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Remote sensing in the study of Brazilian mangroves: review, gaps in the knowledge, new perspectives and contributions for management*

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ABSTRACT

The incidence of anthropogenic pressures and the richness of mangrove areas in Brazil highlight the importance of multiscale/multitemporal studies, by the use of remote sensing technology, to provide information and data for Integrated Coastal Management. This review presents and discusses the applications and limitations of different remote sensing products for the study of Brazilian mangroves, shows the application of these tools for coastal management, and highlights gaps and new perspectives in this field of study. In the last three decades, the use of aerial photography and Landsat images, in a qualitative approach, predominated in the study of Brazilian mangroves, while images of other optical sensors and Synthetic Aperture Radar images, in a quantitative approach, are still expanding. The use of these remote sensing tools has generated very important results for the ecological knowledge of the ecosystem, for the planning and sustainable use of mangroves in the face of human pressures and for decision making in the integrated coastal management, in local, regional and national levels. Despite these advances, there are gaps and new perspectives of studies such as: use of new optical images with high spectral and spatial resolutions for mangrove species mapping; SAR images to estimate above-ground biomass; the use quantitative approaches as OBIA and vegetation index and calibration of remote sensing data with field data to estimate biomass. Here we show a framework to aid in the selection of appropriate remote sensing tools for studying mangroves in the perspective of integrated coastal management.

Keywords: satellite images, aerial photographs, SAR images, geoprocessing techniques.

RESUMO

Sensoriamento remoto no estudo de manguezais do Brasil: revisão, lacunas no conhecimento, novas perspectivas e contribuições para a gestão

A incidência de tensores antrópicos e a riqueza de áreas de manguezal no Brasil destacam a importância de estudos multiescalares, com visão sinóptica e multitemporal sobre esse ecossistema, por meio da utilização do sensoriamento remoto. A presente revisão apresenta e discute as aplicações e limitações de diferentes imagens obtidas por sensoriamento remoto no

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estudo do ambiente e da vegetação de manguezais do Brasil, destaca a aplicação dessas ferramentas para a gestão, bem como evidencia lacunas e novas perspectivas nessa área de estudo. Nas últimas três décadas, o uso de fotografias aéreas e imagens do Landsat, em uma abordagem qualitativa, predominaram no estudo dos manguezais brasileiros, enquanto imagens de outros sensores ópticos e de radar de abertura sintética, em uma abordagem quantitativa, ainda estão em expansão. O uso dessas ferramentas tem gerado resultados muito importantes para o conhecimento ecológico do ecossistema, para o planejamento e uso sustentável dos manguezais em face de pressões antrópicas e para a tomada de decisões na gestão costeira integrada, em nível local, regional e nacional. Apesar desses avanços, existem lacunas e novas perspectivas de estudo, como: uso de novas imagens ópticas com alta resolução espacial e espectral para o mapeamento de espécies vegetais de manguezal; imagens SAR para estimar a biomassa total, uso de abordagens quantitativas como classificações baseada em objeto (OBIA) e índice de vegetação, além da necessidade de calibração de dados de sensoriamento remoto com dados de campo para estimar a biomassa. Esse trabalho apresenta uma estrutura metodológica que auxilia na seleção de ferramentas de sensoriamento remoto apropriadas para o estudo de manguezais na perspectiva da gestão costeira integrada.

Palavras-chave: imagens de satélites de sistemas ópticos, fotografias aéreas, imagens SAR, geoprocessamento digital.

1. Introduction

Mangroves are coastal forests that inhabit saline tidal areas along sheltered bays, estuaries, and inlets in the tropics and subtropics throughout the world, where they fulfill several ecological, environmental and socio-economic functions (Barbier *et al.*, 2011, FAO, 2007). For example, mangrove forests act as a natural buffer, providing coastal land stabilization and protection against storms, tsunamis and sea level rise (e.g., Dahdouh-Guebas *et al.*, 2005; Feagin *et al.*, 2010; Mukherjee *et al.*, 2010). Moreover, this ecosystem forms an ideal habitat for a variety of animal species, including commercially important species, thus supporting offshore fish populations and fisheries (Barbier, 2000; Nagelkerken *et al.*, 2008). Nevertheless, due to pressures from anthropogenic activities and lack of awareness or of perseverance in conservation and management strategies already implemented and/or proposed (Farnsworth & Ellison, 1997; Primavera, 2000; Kovacs, 2000; Armitage, 2002; Dahdouh-Guebas *et al.*, 2002, 2005b; Feagin *et al.*, 2010, Satyanarayana *et al.*, 2013), mangrove forests are disappearing worldwide at rates of 1 - 2% per year (Valiela *et al.*, 2001; Alongi, 2002; FAO, 2007; Duke *et al.*, 2007). This indicates that we face the prospect of a world deprived of the services offered by mangrove ecosystems, perhaps within the next 100 years (Duke *et al.*, 2007).

