais e lançamentos de resíduos de óleo por embarcações de pesca ou lazer. As concentrações de hidrocarbonetos de petróleo na água foram significativamente menores durante o período chuvoso, provavelmente devido a maior diluição dos contaminantes causada pelo aumento da precipitação e do fluxo de água doce no Rio Massangana. As concentrações de hidrocarbonetos alifáticos (HAs) foram determinadas no sedimento através da técnica de cromatografia em fase gasosa acoplada a um detector de ionização em chama (GC-FID) e os hidrocarbonetos policíclicos aromáticos (HPAs) foram determinados através de cromatografia em fase gasosa acoplada a um detector de espectrometria de massas (GC-MS). Os HAs variaram entre <LD e 27,15 µg g^{-1}, e as concentrações de n-alcanos (C_{12}-C_{35}) variaram entre <LD e 6,84 µg g^{-1}. Os resultados indicaram que o material orgânico proveniente de plantas superiores foi a principal fonte de hidrocarbonetos alifáticos, porém sinais de óleo degradado também foram observados em alguns sedimentos. As concentrações de HPAs variaram entre 4,25 e 888,42 ng g^{-1}, e são relativamente baixas quando comparadas a estuários cronicamente impactados. As maiores concentrações foram encontradas próximas do quebra-mar na saída sul do estuário e estão provavelmente relacionadas ao transporte dos contaminantes levados pelas correntes para esta área de menor hidrodinâmica, que favorece a maior deposição dos mesmos. Além disto, os processos de dragagem não ocorrem neste local

possibilitando um maior acúmulo de contaminantes. Os resultados indicaram que os HPAs encontrados nos sedimentos são provenientes de duas fontes distintas: introdução direta do petróleo e de compostos gerados em processos pirolíticos, através da queima de combustíveis ou matéria orgânica. Concentrações relativamente elevadas foram observadas para alguns HPAs individuais, representando moderada probabilidade em causarem danos à biota local. Este estudo mostra que as atividades desenvolvidas no estuário de Suape associadas à presença de manguezais na região contribuem para a introdução de hidrocarbonetos, mesmo que em baixas concentrações. Entretanto, devido ao crescente desenvolvimento do CIPS, incluindo a refinaria Abreu e Lima que iniciará suas operações em breve, é essencial que um programa de monitoramento contínuo seja implantado.

Palavras-chave: estuário, petróleo, contaminação, UV-Fluorescência, GC-MS.

ABSTRACT

Suape Estuary is located on the southern coast of Pernambuco, Brazil, 40 km away from the capital Recife. This estuary is facing a fast paced industrial and port development in the last decades, with setting of the Suape Industrial Port Complex (SIPC) facilities. Many industrial plants work with petroleum derivatives, representing a potential hydrocarbon source to the estuary. Water and sediment samples were collected in order to assess hydrocarbons in Suape Estuary, identifying sources and concentrations during wet and dry seasons. Concentrations of dissolved and/or dispersed petroleum hydrocarbons (DDPH) in the water were determined by UV-Fluorescence technique. The results ranged between 0.05 and 4.59 µg L^{-1} Carmópolis oil equivalents, and 0.01 and 1.39 µg L^{-1} chrysene equivalents, suggesting that Suape Estuary still can be classified as non-polluted. Relatively high concentrations (>1 µg L^{-1}) are possibly associated to residues produced in the port and shipyard activities, as well as eventual industrial discharges and oil residues from recreational and fishery vessels. DDPH concentrations were significantly lower in the wet season, probably as a consequence of rainfall and Massangana River freshwater flux that dilute pollution. Gas chromatography-flame ionization detection (GC-FID) and gas chromatography-mass spectrometry (GC-MS) were used for analyzing aliphatic (AHs) and polycyclic aromatic hydrocarbons (PAHs) in sediments, respectively. AHs ranged from <DL to 27.15 µg g^{-1}, and n-alkanes (C_{12}-C_{35}) ranged from <DL to 6.84 µg g^{-1}. Terrestrial plants are the main source of AHs to the estuary although evidences of degraded oil were also observed in some sediment samples. PAH concentrations ranged from 4.25 to 888.42 ng g^{-1} and are relatively low when compared to chronically impacted estuaries. The highest PAH concentrations were observed at the southern portion of the estuary and are probably related to the local circulation that deposits contaminants in areas of low hydrodynamics. Lack of dredging processes in the area also contributes to contaminant accumulation. Both petrogenic and pyrolitic sources of PAHs have been identified. A few individual PAHs exhibited high concentrations in sediment, representing moderate probability of causing damages to the local biota. In conclusion, human activities at Suape Estuary in combination with local plant waxes contribute to hydrocarbon inputs and accumulation in sediments. Finally, it is suggested that a long term monitoring program must be implemented at Suape Estuary considering the growing development of the SIPC which includes construction of a large oil refinery.

Keywords: estuary, petroleum, contamination, UV-Fluorescence, GC-MS

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INTRODUÇÃO

Estuários são ambientes de transição entre o continente e o oceano e, devido aos seus processos hidrodinâmicos, favorecem o acúmulo de nutrientes e consequentemente o aumento da produtividade biológica (Miranda, 2002). Estes ambientes possuem grande importância ecológica visto que geralmente são mais produtivos do que os rios e zonas oceânicas adjacentes (Miranda, 2002).

Devido à localização privilegiada, próxima ao oceano, com fácil acesso às vias terrestres e a riqueza em recursos naturais dos estuários, muitos centros urbanos têm se instalado em suas margens (González et al., 2006). Miranda (2002) menciona que aproximadamente 60% das grandes cidades do mundo estão próximas a estuários. Junto com esta grande ocupação também pode crescer a ameaça de contaminação nos estuários, já que em algumas destas cidades existe uma falta de infraestrutura, possuindo instalações sanitárias impróprias e destino inadequado dos resíduos.

Além dos centros urbanos, complexos industriais e portuários também se desenvolvem em torno de estuários devido à facilidade de escoamento dos produtos e a menor exposição à forte hidrodinâmica em mar aberto (González et al., 2006). Estes empreendimentos comumente trazem consigo impactos negativos ao ambiente devido ao lançamento de efluentes não tratados ou tratados de forma ineficiente e ao grande desmatamento realizado na fase de implantação.

O estuário de Suape é um bom exemplo de ambiente sob forte influência humana, pois está localizado na Região Metropolitana do Recife e grande parte de sua área está ocupada pelo Complexo Industrial Portuário de Suape (CIPS). Neste complexo estão instaladas mais de 100 empresas e outras 35 estão em fase de implantação, além do Porto de Suape, considerado o maior porto do nordeste brasileiro (SUAPE, 2011). A área de influência deste porto abrange o estado de Pernambuco e parte dos estados de Alagoas e da Paraíba. Entre os grandes empreendimentos em instalação no CIPS, estão uma refinaria de petróleo e três plantas petroquímicas.

A construção do CIPS causou várias modificações na região estuarina de Suape, tais como desmatamento e aterramentos em áreas de mangue, mudanças na hidrodinâmica com o aumento da influência marinha dentro do estuário, modificação quali e quantitativa nas populações de fito e zooplâncton, dentre outras (CONDEPE, 1983; Neumann-Leitão, 1994;

Silva et al., 2004; Paiva; Araújo, 2010; Bezerra Júnior et al., 2011). Além destes impactos já observados, o CIPS também representa uma grande ameaça de contaminação ao ambiente devido aos possíveis lançamentos de resíduos gerados durante a operação das indústrias e atividades portuárias.

Dentre os diversos tipos de contaminação que podem ser causados pelo CIPS, a contaminação por hidrocarbonetos do petróleo é uma das mais importantes, visto que várias empresas deste complexo operam cargas de derivados de petróleo. Inclusive, onze delas realizam a transformação e comércio de artefatos plásticos, embalagens ou resinas, quatro trabalham com o transporte de gás, e dez operam na distribuição e comércio de combustíveis e derivados (álcool, diesel, lubrificantes e graxas) (SUAPE, 2011). Com a implantação da Refinaria do Nordeste S/A (REFINE, RNEST ou Refinaria General José Ignácio Abreu e Lima), a movimentação de petróleo e derivados tende a aumentar substancialmente nesta área.

O projeto da refinaria conta com uma capacidade de refinamento de 200.000 barris de petróleo por dia, dos quais 100.000 serão de petróleo brasileiro. Estima-se uma produção de 60.000 barris de derivados de petróleo por dia, sendo 5.000 já na primeira etapa. A REFINE visa à produção de gás liquefeito de petróleo (GLP), nafta, gasolina, querosene, óleo diesel e óleo combustível. Gurgel et al. (2009) discutem que as emissões atmosféricas (fuligens possuindo hidrocarbonetos voláteis, compostos orgânicos tóxicos, entre outros poluentes), os lançamentos de efluentes líquidos (águas utilizadas no processamento e esgotos sanitários) e os resíduos sólidos (lamas, cinzas de incineradores e borras de filtração) contendo metais, hidrocarbonetos aromáticos, amônia e ácido sulfídrico podem intensificar os danos ao ambiente e à saúde humana em Suape.

Apesar do risco de poluição causado pelas atividades portuárias e futuramente pela Refinaria Abreu e Lima, estudos sobre a contaminação por hidrocarbonetos nas águas e sedimentos nesta região ainda são escassos. Até o momento apenas os estudos acadêmicos realizados por Chagas (2003) e Araújo-Castro (2008) abordaram esta temática, porém ainda não foram publicados em revistas científicas. Alguns relatórios de consultorias feitos e financiados por empresas privadas atuantes no CIPS, que também analisaram hidrocarbonetos, já se encontram disponíveis para consulta pública (PETROBRAS, 2006; PROMAR, 2010), porém sabe-se da existência de outros que ainda não possuem livre acesso.

Deste modo, este trabalho determinou as concentrações de hidrocarbonetos nas águas e sedimentos do estuário de Suape e identificou as possíveis fontes de introdução dos mesmos. Os resultados gerados podem servir de subsídios para a construção de um futuro plano de medidas mitigadoras ou preventivas, a fim de controlar as vias de entrada e os potenciais danos ao ambiente causados pelos hidrocarbonetos.

FUNDAMENTAÇÃO TEÓRICA

Petróleo e Hidrocarbonetos

O petróleo é a principal fonte de energia usada no mundo e é formado por uma mistura complexa de compostos orgânicos e inorgânicos originados após longos processos diagenéticos na matéria orgânica sedimentar, sendo que alguns destes compostos possuem alta toxicidade a organismos marinhos (Samiullah, 1985; Gluyas; Swarbrick, 2003). Os hidrocarbonetos correspondem a cerca de 95% da constituição do petróleo, e os 5% restantes são formados por nitrogênio, enxofre, oxigênio e alguns metais em concentrações traço como: vanádio, níquel, cromo, ferro, sódio, cálcio**,** cobre (UNEP, 1992; NRC, 2003). Devido a esta predominância na composição, os hidrocarbonetos são frequentemente usados na investigação da contaminação por petróleo.

Existem diversas fontes de entrada de hidrocarbonetos do petróleo no meio marinho, como por exemplo, os acidentes envolvendo plataformas ou petroleiros, resultando em grandes derramamentos de óleo. Embora eventos como estes tenham grande repercussão na mídia e alto impacto visual e biológico, a introdução mais comum e também bastante danosa, acontece pela entrada de pequenas quantidades de óleo de forma contínua ou crônica. Este tipo de introdução ocorre por meio de lançamento de efluentes industriais, esgotos urbanos, drenagem fluvial, queima de combustíveis e derivados, atividades portuárias e problemas envolvidos na produção, beneficiamento e transporte do óleo (Zanardi et al., 1999a; Zanardi et al., 1999b; Celino; Queiroz, 2006; Tokhi et al., 2008).

Embora as atividades humanas sejam uma grande fonte de hidrocarbonetos ao ambiente marinho, o aporte destes compostos também pode ocorrer de forma natural, por meio de atividade magmática, síntese por organismos marinhos e terrestres, combustão espontânea de biomassa, diagênese de precursores naturais e erosão de sedimentos continentais (UNEP, 1992; Volkman et al., 1992). A origem destes hidrocarbonetos, se petrogênica ou biogênica, pode ser determinada a partir da análise individual destes compostos, determinando suas composições e distribuições bem como suas proporções relativas no ambiente (Volkman et al., 1992; Zanardi et al., 1999a; Yunker et al., 2002).

Hidrocarbonetos – Composição química

Os hidrocarbonetos podem ser classificados quanto a sua estrutura química em hidrocarbonetos alifáticos e aromáticos (Bícego et al., 2008). Em geral, dos 95% representados pelos hidrocarbonetos na composição do petróleo, 80% são constituídos por hidrocarbonetos alifáticos, sendo 50% cicloalcanos e 30% alcanos, enquanto que os hidrocarbonetos aromáticos correspondem aos 15% restantes (UNEP, 1992).

Hidrocarbonetos Alifáticos

Os hidrocarbonetos alifáticos podem ser saturados, possuindo apenas ligações simples, ou insaturados, com pelo menos uma dupla ligação entre carbonos. Estes compostos não possuem anéis benzênicos em sua estrutura.

Os hidrocarbonetos saturados podem ser subdivididos em alcanos e cicloalcanos, de acordo com a presença ou não de cadeias cíclicas na molécula. Os alcanos possuem somente ligações saturadas sem a presença de cadeias cíclicas e são compostos bastante estáveis. As cadeias de carbono deste grupo podem ser cadeias normais (n-alcanos ou parafínicos) ou ramificadas (isoprenóides) (Fig. 1) (Gluyas; Swarbrick, 2003; Bícego et al., 2008). Os n-alcanos mais comumente encontrados no ambiente possuem desde cadeias mais curtas, 12 a 20 átomos de carbono (C_{12} – C_{20}), até cadeias maiores (C_{21} – C_{35}) (Volkman et al., 1992; Gluyas; Swarbrick, 2003).

Entre os isoprenóides os compostos de maior abundância são o pristano e o fitano, com 19 e 20 átomos de carbono respectivamente. Dependendo das fontes, a proporção entre estes compostos pode variar bastante (Volkman et al., 1992; Gluyas; Swarbrick, 2003). Os cicloalcanos ou naftenos são caracterizados pela presença de cadeias cíclicas, que são anéis formados somente por ligações simples (Fig. 1) (UNEP, 1992; NRC, 2003). O ciclopentano

(C_5H_{10}) e o ciclohexano (C_6H_{12}) são exemplos de cicloalcanos que ocorrem naturalmente em fase líquida e estão em abundância em óleos crus (Gluyas; Swarbrick, 2003). Naftenos de cadeias maiores podem ter mais de um ciclo e podem estar ligados a cadeias retilíneas com ramificações, como os hopanos e esteranos. Estes tipos de naftenos são utilizados como marcadores do óleo, sendo também utilizados na determinação de sua fonte (Volkman et al., 1992; Gluyas; Swarbrick, 2003; Bícego et al., 2008).

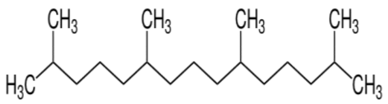
Os alcenos ou olefínicos correspondem aos alifáticos insaturados, contendo uma ligação dupla entre carbonos, e são raramente encontrados naturalmente no petróleo, sendo formados durante o processo de refinamento (UNEP, 1992; NRC, 2003; Lopes et al., 2007). Como exemplo destes compostos, podem ser citados o etileno (C_2H_4) e o propileno (C_3H_6) (Gluyas; Swarbrick, 2003).

Hidrocarbonetos Aromáticos

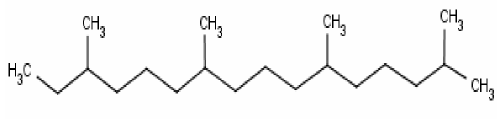
A principal característica deste grupo é a presença de um ou mais anéis benzênicos, que são ciclos formados por ligações simples e duplas intercaladas entre seis átomos de carbono (Fig. 1) (NRC, 2003; Bícego et al., 2008). O benzeno (C_6H_6) é o composto mais simples entre os aromáticos possuindo apenas um anel aromático. Quando possuem dois ou mais anéis benzênicos são chamados de hidrocarbonetos policíclicos aromáticos (HPAs), e são considerados os hidrocarbonetos de maior potencial tóxico para a biota (NRC, 2003).

Propano (n-alcano)

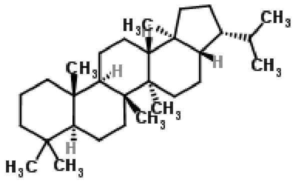
Nonano (n-alcano)



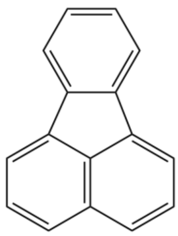
Fitano (isoprenóide)



Pristano (isoprenóide)



Hopano (cicloalcano)



Fluoranteno (aromático)

Figura 1. Exemplos de diferentes tipos de hidrocarbonetos. Fonte:www.chemspider.com

Efeitos sobre o ambiente

A entrada de hidrocarbonetos no ambiente marinho pode resultar em diversos impactos negativos aos organismos (Samiullah, 1985). Os hidrocarbonetos alifáticos, mais abundantes no petróleo, não apresentam alta toxicidade, mas devido a menor solubilidade em água, possuem maior capacidade de adsorção causando recobrimento dos tecidos dos organismos, resultando na morte por asfixia (Samiullah, 1985; NRC, 2003).

Por outro lado, os HPAs mesmo em pequenas concentrações, são elementos potencialmente tóxicos para a biota marinha (NRC, 2003). Após revisar vários artigos científicos, Samiullah (1985) encontrou registros de aumentos nas taxas de mortalidade bem como diminuição no sucesso reprodutivo de algumas populações aquáticas contaminadas por HPAs. Outros estudos, também registraram aumento da mortalidade de larvas de camarões expostos a HPAs, mudanças no equilíbrio celular de moluscos, alterações fisiológicas e celulares em caranguejos e diminuição nas habilidades de forrageio de larvas de peixes que estiveram expostas a estes compostos (Francioni et al., 2007; Carvalho et al., 2008; Bechmann et al., 2010; Dissanayake; Bamber, 2010).

O risco de desenvolvimento de câncer pode aumentar em mamíferos e em populações humanas onde há o consumo de animais com altas concentrações de HPAs (NRC, 2003). Alguns destes compostos, resultantes de processos de combustão, podem ser mais tóxicos do que os encontrados diretamente no petróleo (NRC, 2003). Xia et al. (2013) verificou um aumento no potencial de desenvolvimento de câncer de pulmão em pessoas residentes em centros urbanos, expostas a inalação de HPAs.

Determinação de Fontes de Hidrocarbonetos

Biogênicas ou Petrogênicas

Vários critérios podem ser utilizados para a determinação das fontes de hidrocarbonetos. A própria quantidade destes compostos no local pode dar um indicativo de sua origem, visto que as concentrações de hidrocarbonetos naturalmente introduzidos são baixas quando comparadas com aquelas oriundas de atividades antrópicas (Volkman et al., 1992). Em áreas onde a fonte principal é biogênica as concentrações de hidrocarbonetos alifáticos nos sedimentos podem variar de 5 a 10 µg g^{-1}, enquanto que regiões poluídas por hidrocarbonetos de petróleo podem atingir concentrações maiores que 1000 µg g^{-1} (UNEP, 1992).

Cadeias de n-alcanos com 12 até 35 átomos de carbono são comuns no petróleo, sendo regularmente distribuídas entre cadeias ímpares (contém número ímpar de carbonos) e pares (contém número par de carbonos), sem predominância de uma em relação à outra (UNEP, 1992; Volkman et al., 1992; Bícego et al., 2008). Este padrão de distribuição equilibrada geralmente não ocorre em n-alcanos de origem biogênica, nos quais se verifica uma dominância das cadeias ímpares sobre as pares (UNEP, 1992; Volkman et al., 1992). Deste modo foi desenvolvido um coeficiente chamado Índice Preferencial de Carbono (IPC) que corresponde à razão entre n-alcanos de cadeias ímpares e pares, onde é verificado se há ou não a predominância de um grupo sobre o outro (Bícego et al., 2008). Sedimentos com maior contribuição petrogênica apresentam valores bem próximos de 1, enquanto que sedimentos com predominância de fonte biogênica atingem valores >4 (Gao; Chen, 2008; Maioli et al., 2011) .

Plantas e animais sintetizam cadeias de hidrocarbonetos com diferentes números de carbono. Por exemplo, as plantas terrestres sintetizam em forma de cera hidrocarbonetos geralmente entre C_{23}-C_{33}, já o fitoplâncton sintetiza cadeias <C_{23}, principalmente C_{15}, C_{17} e C_{19} (UNEP, 1992; Gao; Chen, 2008). A partir de razões como C_{31}/C_{19} e das que envolvem n-alcanos de baixo e alto peso molecular (C_{15}-C_{20})/(C_{21}-C_{35}) também é possível estimar a origem do material orgânico, se alóctone (fonte externa) ou autóctone (fonte interna)(Wang et al., 2006; Gao; Chen, 2008).

A razão entre os isoprenóides pristano e fitano (Pri/Fit) também é utilizada na diferenciação das fontes de hidrocarbonetos. Em sedimentos com entrada de hidrocarbonetos de petróleo ambos isoprenóides têm concentrações semelhantes, resultando em valores próximos de 1 para a razão Pri/Fit (Steinhauer; Boehm, 1992; Sharma et al., 2002; Nemirovskaya et al., 2006; Gao; Chen, 2008). Em sedimentos não contaminados as concentrações de fitano são menores que as de pristano, visto que este composto também é originado de lipídios de zooplâncton, levando a valores entre 3 e 5 para a razão Pri/Fit (Steinhauer; Boehm, 1992; Volkman et al., 1992).

Amostras contaminadas por óleo comumente apresentam uma elevação irregular da linha de base nos cromatogramas, sendo esta configuração chamada de Mistura Complexa Não-Resolvida (UCM, em inglês) (Volkman et al., 1992), como pode ser vista na Fig. 2. A explicação mais aceita para a causa da UCM menciona que esta distorção no sinal do equipamento é produto da biodegradação de n-alcanos, que resulta em alcanos ramificados de difícil separação cromatográfica (UNEP, 1992). Essa feição no cromatograma é uma das principais características das amostras contaminadas por petróleo.

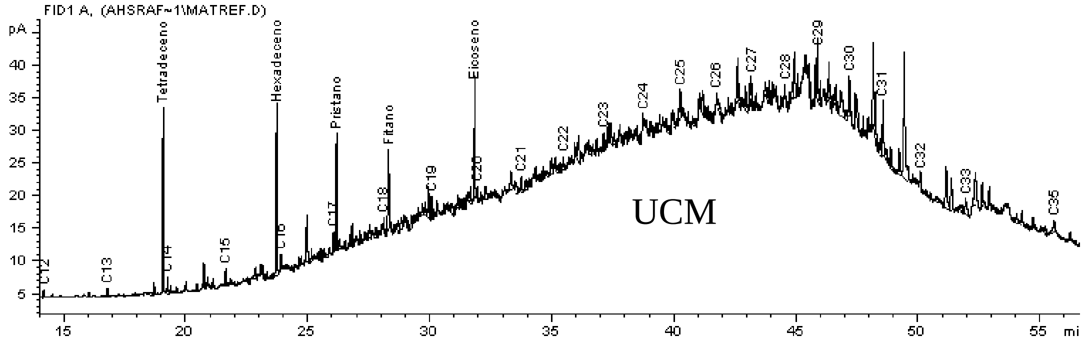


Figura 2. Exemplo de cromatograma de uma amostra contaminada por petróleo, onde está evidenciada a formação da Mistura Complexa Não-Resolvida (UCM)

Petrogênicas ou Pirolílicas

A presença de HPAs no ambiente também é considerada um indicativo de contaminação por óleo, pois embora estes compostos sejam sintetizados por algumas bactérias, plantas e fungos, estas concentrações são, em geral, pequenas quando comparadas com aquelas geradas pela introdução de petróleo no ambiente (Bícego et al., 2008). Depois de identificados no ambiente os hidrocarbonetos aromáticos podem ser atribuídos a fontes pirolíticas (queima) ou petrogênicas (aporte direto de óleo). Esta determinação é feita pela análise das proporções entre alguns HPAs individuais, característicos de cada fonte.

A formação das diferentes espécies de HPAs depende basicamente do calor de formação destes compostos. Deste modo, a determinação da origem dos HPAs tem sido feita a partir da relação entre compostos de mesma massa molecular (isômeros), porém formados em diferentes temperaturas. No caso do petróleo, os HPAs são formados em temperaturas relativamente baixas, originando em maior quantidade compostos mais instáveis. Quando os compostos são formados em temperaturas elevadas, por exemplo, durante processos de combustão, geralmente existe uma proporção maior de compostos mais estáveis.

Considerando-se a proporção entre os isômeros de HPAs de diferentes calores de formação, a origem destes compostos pode ser determinada por meio de várias relações como fenatreno/antraceno e fluoranteno/pireno. Razão fenatreno/antraceno maior que 10 indica origem petrogênica e menor que 10 está associada a fontes pirolíticas (Budzinski et al., 1997). Na razão fluoranteno/pireno, valores maiores que 1 sugerem fontes pirolíticas, enquanto valores menores que 1 indicam fontes petrogênicas (Sicre et al., 1987).

Yunker et al. (2002) utilizaram algumas outras relações para diferenciar fontes pirolíticas e petrogênicas, sendo: antraceno/antraceno + fenantreno (An/178); fluoranteno/fluoranteno + pireno (Fl/Fl+Pi); benzo[a]antraceno/benzo[a]antraceno + criseno (BaA/228); indeno[1,2,3-cd]pireno/indeno[1,2,3-cd]pireno + benzo[g,h,i]perileno (IP/IP+BghiP). Estes mesmos autores mencionam que quando An/178 < 0,10 existe uma maior dominância de fontes petrogênicas, mas para An/178 > 0,10 a dominância maior é de fontes pirolíticas. Para Fl/Fl+Pi as fontes dominantes são petróleo (< 0,40), combustão de petróleo e derivados (0,40-0,50) e combustão de material orgânico vegetal e carvão mineral (> 0,50). BaA/228 < 0,20 sugere aporte direto de petróleo e derivados, 0,20-0,35 indica uma mistura de petróleo com material derivado de processos de combustão e razão > 0,35 aponta uma dominância de fonte pirolítica. Na relação IP/IP+BghiP valores < 0,20 indicam petróleo, 0,20-0,50 sugerem combustão de petróleo ou derivados e valores > 0,50 estão associados a combustão de material vegetal e carvão mineral.

CARACTERIZAÇÃO DA ÁREA DE ESTUDO

Localização e Clima

O Complexo Estuarino-Lagunar de Suape, está localizado a cerca de 40 km da cidade de Recife, litoral sul de Pernambuco, nos municípios de Cabo de Santo Agostinho e Ipojuca, e sua área possui cerca de 135 km², estendendo-se longitudinalmente à linha da costa (Neumann-Leitão, 1994).

Esta região possui clima quente e úmido, pseudotropical do tipo As’ na escala de Köppen, com pluviosidade anual variando de 1.500 a 2.500 mm/ano, e períodos seco de setembro a fevereiro e chuvoso de março a agosto (Silva et al., 2004). Os ventos predominantes são os alísios de sudeste com velocidade média de 2,5 m s^{-1}, constituintes da Massa Equatorial Atlântica e com variação de leste no período chuvoso e de nordeste no período seco (Neumann-Leitão, 1994). A temperatura média anual do ar é de 26° C, com as médias mínimas e máximas anuais aproximadas de 20 ºC e 31 ºC, respectivamente, e umidade relativa em torno de 80% (Neumann-Leitão, 1994).

Hidrografia

Antes da instalação do CIPS o estuário de Suape era caracterizado como sendo um complexo estuarino lagunar, separado do mar por um extenso cordão de recifes de arenito, onde os rios Massangana, Tatuoca, Merepe e Ipojuca desaguavam (Neumann, 1991). Contudo, depois da instalação do porto, apenas os rios Massangana e Tatuoca mantiveram seu curso normal, sendo que os rios Ipojuca e Merepe foram barrados em direção à Baía de Suape pelos aterramentos feitos com a finalidade da construção do porto interno e de um terminal de tancagem (Fig. 3). Atualmente, o rio Tatuoca também está barrado e a entrada de água deste rio no Porto Interno ocorre apenas por três tubulações com pouco mais de 1,5 m de diâmetro cada.

A implantação do porto também acabou reconfigurando a hidrodinâmica e as condições químicas e biológicas do ambiente. O aumento da influência marinha, devido a extinção do aporte de água doce proveniente do Rio Ipojuca, resultou na elevação das concentrações de oxigênio dissolvido e pH dentro do estuário de Suape (Neumann-Leitão, 1994). O maior aporte de água do mar no sistema também causou mudanças na composição das espécies e estrutura trófica da comunidade zooplanctônica do estuário, resultando em uma maior dominância de espécies tipicamente marinhas (Silva et al., 2004).

A construção do molhe em direção ao mar, no sentido perpendicular à linha de costa, também alterou o sentido das correntes costeiras que começaram a erodir a praia e a penetrar com maior força na Baía de Suape (Neumann, 1991). O processo de assoreamento, ocasionado pelo desmatamento nas margens dos rios, e as modificações na dinâmica estuarina, em resposta às construções das instalações portuárias, provocaram a diminuição das profundidades na Baía de Suape (Barros, 2009). Com exceção da região portuária, as profundidades nesta baía e no Rio Massangana não ultrapassam 5 metros, com a presença de muitos bancos arenosos (Barros, 2009).