Brazil shows the second largest mangrove area in the world (13,000 km^2), accounting for 8.5% of the world's coverage and 50% of South America's (FAO, 2007; Spalding *et al.*, 2010). The ecosystem is distributed along the Brazilian coast, from the far north, in Oiapoque River (Amapá State) to the southernmost mangrove limit in Laguna (Santa Catarina State) (Schaeffer-Novelli *et al.*, 1990). Over 80% of Brazil's mangroves are found in a complex of deltaic systems along the north coast, where are found one of the world's largest contiguous mangrove systems (Spalding *et al.*, 2010; Nascimento *et al.*, 2013). On this region, wet conditions allow for the growth of individual trees up to 40 m in height (Spalding *et al.*, 2010). The Brazil northeast coast shows roughly 10.6% of this country's mangroves, where the ecosystems are largely restricted to estuaries and coastal lagoons, with trees reaching up to 30 m (Schaeffer-Novelli *et al.*, 1990; Magris & Barreto, 2010; Spalding *et al.* 2010). Moving southwards occurs about 6.4% of the Brazilian mangroves, where lagoons and estuaries continue to predominate, with a number of important formations behind barrier islands. The trees can reach up to 10 m (Spalding *et al.* 2010). Although, various decrees and laws in three levels of governance: federal (national), state (regional) and municipal (local) legally enforce the conservation and management of Brazilian mangroves (Santos *et al.*, 2014), these forests have been affected by a variety of anthropogenic activities, resulting in losses higher than 50.000 ha between 1980 to 2005 (FAO, 2007).

The richness of mangrove areas in Brazil and the incidence of anthropogenic pressures on this ecosystem highlight the importance of studies and monitoring researches by the use of multi-scale tools, providing information on local, regional and national levels, which are very important for the integrated coastal management. This approach provides synoptic and multi-temporal views of the processes that take place in the environment and vegetation of this ecosystem. Such studies are developed with the use of remote sensing, GIS (Geography Information Systems) and geoprocessing tools.

Remote sensing is the technology to obtain information about an object, area or phenomenon without physical contact, based on the interaction of electromagnetic radiation and the different materials of the scene (Lillesand *et al*., 2008; Novo, 2011). Sensors are devices that capture the electromagnetic energy from objects, phenomena and surface features such as vegetation, soil, rocks, water bodies, houses, buildings and highways, and turn it into data, images, or other products interpretable by humans (Luchiari *et al.*, 2009). To obtain information about an object, area or research phenome-

non, images produced by remote sensors, such as aerial photographs, images obtained by multispectral optical sensors (usually referred as satellite images) and radar imagery are interpreted using techniques of visual analysis and/or digital processing (Jesen, 2009). At this stage, the images are processed and analyzed in GIS environments or by geoprocessing software, which enables the generation of new information or maps derived from the original data (Florenzano, 2002).

Remote sensing GIS-based studies provide a synoptic view, in macro spatial and multitemporal scales, which is not possible to obtain by *in-situ*-based studies. Therefore, these tools can aid in practical issues of coastal management, such as monitoring, at distance, of the fulfillment of environmental laws in coastal areas. In the case of mangrove ecosystem, these tools are specially important for the multitemporal monitoring of these forests and anthropogenic activities, giving subsidies for management, conservation and decision-making support (Santos *et al.*, 2014). In addition, accurate mapping of these environments is essential to the scientists who focus on their ecological functioning (Giarrizzo & Krumme, 2008; Souza-Filho *et al.*, 2011), thus important tools for planning and optimizing the fieldworks, a key step for the establishment of relations between the studied phenomena and the responses observed on the images and data produced by remote sensors.