O regime de marés característico de Suape é semidiurno, com amplitudes de 2,04 m em sizígia e 0,91 em quadratura (PETROBRAS, 2006). As correntes em Suape são geralmente mais velozes na superfície do que no fundo (PETROBRAS, 2006). No Rio Massangana as correntes fluem predominantemente para sudeste durante a vazante e para noroeste na enchente, enquanto que na região portuária as correntes seguem principalmente para sudoeste durante a vazante e para nordeste na enchente (PROMAR, 2010).

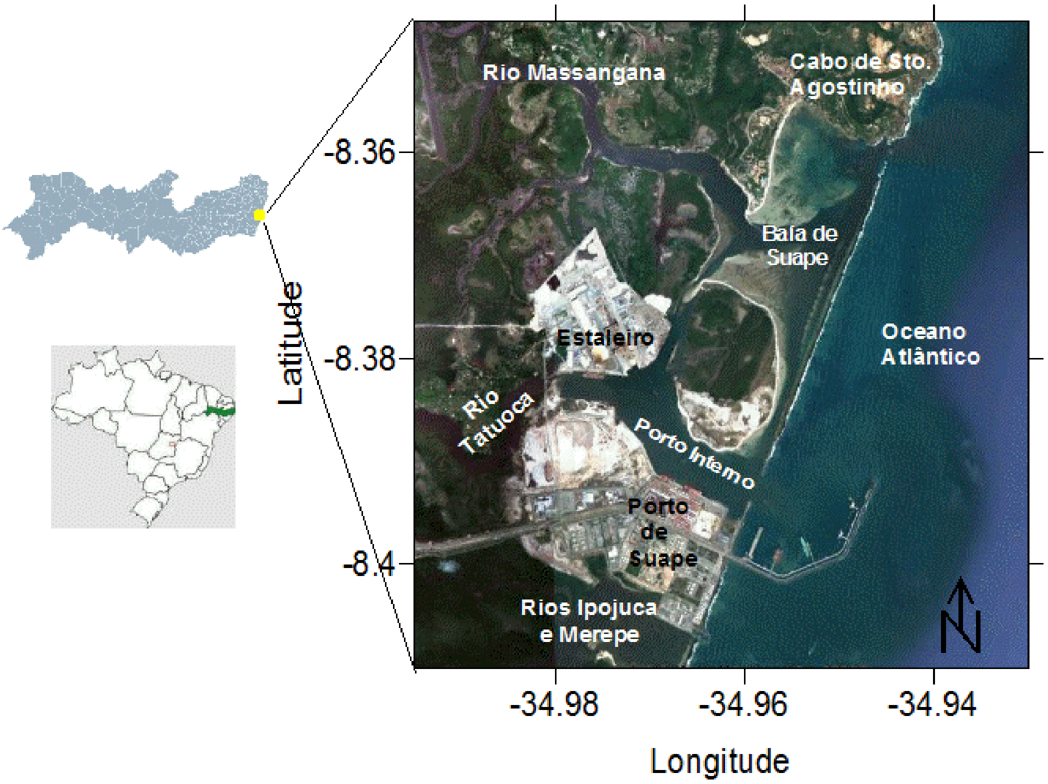


Figura 3: Mapa do Complexo Estuarino-Lagunar de Suape, destacando a presença dos rios Massangana, Tatuoca, Merepe e Ipojuca, bem como o Porto de Suape e o Estaleiro Atlântico Sul.

Sedimento

A região estuarina de Suape, antes da implantação do porto, era constituída por substratos duros naturais, principalmente rochas ou madeiras (mangues) e substratos móveis, representados por areias (variando de finas a grossas), areias lamosas e lamas (CONDEPE, 1983). Entretanto, os processos de dragagem e aterramentos no porto, promoveram uma descaracterização do substrato, dificultando a determinação de um perfil sedimentológico próprio da área (Chagas, 2003). Os sedimentos da baía de Suape e Rio Massangana são formados principalmente de fácies de areia e presença menos representativa de lama, mostrando uma condição de forte hidrodinâmica na área (Barros, 2009). As pequenas quantidades de sedimentos lamosos estão mineralogicamente constituídas de quartzo, calcita, muscovita, ortoclásio, caolinita e esmectita, destacando-se a presença de argilominerais (caolinita e esmectita) que podem indicar locais propícios à concentração de poluentes (Barros, 2009).

OBJETIVO GERAL

Avaliar a contaminação, origem e distribuição de hidrocarbonetos em amostras de água e sedimento do Estuário de Suape.

Metas

- Determinar os níveis de hidrocarbonetos aromáticos totais dissolvidos e/ou dispersos nas águas do Estuário de Suape;
- Analisar as concentrações e composições de hidrocarbonetos alifáticos e aromáticos em amostras de sedimentos no Estuário de Suape;
- Identificar as diferentes origens dos hidrocarbonetos nos sedimentos da região de Suape (biogênico ou antrópico);
- Avaliar o grau de contaminação da região portuária de Suape.

Os resultados deste estudo estão apresentados na forma de dois artigos científicos, escritos no modelo do periódico “Marine Pollution Bulletin”, para o qual os mesmos serão submetidos. No final deste trabalho estão apresentadas algumas conclusões gerais sobre os hidrocarbonetos no Estuário de Suape.

CAPÍTULO I

Petroleum hydrocarbons in water from a Brazilian tropical estuary facing industrial and port development

Rafael Thompson de Oliveira Lemos, Paulo Sérgio Martins de Carvalho and Eliete Zanardi-Lamardo

Abstract

A fast paced industrial and port development is happening at Suape Estuary, Northeast Brazil, but no information about hydrocarbon concentrations in water is available for this area. Based on that, the contamination level of Suape was determined by UV-Fluorescence in terms of dissolved and/or dispersed petroleum hydrocarbons (DDPH), during wet and dry seasons. DDPH concentrations ranged between 0.05 and 4.59 µg L^{-1} Carmópolis oil equivalents, and 0.01 and 1.39 µg L^{-1} chrysene equivalents, indicating that DDPH in the region are still close to baseline levels. Some relatively high concentrations (>1 µg L^{-1}) were possibly associated with port and shipyard operation, occasional industrial discharges and oil derivatives released by fishery and recreational vessels. DDPH concentrations were lower in the wet season in response to increased dilution rates caused by rainfall and Massangana River discharges. Results in this study may be used as baseline for further studies performed in this area.

Keywords: Suape Estuary, water monitoring, DDPH, Carmópolis oil, UV-Fluorescence.

1. Introduction

Suape Estuary is located 40 km southward of Recife, the capital of Pernambuco State, Brazil. One hundred companies comprising diverse activities such as PET production, gas transportation and fuels distribution recently started their operations at the Suape Industrial Port Complex (SIPC) along the estuary margins. SIPC is the major industrial investment in the Brazilian northeast, and additional 35 plants are under construction, including an oil refinery that will start its operations by the end of 2014. SIPC has one of the most modern ports of Brazil, responding for a significant portion of goods imports and exports in northeastern Brazil. Some studies have reported environmental alterations after the SIPC installation, such as: mangrove deforestation (Braga et al., 1989), flooding of mangroves areas (Braga et al., 1989), changes in hydrodynamic patterns (Paiva and Araújo, 2010), structural changes in the zooplankton communities (Silva et al., 2004), and a decrease in biodiversity of ichthyoplankton (Bezerra Júnior et al., 2011).

Besides these impacts, SIPC activities represent a potential source of different kinds of pollutants to the estuary including oil. The most common petroleum sources related to anthropogenic activities are urban runoff, untreated industrial and domestic effluents, burning of petroleum and fossil fuels, harbor activities, oil spills, and problems related to oil production and transport (UNEP, 1992; NRC, 2003).

Monoaromatic and polycyclic aromatic hydrocarbons (PAH) are abundant compounds in petroleum (NRC, 2003), and have been extensively studied as dissolved and/or dispersed petroleum hydrocarbons (DDPH) in areas near ports (Zanardi et al., 1999a; Zanardi et al., 1999b; Bicego et al., 2002), oil spills (Zenetos et al., 2004; Doval et al., 2006; González et al., 2006) and receiving runoff with high load of urban effluents (Wu et al., 2011; Montuori and Triassi, 2012).

The evaluation of aromatic contamination in coastal areas is an important topic, as some PAH molecules are potent carcinogenic agents to both humans and wildlife (Samiullah, 1985; Douben, 2003), while others have been associated to cellular alterations in mussels (Francioni et al., 2007), physiological and cellular modifications in crabs (Dissanayake and Bamber, 2010), mortality of shrimp larvae (Bechmann et al., 2010) and damage on foraging skills of fish species (Carvalho et al., 2008). The approaches to investigate aromatic hydrocarbons in water are in general expensive and require a long time to be performed, but the UV-Fluorescence Method is an efficient, inexpensive and simple tool that gives a fast and general idea about the system integrity pointing out “hot spots” for future investigations (Zanardi et al., 1999b; Doval et al., 2006; Bícego et al., 2009).

Although a fast industrialization process is underway in the vicinity of Suape Estuary, which includes the establishment of an oil refinery, to our knowledge there are no published studies focused on contamination by DDPH in waters from Suape Estuary. The aim of this study is the evaluation of contamination levels by DDPH in Suape Estuary. The experimental design addressed the influence of SIPC industries, river discharges, and other potential sources of oil to the estuarine area of Suape during wet and dry periods of the year, using UV-Fluorescence technique.

2. Study Area

Suape estuary was originally formed by four rivers discharging into Suape Bay: Massangana, Tatuoca, Merepe and Ipojuca (Fig.1). However, after the development of SIPC waters of Merepe and Ipojuca Rivers no longer reach Suape Bay. Currently, Tatuoca River is partially dammed and Suape Bay receives mainly continental waters from Massangana River (Fig. 1). Suape Bay is protected by sandstone reefs with two openings, Northeast and Southeast, through which seawater gets in and out of the estuary (Fig. 1).

Suape estuary is under a regime of hot and humid pseudotropical climate with prevailing southeasterly trade winds, where the wet season lasts from March to August and the dry season from September to February (Silva et al., 2004). The hydrodynamics are characterized by semidiurnal tides with average amplitudes of 2.04 m at spring tide and of 0.91 m at neap tide (PETROBRAS, 2006). Currents inside the bay have higher velocities at surface when compared to the bottom (PETROBRAS, 2006). In Suape Bay currents flow southeast during ebb tides and northwest during flood tides. In inner port, in general currents flow southwest during ebb tides and northeast during flood tides (PROMAR, 2010).

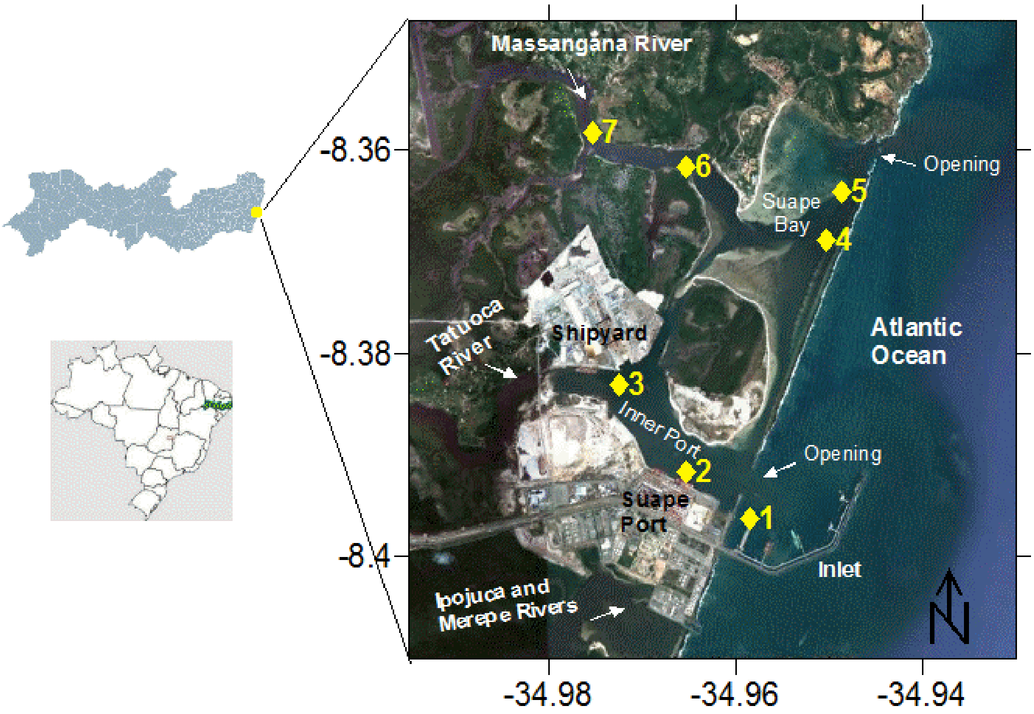


Fig. 1: Sampling stations of sub-surface water in Suape Estuary, during wet and dry season (August 2011 and February 2012, respectively).

3. Material and methods

3.1 Water sampling

Triplicate 1 m deep water samples were collected at 7 sites in Suape Estuary during low tide (Fig. 1). The samples were collected in 8 field campaigns, 4 at the end of the wet season (August/2011) and 4 at the end of the dry season (February and March/2012). Samples were taken with 4 L pre-cleaned amber glass bottles attached to a custom-designed metal frame device. Bottles were released at the bow right before the vessel stopped in order to avoid oil contamination from the engine.

3.2 Analytical procedure

The 4 L water samples were extracted with 20 mL of n-hexane (pesticide grade), added directly to the sampling bottles. Extracts were dried with Na_2SO_4 (previously combusted at 450 °C) and concentrated to 10 mL on a rotary evaporator. DDPH was measured by fluorescence spectroscopy based on the protocol described in IOC (1984) with modifications by Ehrhardt (1983). DDPH fluorescence of extracts was measured using quartz cuvettes in a SpectraMax M3 Molecular Devices Spectrofluorometer, with excitation/emission wavelengths of 310/360 nm.

The concentration of DDPH was calculated based on two analytical curves. One standard curve was based on a dilution series (0 to 2.5 µg L^{-1}) of chrysene (99% purity, Sigma–Aldrich), and a second curve was based on a dilution series (0 to 5.0 µg L^{-1}) of a Brazilian weathered crude oil from Carmópolis oil field.

Chrysene was proposed by IOC (1984) as a standard for DDPH studies, allowing worldwide comparison of results and it has been used by several authors (Atwood et al., 1987; Corbin, 1993; Kornilios et al., 1998; Nayar et al., 2004; Doval et al., 2006). Carmópolis oil was chosen because it comes from one of the largest reserves in the northeastern Brazilian coast, and it has already been used as a standard in Brazilian coastal and open water studies (Zanardi et al., 1999a; Zanardi et al., 1999b; Bicego et al., 2002; Bícego et al., 2009).

The average of blank fluorescence from each campaign was subtracted from the samples. The detection limit (DL) was calculated as three times the standard deviation of all blanks. The DLs expressed in chrysene and Carmópolis oil equivalents were 0.01 µg L^{-1} and 0.04 µg L^{-1}, respectively.

3.3 Statistical analyses

DDPH concentrations expressed as Carmópolis oil equivalents were tested using the software SIGMAPLOT for windows version 11(2008), 2008.

Two nonparametric tests with a significance level of 0.05 were used. Differences between DDPH concentrations among the 7 sites in each season were analyzed by Kruskall-Wallis test. Mann-Whitney U test was used to evaluate differences between seasons.

4. Results and discussion

DDPH concentrations of the individual samples in Suape Estuary, including all field campaigns, ranged from 0.05 to 4.59 µg L^{-1} Carmópolis eq. (Table 1) and 0.01 to 1.39 µg L^{-1} chrysene eq. (Table 2). None of the samples was below DL. The results showed that DDPH concentrations expressed as chrysene equivalents are approximately 30% of those expressed as Carmópolis equivalents.

Considering that Carmópolis oil could be more representative of a petroleum input in the environment, all statistical treatment is based on results expressed as Carmópolis equivalents. During wet season DDPH concentrations expressed as Carmópolis equivalents ranged from a lower median concentration of 0.15 µg L^{-1} at station #4 to a higher median of 0.46 µg L^{-1} at station #2. DDPH concentrations were statistically different between stations #2 and #4 only (Kruskall Wallis test, $H_6 = 14.9$, $p = 0.02$ followed by Dunn's method, $p < 0.05$) (Table 1). In dry season DDPH concentrations ranged from a lower median concentration of 0.18 µg L^{-1} Carmópolis eq. at station #4 to a higher median of 0.41 µg L^{-1} Carmópolis eq. at station #6, but no statistically significant difference was detected among stations (Kruskall Wallis test, $H_6 = 7.6$, $p = 0.27$) (Table 1).

Median DDPH concentrations were higher in dry season than in wet season. Median contamination in the wet season was 0.19 µg L^{-1} Carmópolis eq., while median DDPH in the dry season was 0.26 µg L^{-1}. A statistically significant difference was detected between seasons (Mann-Whitney, U test= 2105, $p = 0.02$) (Table 1).

Analyses of median DDPH concentrations in spring and neap tide showed no statistically significant difference as well (Mann-Whitney, U test= 3150, $p = 0.42$). Median contamination in spring tide was 0.21 µg L^{-1} Carmópolis eq., while in neap tide median DDPH was 0.24 µg L^{-1} Carmópolis eq.

Table 1

Dissolved and/or dispersed petroleum hydrocarbons (DDPH) concentrations in Suape Estuary expressed on µg L^{-1} of Carmópolis oil equivalents in triplicate samples from 7 sites, collected during 4 field campaigns in the wet season (August/2011) and 4 field campaigns in the dry season (February and March /2012).

	Wet Season													Dry Season												
St.	Cruise I			Cruise II			Cruise III			Cruise IV			Median Wet Season	Cruise V			Cruise VI			Cruise VII			Cruise VIII			Median Dry Season
	(07/18/2011)			(07/28/2011)			(08/02/2011)			(08/15/2011)				(02/10/2012)			(02/14/2012)			(02/27/2012)			(03/13/2012)			
#1	0.18	0.12	0.17		0.18	0.18	0.20	0.17	0.21	0.41	0.28	0.22	0.18	0.24	0.20	0.21	0.12	0.10	0.12	0.51		0.40	0.14		0.26	0.20
#2	0.19	0.16		0.60	0.47	0.67		0.29	0.20	0.45	0.48	0.80	0.46^a	0.61	0.80	0.51	0.12	0.12	0.12		0.20	0.26	0.53	0.43		0.35
#3	0.12	0.09	0.07	0.14	0.14		0.21	0.24	0.19	**2.07**	**1.78**	**2.56**	0.19	0.23	0.25	0.24	0.20	0.24	0.26	0.65	0.56		0.16	0.14		0.24
#4	0.15	0.12	0.12	0.11		0.10	0.18	0.36	0.23	0.19	0.12	0.16	0.15^b	0.23	0.15	0.23	0.06	0.10	0.05	**4.01**	**4.29**		0.21		0.15	0.18
#5	0.19	0.10	0.09	0.21		0.16		0.42	0.59	0.15	0.12	0.11	0.16	0.28	0.33	0.24	0.11		0.13	**1.39**	0.92		0.29	0.29	0.34	0.29
#6	0.19		0.19	0.23	0.19	0.17	0.67	0.34	0.34	0.20	0.15	0.21	0.20	0.52	0.44	0.41	0.08	0.14	0.12	**4.13**	**1.99**	**4.59**		0.33	0.36	0.41
#7		0.11	0.15	0.34	0.22	0.42	0.30	0.36	0.23	0.21	0.18	0.17	0.22	0.63	0.49	0.36	0.20	0.17	0.14	**2.71**	**1.54**		0.32	0.21	0.52	0.36
										Overall median			0.19^b													0.26^a

a and b: statistically significant differences detected ($p < 0.05$).
Bold values = higher than baseline (1 µg L^{-1})

Table 2

Dissolved and/or dispersed petroleum hydrocarbons (DDPH) concentrations in Suape Estuary expressed on µg L^{-1} of chrysene equivalents in triplicate samples from 7 sites, collected during 4 field campaigns in the wet season (August/2011) and 4 field campaigns in the dry season (February and March/2012).

	Wet Season													Dry Season												
St.	Cruise I (07/18/2011)			Cruise II (07/28/2011)			Cruise III (08/02/2011)			Cruise IV (08/15/2011)			Median Wet Season	Cruise V (02/10/2012)			Cruise VI (02/14/2012)			Cruise VII (02/27/2012)			Cruise VIII (03/13/2012)			Median Dry Season
#1	0.05	0.03	0.05		0.05	0.05	0.06	0.05	0.06	0.12	0.08	0.06	0.05	0.07	0.06	0.06	0.03	0.03	0.03	0.15		0.12	0.04		0.07	0.06
#2	0.05	0.04		0.18	0.14	0.20		0.08	0.06	0.13	0.14	0.24	0.14	0.18	0.24	0.15	0.03	0.03	0.03		0.06	0.08	0.16	0.13		0.10
#3	0.03	0.02	0.02	0.04	0.04		0.06	0.07	0.05	0.63	0.54	0.77	0.05	0.06	0.07	0.07	0.06	0.07	0.08	0.19	0.17		0.04	0.04		0.07
#4	0.04	0.03	0.03	0,03		0.02	0.05	0.11	0.07	0.05	0.03	0.04	0.04	0.07	0.04	0.07	0.01	0.03	0.01	**1.21**	**1.30**		0.06		0.04	0.05
#5	0.05	0.02	0.02	0.06		0.05		0.12	0.17	0.04	0.03	0.03	0.04	0.08	0.10	0.07	0.03		0.04	0.42	0.28		0.09	0.09	0.10	0.09
#6	0.05		0.05	0.07	0.05	0.05	0.20	0.10	0.10	0.05	0.04	0.06	0.05	0.15	0.13	0.12	0.02	0.04	0.03	**1.25**	0.60	**1.39**		0.10	0.11	0.12
#7		0.03	0.04	0.10	0.06	0.12	0.09	0.10	0.07	0.06	0.05	0.05	0.06	0.19	0.14	0.11	0.06	0.05	0.04	0.82	0.46		0.09	0.06	0.15	0.11
									Overall median				0.05													0.07

Bold values = higher than baseline (1 µg L^{-1})

The relative standard deviation (RSD) of the triplicate samples collected at each site ranged from 1% to 46%. A total of 59% of the samples exhibited RSD below 20%, indicating low variability among replicate samples. These results are comparable to those reported by other authors (Knap et al., 1986; Zanardi et al., 1999a; Bicego et al., 2002).

Differences observed at stations #2 and #4 during wet season are probably related to the different sources of hydrocarbons in each area. At St. #2, located in the Inner Port (Fig. 1), the higher contamination (0.46 µg L^{-1} Carmópolis eq.) is probably related to intense traffic of ships. The pattern of currents in the estuary might also contribute to the highest concentrations in this area, since the samples were taken during ebb tides, when currents are at minimum velocities in the inner port (PROMAR, 2010). St. #4 is on the northern portion of the estuary far from direct hydrocarbons input originated by port activities. Additionally, concentrations at St. #4 are more diluted by Massangana River freshwater during wet season, reflecting the lower median DDPH in this station (0.15 µg L^{-1} Carmópolis eq.) when compared to those in the Inner Port.

In wet season the water samples had smaller DDPH dispersion in relation to the median (Fig. 2). Exception was observed at St. #3, close to a shipyard, where considerable amounts of petroleum products are used routinely. The highest concentrations found in this area during cruise IV (1.78 – 2.56 µg L^{-1} Carmópolis eq.) (Table 1) could be due to an accidental input from shipyard.

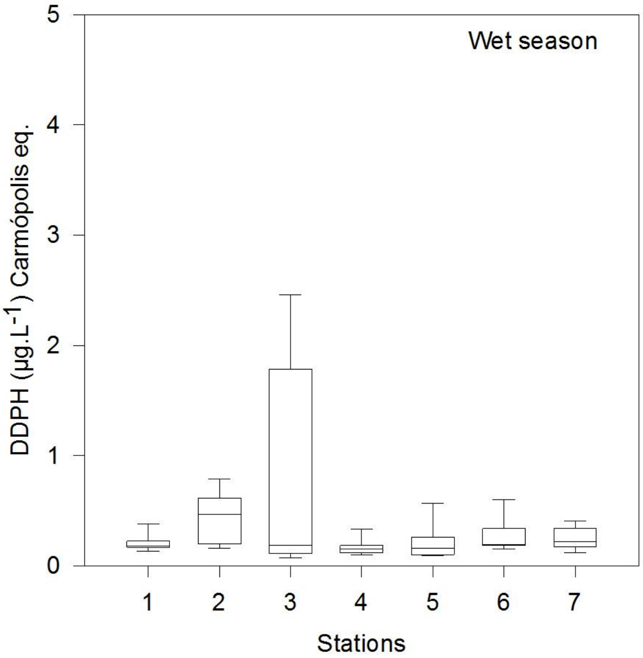


Fig. 2: Dissolved and/or dispersed petroleum hydrocarbons (DDPH) concentrations in water samples from Suape Estuary expressed as Carmópolis oil equivalents collected from 7 stations during wet season (August 2011).

During dry season DDPH in stations #1, #2 and #3 also had low dispersion around the median, but larger variability was observed at stations #4, #5, #6 and #7 (Fig. 3). This high dispersion is related to the highest concentrations detected during cruise VII (sampled at 02/27/2012) in stations influenced by Massangana River discharges. These concentrations may be associated to eventual releases of oil residues by fishery or recreational vessels, regularly observed in this area. Additionally previous studies report the releasing of industrial effluents in this area and mentions that the influence of sewage discharges is low (PETROBRAS, 2006; PROMAR, 2010). The concentrations decreased again to low levels in the following cruise (03/13/2012), showing the importance of the tidal action and the environment hydrodynamics in contaminants dispersion.

Seasonal variations in rivers and estuaries are caused by increased freshwater flow during wet season that dilutes pollution (Montuori and Triassi, 2012). Therefore, rainfall and consequent increase in Massangana River flow rates during wet season promoted the hydrocarbons dilution in Suape Estuary decreasing DDPH contamination.

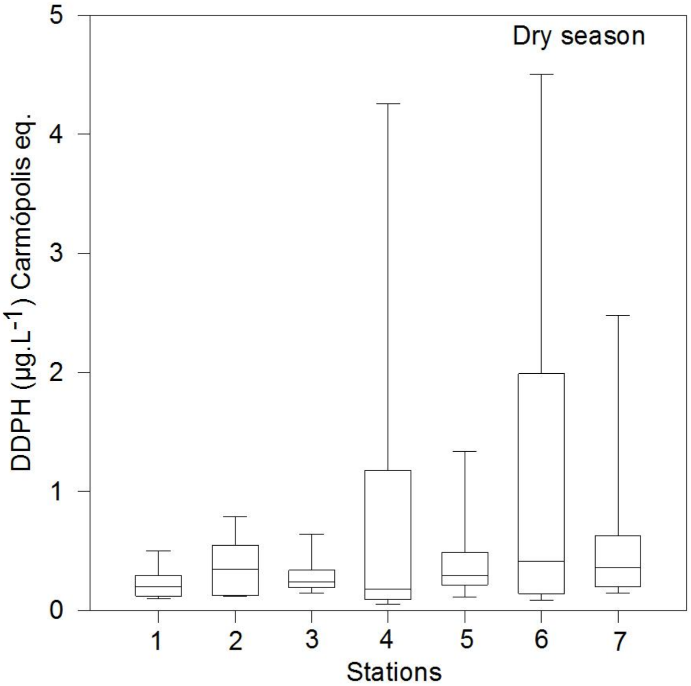


Fig. 3: Dissolved and/or dispersed petroleum hydrocarbons (DDPH) concentrations in water samples from Suape Estuary expressed as oil Carmópolis equivalents collected from 7 stations during dry season (February and March 2012).

Environmental screening using UV-Fluorescence and reporting DDPH results as oil and/or chrysene equivalents have been performed worldwide (Table 3). Bícego et al. (2002) suggested a concentration of 0.31 µg L^{-1} Carmópolis oil eq., as a baseline for non polluted open waters in the South Atlantic Ocean. Even though Suape Estuary is an inshore site, 67% of the detected concentrations were below this value. Concentrations above 1 µg L^{-1} oil eq. are typical of polluted open waters, but DDPH around 5 µg L^{-1} oil eq. are common for non polluted inshore waters (Law, 1981; Zanardi et al., 1999b; Doval et al., 2006; Bícego et al., 2009). In the present study, only 7% of the samples were higher than 1 µg L^{-1} oil eq., and none of them exceeded 5µg L^{-1}, indicating that Suape Estuary can still be considered a non-contaminated area.

Even the highest DDPH in Suape are very low when compared to areas highly contaminated by oil, chronically impacted or after an oil spill event, where concentrations can be over 28 µg L^{-1} oil eq. and 10 µg L^{-1} chrysene eq. (Law, 1981; Salihoglu et al., 1987; Chouksey et al., 2004; González et al., 2006), and sometimes exceeding 100 µg L^{-1} chrysene eq. (Nayar et al., 2004). Concentrations above 200 µg L^{-}

^{1} chrysene eq. were detected in samples from an estuary in Singapore where shipping, petrochemical plant discharges, and oil spillages are frequent (Nayar et al., 2004). DDPH around 25 µg L^{-1} chrysene eq. were observed after a pipeline rupture in the Gulf of Iskenderun, Turkey (Salihoglu et al., 1987). Zanardi et al. (1999b) reported concentrations of 34.2 and 49.6 µg L^{-1} Carmópolis eq. after an oil spill in São Sebastião Channel, Brazil. All these reported values exceed those observed at Suape Estuary.