In the worldwide context, since the last 20 years remote sensing technologies have played a central role in detecting and analyzing changes in the extent and spatial pattern of mangrove forests resulting from natural and/or anthropogenic forces (Heuman, 2011). In the Brazilian context, the first studies using remote sensing images for mangrove analysis started in the 80's, with the use of aerial photographs and satellite images for mapping these forests and detecting spatio-temporal changes (e.g., Espíndola, 1986a, 1986b; Abdon *et al.*, 1986; Herz, 1988; Braga *et al*, 1989; Machado 1992). The use of GIS and remote sensing tools for studying Brazilian mangroves has intensified and spread only from 2002, with publications in refereed journals and increase in the number of dissertations and thesis. This review aims to present and discuss the applications and limitations of different remote sensing tools for the study of Brazilian mangroves, showing the application of these tools for coastal management as well as presenting gaps in knowledge and new perspectives in this field of study.

2. Materials and Methods

A bibliographical research was carried out for scientific works and studies, including the categories of scientific articles, books, dissertations, thesis and full papers published in conference proceedings, which used remote sensing tools to study Brazilian mangroves. For the research of scientific articles we used the database of *Web of Science*, *Scopus* and *Scielo*. To research for books, thesis and dissertations we used the online library catalogs of federal and state Brazilian universities and of the National Institute for Space Research (INPE). Additionally, it was used the Brazilian Digital Library of Thesis and Dissertations (http://bdtd.ibict.br/vufind/), which brings together in one search portal, thesis and dissertations developed in the country and by Brazilians abroad. To research for full papers published in conference proceedings, we considered the online library of Remote Sensing Brazilian Symposium, which contains the collection of the proceedings of these symposia since 1978 to 2015 (http://www.dsr.inpe.br/sbsr2007/biblioteca/).

The key-words used in the bibliographical research were: *mangrove*, *Brazilian mangroves*, *Brazil mangroves, remote sensing*, *satellite images*, *aerial photography*, *radar images*, *SAR images*. We considered only works and studies that used remote sensing tools for studying the environment, ecosystem or vegetation of Brazilian mangroves. In the selected works and studies we analyzed in detail the section material and methods, from which the remote sensing tools and techniques were underlined, the sections results, discussion and conclusions, from which we highlighted relevant and new results for the analysis of vegetation cover (loss due to natural and anthropogenic impacts), vegetation succession, discrimination of physiographic, mangrove vegetation types and mangrove plant species, erosion and progradation in mangroves, and the importance of these tools in the field of Brazilian mangrove and coastal management. The studies were separated and categorized based on the type of tool used and its spatial resolution. The period considered for the bibliographical research started from the oldest record in 1986 (e.g., Espíndola, 1986a, 1986b; Abdon *et al.*, 1986) up to 2015. It was revised a total of 92 works and studies applying remote sensing to study Brazilian mangroves.

3. Results and discussion

Since the late 80's different types of remote sensing images, such as aerial photographs, optical imagery and active microwave (SAR - Synthetic Aperture Radar) data, have been used for analyzing the environment and vegetation of Brazil's mangroves in several studies (Table A in SI-I). These studies apply different techniques to process the information obtained by remote sensing (Table B in SI-I). Visual analysis (qualitative approach), based on interpretation of elements such as color, texture, shape, size, structure and position, was the most commonly used technique in the study of Brazilian mangroves. According to Dadouh-Guebas *et al.* (2006) visual interpretation of aerial photographs is the

most efficient and inexpensive method in the light of ecosystem monitoring research in developing countries, which are often unable to cope with the development or the cost of acquisition of commercial space-borne imaging.

Digital analysis (quantitative approach), using techniques as supervised and unsupervised classifications, segmentation, vegetation index and object-based-image-analysis (OBIA) were applied by less studies of Brazil's mangroves (Table B in SI-I), despite its importance and the recent growth since 2004. In the international context, these techniques have been wildly used with high rates of accuracy (e.g., Green *et al.*; 1998; Kuenzer *et al.*, 2011). In both cases, qualitative and quantitative approaches, it is important to note that since mangroves grow at the land-sea interface, three major features contribute to the pixel composition in remotely sensed imagery: vegetation, soil (usually muddy) and water (Kuenzer *et al.*, 2011). Thus, visual interpretation and automatic techniques must consider this in the mangrove analysis.

In Brazil, the major advance in mangrove studies by quantitative approaches was the introduction of methods based on the spectral response of the targets, supported by computational algorithms (supervised and unsupervised classifications and segmentation), which can also be complemented by visual analysis, giving more accuracy to the method employed. Moreover, quantitative techniques, such as vegetation index enabled other parameters of vegetation to be analyzed, such as green biomass, canopy closure, discrimination of plant species based on the spectral response, which is not possible with qualitative techniques, allowing a better understanding of the ecosystem ecological aspects. More recently, techniques of object-based classifications have been applied in some studies and showed a high potential to large and small scale discriminations.

Different remote sensing tools were applied in the study of Brazilian mangroves (Table A in SI-I), showing different characteristics and spatial resolutions which generate different uncertainties on the discrimination and quantification of vegetation, soil and water. Thus, studies were analyzed according to the type of tool applied, also considering their spatial resolution.

3.1 Studies of Brazilian mangroves by aerial photographs

Aerial photographs record the information of energy reflected by targets in the visible and near infrared regions and have been widely used in the mapping and evaluation of mangrove areas worldwide (Heuman, 2011). Aerial photographs at scales larger than 1:50,000, have high spatial resolution, allowing detailed mapping of mangrove cover as well as the discrimination of mangrove plant species (e.g., Krause *et al.*, 2004; Dahdouh-Guebas *et al.*, 2006). Thus, the use of this tool has been designed for obtaining information on local to regional scales, especially in cases which past data are not available and field data were not collected (Kuenzer *et al.*, 2011; Reis-Neto, *et al.* 2011). Moreover, aerial photographs are very suitable for highly detailed mapping in very small and narrow coastal environments as well as for the evaluation of mapping procedures performed with lower-resolution data (Kuenzer *et al.*, 2011).

One of the limitations of the use of aerial photographs is for mangrove mapping over large geographic areas (Heuman, 2011), due to the need to obtain a large number of aerial photos to cover the area of interest. The quality of images obtained by aerial photographs, particularly images before the 90's, and shading problems caused by clouds should also be considered. Furthermore, the application of quantitative techniques is also limited and in general visual analysis is applied, which could introduce interpretation and discrimination errors due to subjectivity of the interpreter. On the other hand, this material provides information on a broad timescale in periods prior to the availability of satellite images and is useful for detecting long-term spatio-temporal changes and monitoring of mangrove forests (Dahdouh-Guebas *et al.*, 2006; Heuman, 2011). Aerial photographs are more accessible to developing nations in which the majority of the world's mangroves grow and they can provide very rapid assessments for monitoring changes (Dahdouh-Guebas *et al.*, 2006) in times of crisis (Heuman, 2011).

In Brazil, the first three initial studies of mangrove areas by aerial photographs used photo-interpretation (visual analysis) of such material into analogical form in black and white (e.g., Herz, 1988; Braga *et al.*, 1989; Machado, 1992). The most pioneering study using this tool was the thesis of Herz (1988), developed in the Southeastern Brazil (Estuarine System of Cananéia-Iguape, São Paulo). This author used aerial photographs to discriminate different types of mangrove forests, based on visual interpretation, especially on the elements of tone and texture, classifying them into tall dense mangrove, short dense mangrove, scattered mangrove and salt marsh. In addition to these tools, Herz (1988) also used quantitative techniques to classify satellite images TM/Landsat and spectroradiometer on the field to record the spectral responses of different mangrove species.

The study of Braga *et al.* (1989) was the second published work. These authors used aerial photographs from 1974 and 1988 to discriminate and quantify changes in mangrove forests due to the introduction of human activities, such as a port and infrastructure to an industrial complex, in Northeastern Brazil (Suape, Pernambuco). Based on the photo-interpretation and tem-

poral analysis, these authors discriminated three conservation status of mangrove forests: preserved, degraded and regenerated. They also quantified the area of loss, flooding and landfill of mangroves. In the photo-interpretation, Braga *et al.* (1989) considered many elements as: size, prevalence, form, texture, density, hue, and other factors such as topography and hydrography.

The third study published was the master thesis of Machado (1992). This author used a time series analysis of analogical aerial photographs of the years 1977, 1986 and 1987 to evaluate an oil spill impact on the vegetation cover of mangrove forests located in Southeastern Brazil (Canal de Bertioga, São Paulo). This study discriminated changes in mangrove cover, which may be associated with different stages of the vegetation responses due to the effect caused by the oil. Among the changes, were highlighted: gaps, bare soil, clearing and spaced canopy, decreased in density. The main photo-interpretation elements considered by this author were tone, texture and shape.