Even though each oil type has its own fluorescence, this methodology has been used as a rapid screening and allows data comparison for coastal and inshore areas of the world undergoing similar human pressure. Through the DDPH fluorescence detection the authors have proposed different contamination levels to the environment. DDPH concentrations lower than 1 µg L^{-1} (chrysene and oil eq.) have been considered as baseline for marine waters (De Domenico et al., 1994; Persad and Rajkumar, 1995; Wattayakorn et al., 1998; Zanardi et al., 1999a; Bicego et al., 2002). Areas where DDPH are usually between 1-10 µg L^{-1} (chrysene and oil eq.) are associated to a chronic contamination (Atwood et al., 1987; Wattayakorn et al., 1998). Regions under great urban pressure or located next to oil spillage accidents, usually exhibit high contamination of DDPH between 10-40 µg L^{-1} (chrysene eq.) or >10 µg L^{-1} (oil eq.) (Salihoglu et al., 1987; Wattayakorn et al., 1998; Zanardi et al., 1999b; González et al., 2006). Environments with concentrations over 40 µg L^{-1} chrysene eq. suggest an acute contamination with a higher probability of causing biological effects (Wattayakorn et al., 1998; Nayar et al., 2004).

Table 3

Dissolved and/or dispersed petroleum hydrocarbons (DDPH) concentrations using UV-Fluorescence expressed as chrysene and oil equivalents in different areas of the world.

Authors	Area	Environment	Chrysene (µg L^{-1}) range	Oil (µg L^{-1}) range
Atwood et al. (1987)	Gulf of Mexico	Inshore	1 - 10	
Salihoglu et al. (1987)	Gulf of Iskenderun	Inshore	Av. 25	
Corbin et al. (1993)	Caribbean coast	Open water	1.3 - 2.7	
Persad and Rajkumar,(1995)	Caribbean sea	Open water	0.11 - 0.78	
Kornilios et al. (1998)	Mediterranean sea	Inshore	0.09 - 0.32	
Wattayakorn et al. (1998)	Gulf of Thailand	Inshore	0.01 - 76.2	
Nayar et al. (2004)	Ponggol Estuary, Singapore	Estuary	4.42 - 248.94	
Zenetos et al. (2004)	Gulf of Southern Evoikos, Greece	Inshore	0.10 - 1.41	
Domenico et al. (1994)	Harbor area in Sicily coast	Inshore	0.06 - 0.37	1.36 - 5.97
Doval et al. (2006)	Rias Baixas embayments, Spain	Estuary	Av. 1.3	Av. 6.30
Gonzales et al. (2006)	Galicia coast, Spain	Inshore	0.09 - 4.84	0.19 – 28
Law et al. (1981)	UK Marine Waters	Inshore/ off shore		1.1-74
Zanardi et al. (1999a)	São Sebastião Channel	Inshore		0.36 - 2.50
Zanardi et al. (1999b)	São Sebastião Channel	Inshore		0.15 - 49.60
Bícego et al. (2002)	South Atlantic ocean	Open water		0.07 - 0.75
Chouksey et al. (2004)	Bassein–Mumbai, India	Open sea		1.7 - 3.70
Chouksey et al. (2004)	Bassein–Mumbai, India	Estuary		3.3 - 21.30
Present study	Suape Estuary	Estuary	0.01 – 1.39	0.05 - 4.59

Av.= only average concentration was reported by the authors

Considering the concentrations and conclusions reported worldwide by different authors, this paper summarized the classification levels of contamination in Table 4. More than 90% of DDPH concentrations observed in Suape Estuary are in the baseline category for both oil eq. and chrysene eq. Some unusual high concentrations (>1 µg L^{-1}) suggest eventual inputs associated to anthropogenic sources such as port and shipyard operation, eventual industrial discharges and some fuels or oil derivatives released from fishery and recreational vessels at Massangana River. In addition, it is also important to consider potential atmospheric sources such as soot from industries of the SIPC and the sugar cane burning, which have been reported as a potential PAH source to environments in the vicinity of sugarcane crops (Maioli et al., 2011). Even though Suape estuary is not highly contaminated by hydrocarbons, evidences of oil and derivatives input show the importance of a continuous monitoring in order to avoid future chronic inputs or higher contamination levels.

Table 4: Summary of dissolved and/or dispersed petroleum hydrocarbon (DDPH) contamination levels (chrysene or oil equivalents) according to several studies all over the world.

Contamination Level	Chrysene eq. (μg L^{-1})	Oil eq. (μg L^{-1})
Baseline	0-1	0-1
Chronic	1-10	1-10
High	10-40	>10
Acute	>40	

5. Conclusions

Results in this study indicate that Suape Estuary is still not highly contaminated by hydrocarbons. High hydrocarbon concentrations in the estuary were probably a consequence of port and shipyard operation. Additionally, industrial discharges and eventual fuels or oil derivatives released by fishery and recreational vessels at Massangana River may occur. Seasonal differences in DDPH were observed, suggesting that rainfall and Massangana river flow might increase the hydrocarbons dilution during wet season. These results provide an important baseline for DDPH contamination levels at Suape Estuary, and a continuous monitoring may provide information about potential increases in hydrocarbon contamination with further industrial development.

Acknowledgements

The authors gratefully acknowledge support of this research by Conselho Nacional de Pesquisa (CNPq, Proc n°478589/2010-7). The authors thank the OrganoMAR group and Transpetro Company staff for assistance with sample acquisition and associated measurements. Lemos thanks CNPq for the Brazilian Graduate Research Fellowship.

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CAPÍTULO II

Contamination and source evaluation of aliphatic and aromatic hydrocarbons in Suape Estuary, Pernambuco, Brazil

Abstract

Suape Estuary, located on the northeastern Brazilian coast, is facing a fast development due to setting up of the Suape Industrial Port Complex (SIPC). Several plants at the SIPC operate petroleum derivatives and an oil refinery will soon start its operations. Such activities represent a significant risk of hydrocarbon contamination to the estuary, but no information about these compounds has been published yet. In order to investigate hydrocarbons distribution and sources, sediment samples from Suape Estuary were collected in two different periods of the year and aliphatic (AH) and polycyclic aromatic (PAH) hydrocarbons were determined. AH concentrations ranged from <LD to 27.15 µg g^{-1}, indicating land plants contribution with signs of degraded oil at some sites. PAHs ranged from 4.25 to 888.42 ng g^{-1}, and these results suggest a low contamination level at Suape Estuary. Exception was observed at the South entrance of the Bay, presenting moderate contamination, probably due to local currents circulation and lower hydrodynamics that accumulate contaminants in this area. The sources of PAHs were both petrogenic and pyrolytic. The petrogenic was probably a result of shipping activities, transport of fossil fuels, shipyard activities and industrial discharges. The pyrolytic source was possibly associated to product of industrial soot, fossil fuel combustion and burning sugar cane plantations surrounding Suape area. Although relatively high PAH concentrations were eventually observed at some sites, such compounds are lower than those believed to cause damages to the biota.

Keywords: petroleum contamination, Suape Port.

1. Introduction

Hydrocarbons (HC) are organic compounds consisting of hydrogen and carbon. They occur naturally in marine environment and can be originated from biosynthesis, biomass burning, continental erosion, oil seeps and diagenetic processes (UNEP, 1992). However, high HC concentrations are frequently attributed to anthropogenic sources such as industrial and urban effluents, atmospheric deposition, shipping activities, oil spills and oil production and transportation (UNEP, 1992; NRC, 2003).

HCs may be separated into two groups: aliphatic and aromatic hydrocarbons. Among the latter, polycyclic aromatic hydrocarbons (PAH) are considered the most toxic, and have been associated to ecological and physiological impacts in marine organisms (Samiullah, 1985; Francioni et al., 2007; Carvalho et al., 2008; Bechmann et al., 2010; Dissanayake and Bamber, 2010) and potentially may cause carcinogenic effects in mammals including the man (Samiullah, 1985; Douben, 2003; Xia et al., 2013). The aliphatic hydrocarbons (AH) are predominant in petroleum composition (~80%) and are less toxic than PAHs. The AHs are used to determine origin of HCs because the distribution of individual AHs is different in biogenic and anthropogenic sources (Volkman et al., 1992; Gao and Chen, 2008). The identification of anthropogenic HCs sources helps the development of management plans in order to prevent future environmental contamination.

Estuaries are one of the most productive environments of the world due to its chemical and dynamic processes that promote high nutrients concentration and consequently high primary production (Hobbie, 2000). However, estuarine and coastal environments surrounded by harbor and urban areas have been under high human pressure and are frequently reported as contaminated by hydrocarbons (Chen and Chen, 2011; Tam et al., 2011; Wagener et al., 2012). In the Brazilian northeastern coast, Suape Estuary can be appointed as a good example of environment influenced by human activities (Koening et al., 2003; Silva et al., 2004; Paiva and Araújo, 2010). This estuary is 40 km south of Recife and has been altered by the construction and development of the Suape Industrial Port Complex (SIPC). Currently SIPC represents the most important industrial and port complex in the Brazilian northeast, with a large port and more than one hundred companies operating (SUAPE, 2011). The risk of HCs contamination in this estuary tends to increase with the SIPC development due to intensification of ship traffic, fuel transportation, plants operation and shipyard activities. In addition, a petroleum refinery will start its operation in the area, at the end of 2014, representing a potential HCs source to the estuary.

Besides the importance of studies about HCs contamination, to our knowledge, there are no published data about HCs in this estuary. Even though the SIPC activities are recent compared to others contaminated industrial and port complex, it is of great importance to determine HC concentrations at present as well as investigate its sources in order to avoid future pollution. Based on that, this study focused on HC analyses in sediment samples from Suape Estuary in order to evaluate the contamination levels and sources of AHs and PAHs in the estuary.

2. Study area

Suape Estuary is formed by the encounter of the waters from Atlantic Ocean and the Massangana and Tatuoca Rivers discharges. Nowadays, the Tatuoca River flow is partially dammed and Massangana is the main freshwater source to the estuary. Studies at Massangana River indicated that the industrial effluents discharged into the river have already decreased its water quality (PETROBRAS, 2006; PROMAR, 2010). At the Inner Port, which is naturally protected by a sandstone reef barrier, are located the Suape Port and the Atlântico Sul shipyard (Fig. 1), and the associated intense navigation and shipping operations in these areas, represent important potential sources of hydrocarbons. Sediments distribution depends on river discharges and dredging operations along the navigation channel.

Currents in Suape Estuary are stronger at surface than at bottom (PETROBRAS, 2006), and more intense in Massangana River than Suape Bay (PROMAR, 2010). In Massangana river and Suape Bay currents flow is predominantly southeast during ebb tides and northwest during flood tides. In the Inner Port southern estuary, currents flow southwest during ebb tides and northeast during flood tides (PROMAR, 2010). Suape estuary is under a regime of hot and humid pseudotropical climate with prevailing southeasterly trade winds and wet season lasting from March to August (Silva et al., 2004).

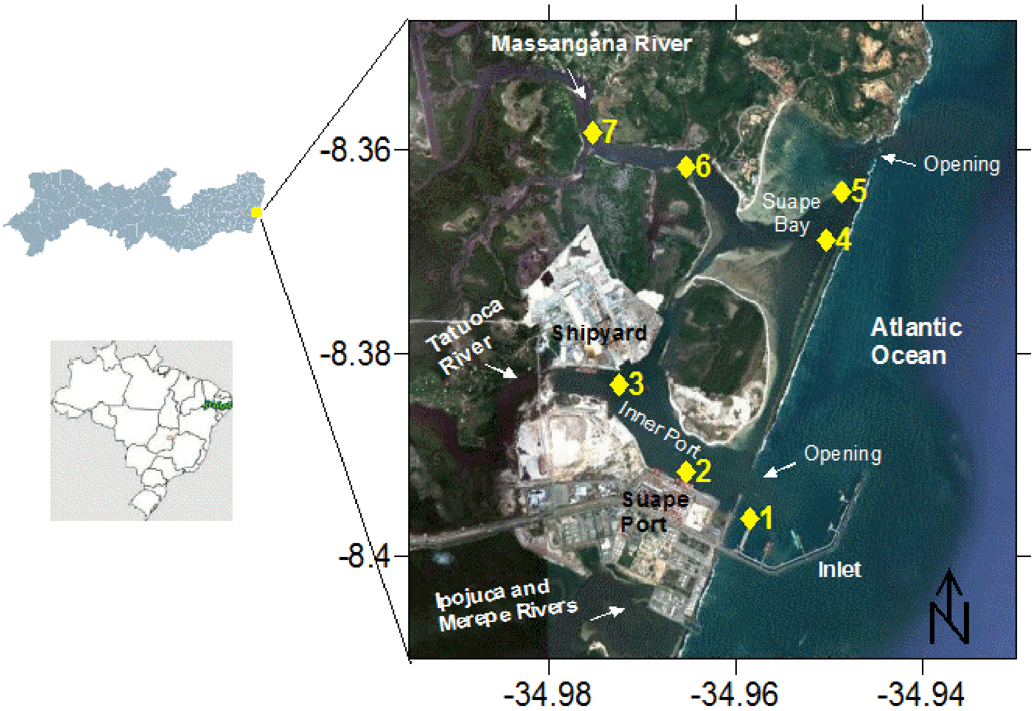

Fig. 1: Suape estuary and sediment sampling stations.

3. Materials and methods

3.1. Sampling

Sediments samples were collected at 7 stations in Suape Estuary (Fig. 1), during two sampling periods: July/2011 and February/2012. Samples were collected using a stainless steel van Veen grab sampler. Surficial sediments (top 2 cm) were sampled and kept in the dark at -18 °C until laboratory analyses.

3.2. Chemical analyses

Sediment samples were freeze-dried and before the extraction a mix of compounds containing n-hexadecene, n-eicosene and 5 deuterated PAHs (d_8-naphthalene, d_{10}-acenaphthene, d_{10}-phenanthrene, d_{10}- fluoranthene and d_{12}-chrysene) were added in all samples as surrogate. Aliquots of 20 g were Soxhlet extracted for 8 h with a mixture of n-hexane and dichloromethane (1:1, v/v) according to UNEP (1992). Copper was added to the Soxhlet apparatus for removing sulfur from the samples. The organic extracts were concentrated in a rotary evaporator, purified and fractionated by alumina-silica gel chromatography. The first eluted fraction (F1) contained AHs while the second fraction (F2) contained PAHs. Before chromatographic analysis tetradecene and d_{12}-benzo[b]fluoranthene were added to the extracts as internal standards. The surrogate recovery of AHs ranged from 61% to 94% and PAHs ranged from 45% to 104%.

AHs were determined in an Agilent Technologies 6890 gas chromatograph (GC) equipped with an HP-5 fused silica capillary column (50 m × 32 mm i.d. × 0.17 µm film thickness) and a flame ionization detector (FID). Hydrogen was used as the carrier gas. The GC oven was programmed from 40 °C to 60 °C at 20 °C min^{-1}, to 290 °C at 5° C min^{-1} (holding for 5 min at 290 °C) and to 300 °C at 10 °C min^{-1} (with a final hold for 10 min). Injector and detector temperatures were set to 300 °C and 325 °C, respectively. Individual n-alkanes were determined from C_{12} to C_{35} as well as isoprenoids pristane and phytane.