These three pioneer studies using remote sensing tools (aerial photography) and qualitative interpretation techniques to study Brazilian mangroves had and still have importance for the ecosystem management. For example, they serve as past database on the extent and conservation status of mangroves. They also quantified losses in mangrove area due to anthropogenic pressures, as oil and land use for port and industrial complexes, important data for the development of coastal environmental planning. These studies gave light to the importance of using these tools and multi-temporal approaches to generate fundamental data and information for coastal management.

With the increasing development of GIS and geoprocessing software for digital image analysis, analogical aerial photographs have become digitized and thus they can be analyzed in computing environments. More recently, the production of digital aerial photographs and color orthophotos allowed these images to be directly used in GIS, expanding the possibilities of analysis. The use of these tools, especially considering historical data, in the study of Brazilian mangroves has allowed the evaluation and monitoring of large-scale changes due to anthropogenic pressures, as loss and vegetation dynamics in areas under pressure from urban and industrial expansion (e.g., Bernardy, 2000; Oliveira, 2001; Melo, 2008; Menghini, 2008; Cunha-Lignon *et al.*, 2009; Santos, 2009; Santos A.L.G., 2010) and mangroves impacted by oil spill (e.g., Santos *et al.*, 2012). Others authors have been using aerial photographs to map mangrove forests and to discriminate anthropogenic pressures on these areas (e.g., Lardosa, 2011) and to assess mangrove vulnerability to urban occupation (e.g., Coelho, 2008).

Aerial photographs have also been used to assess the vegetation dynamics of Brazilian mangroves from natural processes such as: erosion, progradation, natural recovery (e.g., Vale, 1999, 2004; Cunha-Lignon, 2005; Reis-Neto *et al.*, 2011, 2013), gap dynamics (e.g., Espinoza, 2008; Espinoza, *et al.*, 2009); discrimination of mangrove plants species (e.g., Krause *et al.*, 2004) and shifts between salt marshes and mangrove (e.g., Portugal, 2002; Lugli, 2004). From these works we highlighted the study of Portugal (2002), which used a spatio-temporal analysis of aerial photographs, combined with data from mangrove forest structure, microtopography survey and sedimentary dynamics, to developed scenarios of mangrove dynamics in response to sea level elevation. This study revealed a dynamic behavior of mangroves, involving propagation of pulses (toward the bay) and colonization of pulses toward a hypersaline plain (salt flats).

Thus, these studies demonstrate the importance of aerial photographs to study the dynamics of vegetation and to monitor natural changes in mangrove extent and cover, contributing to the ecological knowledge of the ecosystem as well as the identification and monitoring of human impacts, both information important for the ecosystem and coastal management.

3.2. Studies of Brazilian mangroves by medium-resolution optical imagery

Medium-resolution optical imagery (spatial resolution between 5 and 80 meters) provides a multitemporal and synoptic view of extensive areas, making available information in different bands of the electromagnetic spectrum (Florenzano, 2002). Currently there is a significant number of medium-resolution optical sensor systems that can be used to accurately map coastal wetlands (Rodrigues & Souza-Filho *et al.*, 2011) such as: MSS (Multispectral Scanner), TM (Thematic Mapper) and ETM (Enhanced Thematic Mapper) from the Landsat satellites; CCD (High Resolution Imaging Camera) and IRMSS (Infrared Multispectral Scanner) from CBERS satellites (China-Brazil Earth Resources Satellite Program); ASTER satellite (Advanced Spaceborne Thermal Emission and Reflection Radiometer); HRV (Haute Resolution Visible) from SPOT satellite (*Système Probatoire d'Observation de la Terre*); LISS (Linear Imaging Self-Scanning Sensor) from IRS satellite (Indian Remote Sensing Satellite) and AVNIR (Advanced Visible and Near Infrared Radiometer) from ALOS satellite (Advanced Land Observing Satellite). From this diversity, images from Landsat, CBERS and IRS are freely available from the INPE's website.

Medium-resolution techniques are excellent for the mapping of ecosystems (however, usually not at the species level), the monitoring of large-scale changes, the analyses of regional environmental relationships,

and the assessment of the condition of mangroves (vigor, age, density, etc.). Global mangrove loss numbers have been derived solely from the analysis of medium-resolution data (Kuenzer *et al.*, 2011).

From the diversity of medium-resolution images, the freely availability of Landsat images has increased the use of satellite images in different areas of knowledge, especially for management purposes. In the remote sensing of Brazilian mangroves, the first studies using satellite images were developed in the INPE using Landsat MSS and TM images. The studies of Abdon *et al.* (1986, 1988) were the pioneers to use these images in a multitemporal analysis to map and detect deforestation in mangrove areas, as well as, to classify mangrove forest structure in tall and short stands.