PAHs were determined in an Agilent Technologies 6890 gas chromatograph equipped with an HP-5MS fused silica capillary column (30 m × 25 mm i.d. × 0.25 µm film thickness) and a 5973N mass spectrometer (MS) in the selected ion monitoring (SIM) mode. Helium was the carrier gas and the GC oven was programmed identically to the GC-FID runs. The 16 priority PAHs, according to the U.S. Environmental Protection Agency (US-EPA), were identified and quantitated: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene and benzo[ghi]perylene. PAHs identification was based on the GC retention times of each analyte in certified standards and the individual mass spectra. Five different concentrations of certified standards were used to calibrate the instruments. Aliphatic and aromatic concentrations are given on a dry weight basis.

Quality control was based on the analysis of procedural blanks, sample duplicates, blank and matrix spikes and certified reference material (IAEA-417). More details on the analytical procedures are described by UNEP (1992) and Martins et al. (2004).

Sediment grain size determinations and Organic matter (OM) were performed following Suguio (1973). Based on the percentage of sand, silt and clay, sediments were classified in different categories according to Shepard (1954).

Correlations between grain size, OM, AHs, n-alkanes and PAHs were investigated by using Pearson's product-moment correlation with a significance level of 0.05.

4. Results and discussion

4.1. Grain size

Sediments grain size distribution varied according to the hydrodynamics of sampling sites. Sts. #1, #2 and #3, close to the port activities, had sediments dominated by finer grains (silt + clay). These stations are located in Inner Port area, where hydrodynamics is less intense than in the northern portion of the estuary (PROMAR, 2010), allowing deposition of finer particles (Table 1). Sts. #4 and #7 presented a predominance of sand but considerable amounts of fine particles were also present (Table 1). Sediments from St. #7 were collected in the river margin where currents are weaker than in the main channel, allowing some finer grains to sink (Christofoletti, 1981). St. #4 is also located in a more protected area, behind the reef barrier, and it is more susceptible to fine particles deposition. Sediments from Sts. #5 and #6, were predominantly sand (Table 1). St #6 is located in the channel of the river where currents are usually more intense than in the margins, carrying the finer particles and allowing only coarse grains to sink (Christofoletti, 1981). The coarse sediments predominance in St. #5 is probably due to its proximity to the marine region, an area with higher hydrodynamics.

Sediments in stations #1, # 2 and #3 ranged from clayey silt to sand clay; Sts. #4 and #7 were predominantly clayey sand and Sts. #5 and #6 were classified as sand (Table 1). OM was significantly correlated to finer grains ($r = 0.69$, $p < 0.05$). The lowest OM was observed in Sts. #5 and #6, dominated by sand.

4.2. Aliphatic hydrocarbons

4.2.1. Total aliphatic hydrocarbon (AH) and n-alkanes

AHs were considered as the sum of the resolved, including isoprenoids pristane and phytane, and unresolved compounds. The AHs in all samples from Suape Estuary ranged from <DL to 27.15 $\mu g\ g^{-1}$ (Table 2) with the highest concentration observed at St. #7 during sampling I. AHs in Suape were significantly correlated to OM ($r = 0.75$, $p < 0.05$) and UCM ($r = 0.88$, $p < 0.05$).

Table 1

Grain size composition (sand, silt and clay in %), sediment classification (Shepard, 1954) and % organic matter (OM) in sediments from Suape estuary during the two sampling periods: July 2011(Sampling I) and February 2012 (Sampling II).

	Sampling I					Sampling II				
St.	Sand	Silt	Clay	Shepard (1954)	OM	Sand	Silt	Clay	Shepard (1954)	OM
1	2.60	55.00	42.40	CS	8.10	68.53	12.94	18.53	CSa	4.20
2	28.57	27.84	43.59	SaSC	5.77	1.85	29.82	68.33	SC	7.57
3	1.33	39.47	59.20	SC	7.60	46.15	27.96	25.89	SaSC	7.23
4	52.54	21.78	25.68	CSa	8.07	89.30	8.56	2.14	As	4.57
5	98.66	1.08	0.27	Sa	1.03	99.49	0.41	0.10	As	1.53
6	97.79	1.76	0.44	Sa	1.57	100	0.00	0.00	As	1.37
7	53.75	14.45	31.80	CSa	10.60	73.52	9.25	17.23	CSa	9.60

Shepard (1954): CS: clayey silt; SaSC: sand silt clay; SC: silt clay; Sa: sand; CSa: clayey sand.

Marine sediments with abundant organic material may have AHs concentrations as high as 100 µg g^{-1}, but concentrations higher than that are indicative of petroleum contamination (Volkman et al., 1992; Readman et al., 2002). AH concentrations commonly found in intertidal and estuarine unpolluted environments are usually around 10 µg g^{-1} and can reach 30 µg g^{-1} under high input of organic matter from terrestrial plants (Volkman et al., 1992). The highest AH concentrations in Suape were in the range of those detected in estuaries under high OM input.

AH concentrations in Suape Estuary may be considered low when compared to areas receiving high loads of sewage and urban runoff such as the Patos Lagoon Estuary (Medeiros et al., 2005) and Black Sea (Readman et al., 2002) or port areas with large crude oil circulation as San Jorge Gulf (Commendatore et al., 2000), in which concentrations exceed 100 µg g^{-1}. In Suape Estuary sewage discharges are not high (PETROBRAS, 2006; PROMAR, 2010) and the rivers flowing into Suape Bay do not receive effluents of large urban areas. Additionally, only light fuels are transported in Suape Port and the quick degradation of these compounds in the environment result in low hydrocarbon concentrations. AH concentrations in Suape are too low when compared to chronically contaminated Brazilian regions in the vicinity of metropolitan areas and large ports including São Vicente Estuary System (Bícego et al., 2006) and Guanabara Bay (Wagener et al., 2012) where contamination exceeds 2,000 µg g^{-1}. The lower AH concentrations at Suape Port, compared to these contaminated harbors, might be a response of the lower operation time that Suape Port has. In sediments collected at St. #3, near the shipyard, the AH concentrations were 3.97 and 8.02 µg g^{-1} and are too low when compared to other areas close to shipyard activities, where concentrations exceed 900 µg g^{-1} (Bícego et al., 2006; Wagener et al., 2012).

Table 2

Concentration (µg.g^{-1}) of total aliphatics (AH), Σn-alkanes, unresolved complex mixture (UCM), pristane and phytane, and ratios of C_{31}/C_{19}, carbon preference index (CPI), low molecular weight / high molecular weight (LMW/HMW), unresolved complex mixture / resolved compounds (UCM/R) and pristane / phytane (Pri/Phy) in sediments from Suape Estuary during the two sampling periods: July 2011 (Sampling I) and February 2012 (Sampling II).

		Sampling I							Sampling II						
Stations	DL	#1	#2	#3	#4	#5	#6	#7	#1	#2	#3	#4	#5	#6	#7
AHs		8.57	5.70	3.97	15.10	0.89	0.97	27.15	11.35	6.96	8.02	1.45	0.50	<DL	8.41
Σn-alkanes		2.79	1.21	1.73	4.30	0.01	0.08	6.84	0.72	2.06	1.79	0.80	0.06	<DL	4.09
C_{31}/C_{19}		30.5	35.8	38.9	46.6	NC	NC	22.6	11.4	46.1	NC	NC	NC	NC	13.4
CPI		5	6	6	7	NC	NC	6	4	6	7	6	4	NC	6
LMW/HMW		0.1	0.1	0.3	0.1	NC	2.8	0.1	0.1	0.1	0.1	0.1	NC	NC	0.1
UCM	5.34	<DL	<DL	<DL	6.98	<DL	<DL	15.00	9.38	<DL	<DL	<DL	<DL	<DL	<DL
UCM/R		NC	NC	NC	0.9	NC	NC	1.2	4.7	NC	NC	NC	NC	NC	NC
Pristane	0.01	0.04	<DL	0.02	0.03	<DL	<DL	0.02	<DL	0.03	<DL	<DL	<DL	<DL	<DL
Phytane	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	<DL	<DL	<DL	<DL	<DL
Pri/Phy		2.0	NC	1.8	3.5	NC	NC	1.3	NC	2.6	NC	NC	NC	NC	NC

NC = no calculated

<DL = below detection limit

CPI = (1/2)[(C25 + C27 + C29 + C31 + C33)/(C24 + C26 + C28 + C30 + C32) + (C25 + C27 + C29 + C31 + C33)/(C26 + C28 + C30 + C32 + C34)]

Concentration of Σ n-alkanes (C_{12}-C_{35}) in sediments from Suape were low, ranging from <DL to 6.84 µg g^{-1} (Table 2). N-alkanes were significantly correlated with OM ($r = 0.88$, $p < 0.05$), but had no significant correlation with fine grains ($r = 0.38$, $p > 0.05$) and sand sediments ($r = -0.38$, $p > 0.05$). According to these results, n-alkanes accumulation in Suape is more dependent on organic matter than grain size distribution. These concentrations observed at Suape are comparable to those reported for sediments collected in the São Sebastião Channel (São Paulo, Brazil), where it is located the São Sebastião Port and an important PETROBRAS oil terminal (Zanardi et al., 1999a). The authors attributed the low concentration mainly to the strong currents registered in the area. The hydrodynamic pattern at Suape Bay may also corroborate to dispersing, diluting and even removing HCs from the area.

The distribution of n-alkanes may indicate the origin of hydrocarbons in the environment. N-alkanes derived from biogenic sources may be differentiated according to the number of carbons in the chain. Phytoplankton normally synthesizes odd chained hydrocarbons with 25 carbons or less ($<C_{25}$), mainly C_{15}, C_{17} and C_{19} (Blumer et al., 1971; UNEP, 1992). Terrestrial plant waxes are dominated by odd chains, between C_{23} and C_{33}, predominantly C_{27}, C_{29} and C_{31} (UNEP, 1992). In the present work, major concentration of C_{27}, C_{29} and C_{31} indicated high contribution of n-alkanes from plant waxes (Fig. 2). This has been also observed in other two Brazilian estuaries (Maioli et al., 2010) and in Jiaozhou Bay, China (Wang et al., 2006).

The ratio C_{31}/C_{19} is used to distinguish biogenic n-alkane inputs from phytoplankton and marine organisms (autochthonous) and land plant waxes (allochthonous). Values greater than 0.4 are attributed to non-marine sources while values lower than 0.4 are typical from marine sources (Gao and Chen, 2008). The calculated C_{31}/C_{19} ratios at Suape were a lot higher than 0.4, indicating a predominance of land plant waxes (Table 2). The plant waxes contribution to Suape Estuary is probably from mangroves on the margins of Tatuoca and Massangana rivers.

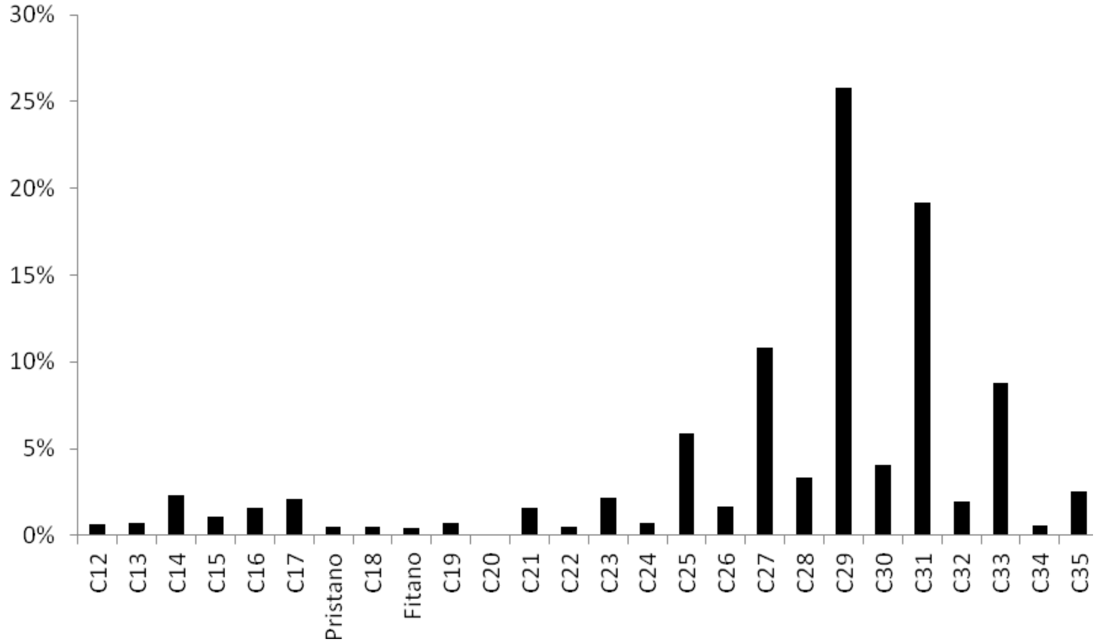

Fig. 2. Relative abundance of n-alkanes in sediment samples from Suape Estuary showing higher concentrations to C_{27}, C_{29}, and C_{31} chains.

Other approaches have been applied to differentiate biogenic and petrogenic sources of HCs, considering the ratio between odd and even chained n-alkanes, low and high molecular weight hydrocarbons, the presence of unresolved compounds, among others. N-alkanes from C_{15} to C_{35} are commonly present in sediments and the chains with odd and even carbon numbers are distributed depending on the source (Volkman et al., 1992). Petroleum hydrocarbons have a regular distribution of odd and even chains. Conversely, biogenic sources are dominated by odd chains (Volkman et al., 1992). The Carbon Preferential Index (CPI) is also a widely used tool that considers the ratio between odd and even hydrocarbons and helps in the investigation of aliphatic hydrocarbon sources (Bícego et al., 2006; Wang et al., 2006; Gao and Chen, 2008; Maioli et al., 2011; Wagener et al., 2012). Sediments that present ratios close to 1 are attributed to oil input, ratios higher than 4 indicate biogenic sources and intermediate ratios suggest mixed sources (Colombo et al., 1989; Gao and Chen, 2008). CPI calculated for sediments from Suape Estuary ranged from 4 to 7, suggesting predominance of hydrocarbons from biogenic origin (Table 2). Although CPI index has been widely used it may underestimate oil residue when there is high terrestrial plants input associated to intense n-alkanes degradation (Wagener et al., 2012).

Other tool used to distinguish n-alkanes origin is the ratio between low molecular weight (LMW = $nC_{12} – nC_{20}$) and high molecular weight (HMW = $nC_{21} – nC_{35}$). Values lower than 1 have been reported to hydrocarbons from higher plants, marine animals and sedimentary bacteria; ratios close to 1 are more related to petroleum and plankton sources; and values greater than 2 are attributed to input of fresh oil in sediments (Wang et al., 2006; Gao and Chen, 2008). Some samples from Suape did not have LMW compounds so it was not possible to calculate the ratio. Among samples with LMW and HMW n-alkanes, ratios ranged from 0.1 to 0.5 indicating a biogenic source in almost all samples (Table 2). An exception occurred at St. #6, during sampling I, with LMW/HMW ratio of 2.8. This could suggest fresh oil input to sediments. However, looking at the hydrocarbons distribution of this sample (data not shown), it was observed only some n-alkanes, unlike expected to an oil contaminated sample.

4.2.2. Unresolved Complex Mixture (UCM)

The Unresolved Complex Mixture (UCM) is considered one of the best evidences of petroleum pollution and is probably caused by a group of branched and cyclic compounds that are not able to be resolved by the GC capillary column. The complex mixture is resistant to degradation and tends to accumulate in sediments (Volkman et al., 1992; Bícego et al., 2006; Gao and Chen, 2008). In the chromatograms, the complex mixture is identified as a baseline rise that indicates petroleum residues (Volkman et al., 1992). The UCM is an evidence in sediments contaminated by biodegraded petroleum and by some refined fractions such as lubricating oils (Gough and Rowland, 1990). UCMs in Suape Estuary were identified in some sediment samples but as a low baseline rise (Fig. 3). There was no significant positive correlation between UCM and fine sediment particles ($r = 0.01$, $p > 0.05$) in opposite to that reported by Bouloubassi and Saliot (1993).

UCM concentrations ranged from <DL to 15.00 $\mu g\ g^{-1}$ (Table 2) and were lower than those reported for areas considered chronically polluted (Readman et al., 2002; Bícego et al., 2006; Wagener et al., 2012). A positive correlation between UCM and total AHs ($r = 0.88$, $p < 0.05$) was observed in the sediment samples. When UCM is the major constituent of samples with AHs >7 $\mu g\ g^{-1}$, there is a strong indication of degraded petroleum compounds deposited in the sediments (Wagener et al., 2011). Stations #7 in sampling I and #1 in sampling II presented AHs >10 $\mu g\ g^{-1}$ with UCMs representing the most of AHs, 55% and 82%, respectively, suggesting degraded petroleum in these sites.

In addition, a ratio between UCM and Resolved Aliphatic Hydrocarbons (UCM/R) may be used to investigate petroleum inputs. Values greater than 4 are attributed to petroleum residues (Readman et al., 2002; Maioli et al., 2010; Wagener et al., 2010). In this study, only St. #1 during sampling II had a value above 4.

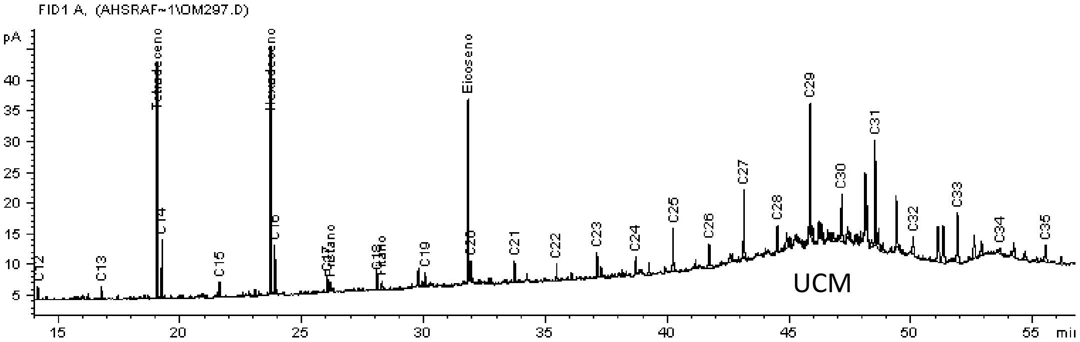

Fig. 3. Chromatogram of sediments collected during sampling II at St. #1 in Suape Estuary, evidencing an unresolved complex mixture (UCM).

4.2.3. Isoprenoids

Pristane (C_{19}) and Phytane (C_{20}) are the most abundant isoprenoids in petroleum, and are commonly present in sediments (Volkman et al., 1992; Gao and Chen, 2008). The proportion of pristane to phytane may vary widely depending on the source. As a consequence, they are also used to investigate petroleum contamination. In general, uncontaminated sediments with biogenic influence have a predominance of pristane over phytane, exhibiting a Pri/Phy ratio between 3 and 5 (Steinhauer and Boehm, 1992). In sediments contaminated by petroleum the values are around 1 (Steinhauer and Boehm, 1992).

In sediment samples from Suape Estuary, concentrations of both isoprenoids were low and in many samples they were <DL (Table 2). At St. #7, sampling I, this ratio was close to 1 suggesting the presence of petroleum. Pri/Phy ratio of 3.5 at St. #4 during sampling I indicates biogenic predominance. In the other samples where it was possible to calculate Pri/Phy ratio, the values were close to 2. Considering the low AH and UCM concentrations at these stations, in Suape the Pri/Phy around 2 seems to be more related to biogenic sources.

AH concentrations in Suape did not exceed 100 µg g^{-1} and CPI values >4 and LMW/HMW < 1, indicate a predominance of biogenic sources to these sediments. However the predominance of UCM associated to Pri/Phy (St. #7, sampling I) and UCM/R (St. #1, sampling II) ratios, suggest also the oil presence at these stations. At Suape Port (St #2) and shipyard (St. #3), AHs indicated biogenic sources, but it is important to note that dredging operations may lead to unclear results, since sediments and, consequently, contaminants are removed periodically.

4.3. Polycyclic aromatic hydrocarbons (PAH)

The total PAHs were considered as the sum of the 16 priority aromatic hydrocarbons according to US-EPA and ranged from 4.25 to 888.42 ng g^{-1} (Table 3). PAHs distribution in Suape Estuary showed higher concentrations at St. #1 (324.79 and 888.42 ng g^{-1}) and lower (<130 ng g^{-1}) at the other stations (Table 3). With exception of St. #1, PAHs had positive correlation with the sediments fine fraction ($r = 0.67$, $p < 0.05$) and OM ($r = 0.62$, $p < 0.05$), suggesting PAH partition to organic matter and finer particles (Law, 1981; Wang et al., 2006).

Table 3: Individual and total PAH concentrations (ng g^{-1}), Threshold Effect Level (TEL) and Effect Range-Low (ERL) in sediments from Suape Estuary during the two sampling periods: July 2011 (Sampling I) and February 2012 (Sampling II).

	DL	Sampling I							Sampling II							TEL	ERL
Stations		#1	#2	#3	#4	#5	#6	#7	#1	#2	#3	#4	#5	#6	#7		
Naphthalene	0.68	11.21	1.85	7.52	7.85	<DL	<DL	8.17	11.18	4.34	0.77	1.33	<DL	<DL	1.55	34.6	160
Acenaphthylene	0.68	1.69	<DL	<DL	1.40	<DL	<DL	0.72	0.77	<DL	<DL	<DL	<DL	<DL	<DL	5.87	44
Acenaphthene	0.20	8.06	<DL	1.00	0.30	<DL	<DL	0.37	43.38	<DL	<DL	<DL	<DL	<DL	<DL	6.71	16
Fluorene	0.25	6.69	0.51	2.49	1.84	0.28	0.42	2.54	25.21	1.61	0.37	0.37	<DL	0.26	0.56	21.2	19
Phenanthrene	0.55	33.57	2.93	28.64	14.30	4.64	3.46	19.87	68.91	7.99	1.44	2.46	1.84	1.89	3.62	86.7	240
Anthracene	1.08	18.51	8.46	44.60	21.07	<DL	<DL	24.29	10.26	26.80	7.19	1.35	<DL	<DL	<DL	46.9	85.3
Fluoranthene	0.40	40.47	2.33	6.90	11.50	0.73	0.53	7.44	131.85	5.75	1.15	0.89	0.53	0.40	2.44	113	600
Pyrene	0.40	43.76	6.26	24.04	17.85	3.69	2.62	19.51	110.47	14.79	2.97	1.98	2.24	1.71	5.02	153	665
Benz[a]anthracene	2.15	16.23	<DL	<DL	3.06	<DL	<DL	<DL	68.00	<DL	<DL	<DL	<DL	<DL	<DL	74.8	261
Chrysene	2.15	22.95	<DL	<DL	3.93	<DL	<DL	<DL	80.82	<DL	<DL	<DL	<DL	<DL	<DL	108	384
Benzo[b]fluoranthene	1.14	14.53	<DL	<DL	1.88	<DL	<DL	1.46	53.25	<DL	<DL	<DL	<DL	<DL	<DL		
Benzo[k]fluoranthene	1.14	11.75	<DL	<DL	3.05	<DL	<DL	<DL	36.01	<DL	<DL	<DL	<DL	<DL	<DL		
Benzo[a]pyrene	1.14	21.34	<DL	<DL	4.83	<DL	<DL	1.48	62.87	<DL	<DL	<DL	<DL	<DL	<DL	88.8	430
Indeno[1,2,3-cd]pyrene	2.20	28.87	<DL	<DL	7.50	<DL	<DL	2.47	79.03	<DL	<DL	<DL	<DL	<DL	<DL		
Dibenz[a,h]anthracene	1.52	7.53	<DL	<DL	<DL	<DL	<DL	<DL	22.95	<DL	<DL	<DL	<DL	<DL	<DL	6.22	63.4
Benzo[ghi]pyrene	0.92	37.66	2.07	2.47	12.16	<DL	<DL	4.86	83.47	2.91	0.99	1.19	<DL	<DL	1.68		
Σ16PHAs		324.79	24.41	129.95	112.51	9.34	18.71	93.18	888.42	64.18	14.89	9.57	4.62	4.25	14.87		
P/Na		1.81	0.35	0.64	0.68	NC	0.30	0.82	6.72	0.30	0.20	1.82	NC	NC	NC		
Fl/ Py		0.92	0.37	0.29	0.64	0.20	0.20	0.38	1.19	0.39	0.39	0.45	0.24	0.23	0.49		
Fl/Fl + Py		0.48	0.27	0.22	0.39	0.17	0.17	0.28	0.54	0.28	0.28	0.31	0.19	0.19	0.33		
An/178		0.36	0.74	0.61	0.60	NC	0.77	0.55	0.13	0.77	0.83	0.35	NC	NC	NC		

DL = detection limit; NC = no calculated; P/An = phenanthrene/anthracene, Fl/Py = fluoranthene/pyrene, An/178 = anthracene/anthracene + phenanthrene; Fl/Fl + Py = fluoranthene/fluoranthene + pyrene.

PAH concentrations in Suape are considered low when compared to other contaminated areas around the world. Concentrations of 24.41 and 64.41 ng g^{-1} at the Suape Port (St. #2) are much lower than those reported in sediments from Guanabara Bay, close to Rio de Janeiro Harbor, where PAHs exceeded 40,000 ng g^{-1}, an area with high chronic contamination (Wagener et al., 2012). The same study found concentrations over 7,000 ng g^{-1} in sediments close to a shipyard. These levels are some orders of magnitude higher than those observed near shipyard in the Suape Estuary (18.89 and 129.95 ng g^{-1}). In Kaohsiung Harbor, Taiwan, Σ17PAH ranged from 472 to 16,201 ng g^{-1} and the highest concentrations were observed in industrial zone docks (Chen and Chen, 2011). The low concentrations observed in Suape port area, when compared to these other ports, are possibly related to the frequent dredging operations associated to the shorter time that Suape area has been exposed to these contaminants (just 30 Years).

Considering that PAHs deposition is directly correlated with fine particles and OM contents in the sediments, mangrove environments are a major concern about PAHs contamination since it has typically both characteristics. In Suape Estuary, the Massangana River, which is surrounded by a marginal mangrove, showed concentrations from 4.25 to 93.18 ng g^{-1}. These concentrations are much lower than those detected in mangroves from Hong Kong (356 to 11,098 ng g^{-1}) where high amounts of sewage discharges as well as livestock and industrial effluents are observed (Tam et al., 2011). This difference probably is due to the fact that urbanization and industrialization processes in Suape are relatively new and this area is still not highly contaminated. However, the area is under a growing development and the situation might be different in a few years.

PAHs in Suape were in the same range of those observed at Sarno River and its estuary (5.3 to 678.6 ng g^{-1}), an industrial area under influence of industrial discharges and atmospheric emissions from the local plants (Montuori and Triassi, 2012). These authors related higher contamination (>400 ng g^{-1}) to areas with low hydrodynamics. The highest PAH concentrations in Suape (324.79 and 888.42 ng g^{-1}) were observed in St. #1, which is located in a protected area, behind a inlet, where hydrodynamics is lower than in Suape Bay, possibly allowing higher contaminants deposition (Fig. 1).

Although PAHs in Suape estuary were low when compared to contaminated areas, these concentrations are higher than those reported in pristine regions (<10 ng g^{-1})

that are normally more distant from land inputs, have oligotrophic waters with low sedimentation flux and high hydrodynamics, promoting faster dispersion (Wagener et al., 2011). Baumard et al. (1998) proposed a classification with four different PAH contamination levels: 1) low, 0–100 ng g^{-1}; 2) moderate, 100–1000 ng g^{-1}; 3) high, 1000–5000 ng g^{-1}; and 4) very high, >5000 ng g^{-1}. Most of the sediment samples (10 out of 14) from Suape Estuary are in the low contamination range (Table 3). Two samples taken during the sampling I, at St.#3 and St. #4, were on the low limit of the moderate classification with 112.51 and 129.95 ng g^{-1}, respectively. The two other samples, both from St. #1 (324.79 and 888.42 ng g^{-1}) are also classified as moderated contaminated sediments. In order to compare contamination levels worldwide, the classification of other estuaries is presented in Table 4. Overall, the Suape sediments were less contaminated than other environments under high human pressure and with petroleum hydrocarbons input from port and shipyard activities, sewage and industrial effluents, petroleum combustion, etc (Table 4).

Table 4

PAHs concentration (ng g^{-1}) in several areas of the world. Contamination levels are based on Baumard et al. (1998).

Area	Number of PAHs	Σ16PAHs (ng g^{-1})	Contamination Level	Authors
Guanabara Bay, Brazil	16	50 – 78,523	Low to very high	Wagener et al. (2012)
Kaohsiung Harbor, Taiwan	15	472 – 16,207	Moderate to very high	Chen and Chen (2011)
Mangrove swamps, Hong Kong	15	356 – 11,098	Moderate to very high	Tam et al. (2011)
Marmara Sea, Turkey	8	135 – 6,009	Moderate to very high	Taşkin et al. (2011)
Jiaozhou Bay, China	16	16 – 2,164	Low to high	Wang et al. (2006)
Todos os Santos Bay, Brazil	16	7.6 – 2,226	Low to high	Wagener et al. (2010)
Sundarban mangrove Wetland, India	16	132 – 2,938	Moderate to high	Domínguez et al. (2010)
Salt Marsh-Tidal Creek Systems, USA	16	147 – 9,671	Moderate to very high	Garner et al. (2009)
Suape Estuary, Brazil	16	4.25 - 888.42	Low to moderate	Present study

PAHs are known by their toxicity and depending on the concentration they can affect the local biota (Samiullah, 1985; Douben, 2003). In order to evaluate the PAH potential toxicity effects, the individual concentrations of each compound were compared to the threshold effect level (TEL), probable effect level (PEL) (CCME, 1999), and the effect range-low (ERL) and effect range median (ERM) (Long et al., 1995).

TEL is based on many bioassays studies, and it ranks concentrations with low probability of being toxic to the benthic biota. Concentrations greater than PEL are related more frequently to toxic effects (CCME, 1999). Among all studied sites, only St. #1 had compounds with concentrations higher than TEL. In sampling I acenaphthene and dibenz(a,h)anthracene were higher than TEL (6.71 and 6.22 ng g^{-1}, respectively) (Table 3). In sampling II, individual concentrations of acenaphthene, fluorene, fluoranthene and dibenz(a,h)anthracene exceeded TEL (6.71, 21.2, 113 and 6.22 ng g^{-1}, respectively) (Table 3). None of these compounds were higher than PEL.

These data were also compared to ERL and ERM. Concentrations below ERL represent a rare probability of biological effects. Intermediate contamination levels between ERL and ERM occasionally cause impacts benthic biota. Concentrations above ERM suggest that biological effects may be frequently observed (Long et al., 1995). Only acenaphthene and fluorene in sediments from St. #1, sampling II, were higher than ERL, but lower than ERM. The PAH concentrations higher than TEL and ERL represent a potential threat of causing damages to the local biota.

The sum of 16 PAHs observed for sediments from Suape was lower than the proposed as ERL (4,022 ng g^{-1}) (Long et al., 1995). Similar results were observed in areas of Jiaozhou Bay influenced by anthropogenic activities where Σ16PAH concentrations (148 – 2,160 ng g^{-1}) were also below ERL (Wang et al., 2006).

The PAHs sources may be identified according to their molecular weight distribution. Low molecular weight (LMW) PAHs are compounds with two or three aromatic rings. High molecular weight (HMW) PAHs have four to six aromatic rings. LMW PAHs are commonly predominant in petrogenic sources (direct input of oil and derivatives) and HMW PAHs are associated to pyrogenic sources (combustion of fossil fuels and organic matter) (Wagener et al., 2010; Huang et al., 2011; Martins et al., 2011; Montuori and Triassi, 2012). LMW PAHs were more abundant in most sediment samples from Suape Estuary when compared to HMW PAHs, indicating a predominance of petrogenic sources. The opposite was observed at St. #1 where the major compounds were HMW PAHs, suggesting a higher input of combusted compounds. LWM PAHs are more easily degraded and dispersed than HWM compounds (Montuori and Triassi, 2012). Therefore the predominance of HWM PAHs in St.1 might also indicate that the LMW were degraded before reaching this area (which has lower hydrodynamics) and these sediments accumulated mainly the heavier compounds.

PAHs from petrogenic sources are formed at lower temperatures and have more unstable compounds (alkylated) than those from pyrolytic sources (Budzinski et al., 1997; Yunker et al., 2002). Based on that, ratios between individual compounds have been proposed to differentiate PAH sources. The most frequently used are phenanthrene/anthracene (P/An), fluoranthene/pyrene (Fl/Py), anthracene/anthracene + phenanthrene (An/178), and fluoranthene/fluoranthene + pyrene (Fl/Fl + Py) (Sicre et al., 1987; Budzinski et al., 1997; Yunker et al., 2002; Bícego et al., 2006; Wang et al., 2006; Tam et al., 2011). However, some other ratios have been also used: benz[a]anthracene/benz[a]anthracene + chrysene (BaA/228), and indeno[1,2,3- ,d] pyrene/indeno[1,2,3- c,d]pyrene + benzo[g,h,i]perylene (IP/IP + BghiP) (Budzinski et al., 1997; Yunker et al., 2002; Bícego et al., 2006; Tam et al., 2011).

Anthracene, phenanthrene, fluoranthene and pyrene were detected in almost all sediment samples. Thus, the proposed ratios between them were used to identify PAH sources at Suape. The ratio P/An > 10 suggests predominance of petrogenic inputs and P/An < 10 indicates pyrolytic sources (Budzinski et al., 1997). Fl/Py ratio < 1 are attributed to petrogenic sources and values >1 are associated to pyrolytic sources (Sicre et al., 1987). Sometimes the two ratios lead to contradictory conclusions. In these cases, it is more appropriate to plot them in a single graph for distinction of data (Budzinski et al., 1997; Tam et al., 2011) as it can be observed in Fig. 4. Sediments from Suape resulted in P/An ratios predominantly below 10 while Fl/Py ratios were mostly below 1, suggesting a mixture of pyrolytic and petrogenic sources (Table 3, Fig. 4). Only sediments from St. #1, in the sampling II, showed a clear evidence of pyrolytic sources.

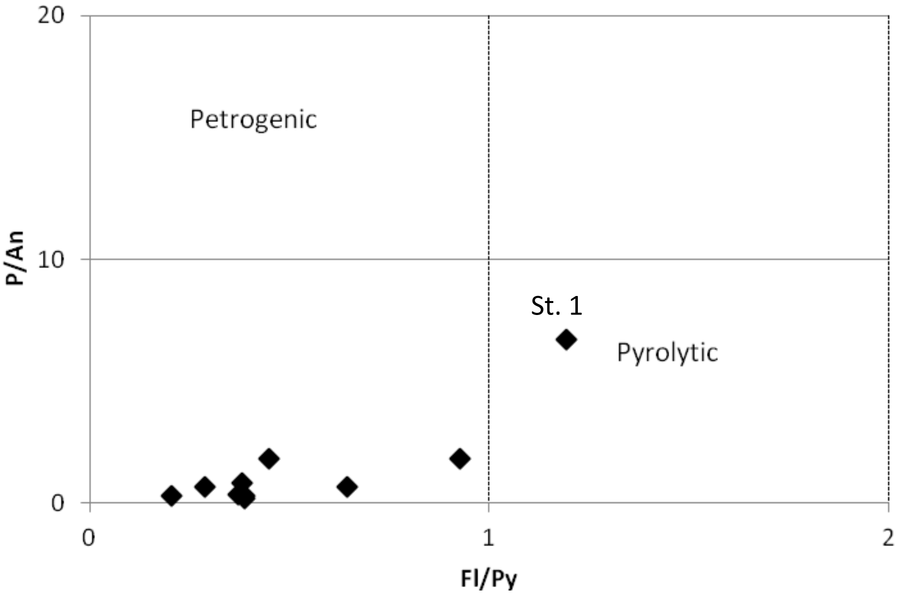

Fig. 4. Phenanthrene/anthracene (P/An) and fluoranthene/pyrene (Fl/Py) ratios in sediments from Suape Estuary.

Results of P/An and Fl/Py ratios were confirmed by An/178 and Fl/Fl+Py ratios. An/178 ratio < 0.10 suggests a dominance of petroleum contamination and ratio > 0.10 indicates a predominance of combustion sources. Fl/ Fl + Py ratios < 0.40 are associated to petroleum, intermediate ratios of 0.40–0.50 indicate petroleum combustion, and ratios > 0.50 are attributed to combustion of coal, grasses and wood (Yunker et al., 2002; Bícego et al., 2006). These ratios were calculated to sediments from Suape Estuary and a pattern of petrogenic and pyrolytic mixed sources was identified (Table 3, Fig. 5). Once again, St. #1 exhibited a predominance of pyrolytic contamination with petroleum combustion dominating in the sample from sampling I and organic matter combustion prevailing in the sample from the second sampling period. These results are in agreement with the above discussion since the dominance of HMW compounds at St. #1 suggests a pyrolytic source of PAHs to this site. The predominant input of pyrogenic compounds at St. #1 is also indicated by the presence of relatively high concentrations of pyrene, crhysene and benzo[a]pyrene, frequently observed in pyrolytic sources (Pereira et al., 1999) (Table 3).

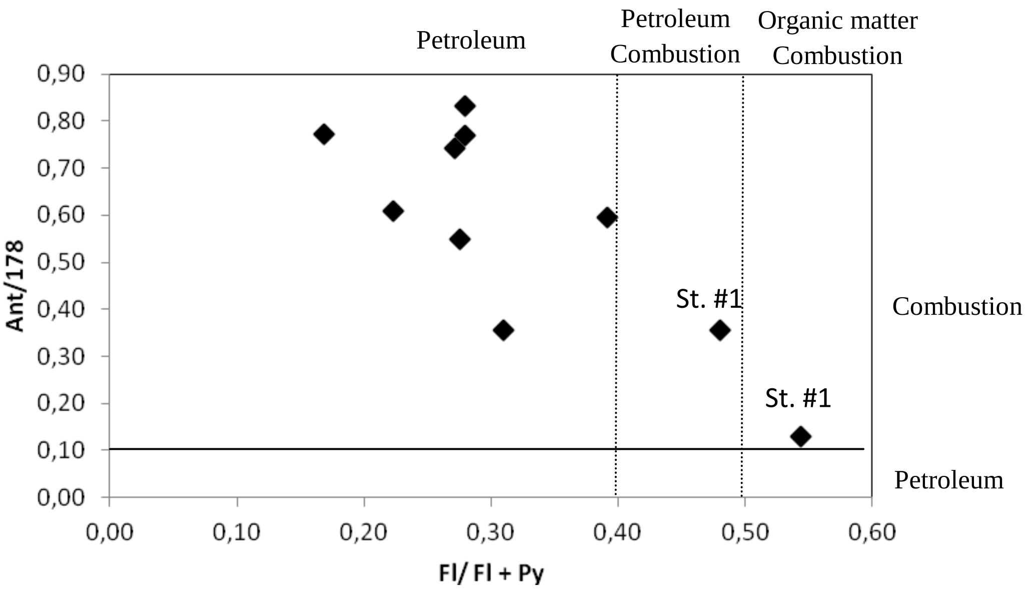

Fig. 5. Anthracene/anthracene + phenanthrene (An/178); fluoranthene/fluoranthene + pyrene (Fl/Fl + Py) ratios in sediments from Suape Estuary.

Petrogenic PAHs at Inner Port are probably related to traffic of ships, fuel transportation and oil residues released by shipyard activities. Conversely, PAHs identified at Suape Bay and Massangana River might be originated from industrial discharges or oil releases from recreational and fishery vessels commonly observed in the area. Pyrolytic PAHs at Suape may be a consequence of oil combustion and soot released from industrial plants. Alternatively, they may be originated from sugar cane burning in the vicinities of Suape. Sugar cane burning has been reported as a potential cause of increased PAH concentrations in environments near crops (Maioli et al., 2011). Water circulation in Suape Bay tends to carry contaminants to the southern opening during ebb tide when currents are weaker (PROMAR, 2010). In this area the HMW PAHs, as well as the pyrolytic compounds, are accumulated in sediments because they have low solubility in water and low vapor pressure, with significant refractory behavior contrasting to the LMW, which are quickly dispersed and degraded in water (Montuori and Triassi, 2012).

5. Conclusion

Suape Estuary is characterized by low contamination levels. Some sites presented moderate contamination, especially the southern entrance of the estuary. Results from both aliphatic and aromatic hydrocarbons are complementary, and show the presence of biogenic (land plants) associated to anthropogenic sources (petrogenic and pyrolytic). AH and PAH results showed evidences of oil degradation at the southern entrance to the estuary, a protected area with low hydrodynamics. At other sites, evidences of degraded oil are not so clear yet, probably due to the fact that Suape industrial complex is relatively new and it has been exposed to petroleum contamination for just a short period of time. Regular dredging operations might also contribute for removal of contaminants from the area. PAH compounds are probably a consequence of shipping activities, fuel transportation, shipyard activities, industrial discharges, oil combustion, industrial soot and burning of sugar cane leaves prior to harvesting. Some individual PAHs at Suape Estuary indicate the possibility of causing occasional damages to the local biota.

Acknowledgements

The authors would like to thank the support of this research by Conselho Nacional de Pesquisa (CNPq, Proc n°478589/2010-7). We also thank the OrganoMAR group and Transpetro Company staff for helping in the sample acquisition and associated measurements. Great acknowledge Dr. Roberto Barcellos for the support and the availability of the laboratory where grain size analyses were performed. Lemos also thanks CNPq for the Brazilian Graduate Research Fellowship.

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CONCLUSÕES

- As concentrações de hidrocarbonetos na água e nos sedimentos do Estuário de Suape são baixas sugerindo que o ambiente não apresenta altos índices de contaminação.

- Algumas concentrações relativamente mais elevadas de hidrocarbonetos de petróleo dissolvidos e/ou dispersos na água do Estuário de Suape, observadas no decorrer do estudo, sugerem eventuais entradas de óleo pelas atividades realizadas no porto e no estaleiro assim como descargas industriais, resíduos lançados por pequenas embarcações.

- No período chuvoso as concentrações de hidrocarbonetos na água são menores devido ao processo de diluição decorrente do aumento do nível de precipitação e fluxo de águas continentais no estuário.

- No Estuário de Suape existem diversas fontes de hidrocarbonetos nos sedimentos. Os hidrocarbonetos alifáticos mostram uma contribuição significativa de material orgânico natural, principalmente oriundo dos manguezais presentes na região, juntamente com compostos originados do petróleo. Os resultados de HPAs sugerem duas fontes distintas: petrogênicas, relacionadas às atividades portuárias e do estaleiro, transporte de combustíveis, prováveis resíduos de óleo lançados por pequenas embarcações e eventuais descargas industriais; e fontes pirolíticas, possivelmente originadas da queima de combustíveis fósseis, fuligem lançada pelas indústrias localizadas no CIPS e compostos gerados na queima da cana-de-açúcar das plantações próximas ao estuário.

- Os resultados de AHs e HPAs indicam haver uma maior acumulação e degradação de óleo na entrada Sul do estuário, próxima ao quebra-mar, que é uma área mais protegida e de baixa hidrodinâmica.

- A maior parte dos HPAs individuais em Suape indica uma pequena probabilidade de causar efeitos negativos na biota. Porém alguns compostos detectados em concentrações um pouco mais elevadas podem representar potenciais ameaças aos organismos bentônicos.

- Nas proximidades do Porto de Suape e do estaleiro as concentrações de hidrocarbonetos na água podem indicar com maior eficiência a entrada de óleo no ambiente, visto que as constantes dragagens no canal portuário impedem o acúmulo de contaminantes no sedimento, dificultando a identificação dos mesmos.

PERSPECTIVAS FUTURAS

Um programa de monitoramento contínuo para avaliação da contaminação por hidrocarbonetos no estuário de Suape deve ser proposto e implantado, incluindo matrizes biológicas para um melhor entendimento dos efeitos causados sobre a biota local. É importante considerar que a região de Suape está em pleno desenvolvimento e que a refinaria Abreu e Lima está prestes a iniciar suas operações, o que pode acarretar num aumento do nível de contaminação desta região num curto prazo.

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