After these, most studies have used images of Landsat TM and ETM + (Table A in SI-I), due to the freely available and longevity of its sensors. Fewer studies employ images of other optical medium resolution sensors (Table A in SI-I). In overall, medium-resolution optical imagery has been applied to discriminate, measure and quantify the extent and changes of Brazilian mangroves at regional (e.g., Souza-Filho, 2005; Maia & Lacerda, 2006) and local scales (e.g., Pires, 1992; Noernberg *et al.,* 2006; Vieira, 2007; Medeiros 2009; Silva, 2009; Santos *et al.*, 2014). Nevertheless, a recent study (e.g., Magris & Barreto, 2010) was developed at the national scale and mapped mangroves as well as assessed the protection of this environment across coastal protected areas in the entire Brazilian coast. These authors used Landsat TM images and visual interpretation. They found that most of the Brazilian mangroves (83%) are located within protected areas, mainly of sustainable use, but they are concentrated on the North and Southeast coast. According to them, new protected areas should be established in other eco-regions, such as in the northeastern, in order to ensure sustainable management of mangrove resources. This is an important study because it is the most recent mapping of Brazil's mangroves at the national scale, and addressed important issues for the management and conservation of this ecosystem.

The availability of medium spatial resolution satellite images for about three decades has enabled temporal studies of mangrove vegetation cover (Kuenzer *et al.*, 2011). These images are useful to assess the extent and intensity of changes, but they are not suitable for analysis on detailed scales, due to the coarse spatial resolution (Krause *et al.*, 2004).

Time series of medium spatial resolution images have allowed the identification and quantification of anthropogenic changes in the coverage of Brazilian mangroves, such as: losses of mangroves due to landfills and human occupation (e.g., Bonetti-Filho, 1996; Martins, 2008; Martins & Wanderley, 2009; Araújo, 2010), aquaculture activities, tourism, urban expansion, agriculture (e.g., Guimarães, 2007; Guimarães *et al.*, 2009; Medeiros, 2009; Santos *et al.*, 2009; Jesus, 2010; Silva, 2012; Santos *et al.*, 2014; Godoy, 2015), road construction (e.g., Krause *et al*., 2004) and detection of cryptic ecological degradation, a process in which occurred increase of macrophytes flats in mangrove areas, masking the degradation of the site due to hydrological changes (e.g., Cunha-Lignon & Kampel, 2011).

Natural changes have also been detected by these tools, such as loss of mangroves by erosion processes (Krause *et al.*, 2004; Araújo, 2010; Jesus, 2010; Silva, 2010), increase in mangrove area by progradation processes as dense settlement and development of this vegetation on tide muddy plains and barrier islands (e.g., Alves *et al.*, 2003, Cunha-Lignon *et al.*, 2011; Silva, 2012) and expansion into new sedimentation areas and in old saltwork area (e.g., Reis-Neto *et al.* 2013; Godoy, 2015), detection of vegetation regeneration (e.g., Araújo, 2010), as well as mangrove dynamics, including increase and decrease of area and the intrinsic relationship between mangroves and salt flats (e.g., Almeida, 2010; Almeida, *et al*., 2011). Kampel *et al.* (2005) used a multi-temporal analysis of TM/Landsat-5, ETM+/Landsat-7 and CCD/CBERS to detect mangrove area changes and dynamics, and their results confirmed the use of CCD/CBERS imagery as an appropriate source of information to monitor this important ecosystem at reduced costs, as also highlighted by Santos *et al.* (2014) and Santos & Bitencourt (2013).

Silva *et al.* (2013) used multi-temporal analysis of TM/Landsat-5 to map changes in mangrove forests, detecting that mangrove forest in protected areas showed an expansion in extent. By these results, the authors highlighted the importance of protected areas in mangrove forests, mainly in urban and metropolitan areas. Also in this perspective, the study of Lardosa *et al.* (2013) surveyed and updated cartographic data, including satellite images of TM/Landsat-5 and SPOT to produce an essential tool for the management of mangrove ecosystem, in the State of Rio de Janeiro, which is a base to implement a Mangrove Conservation Policy.

The findings showed here by the use of medium resolution satellite images are important information for the regional and local management of the ecosystem, subsidizing the development of adequate management strategies, according to the natural or anthropogenic changes affecting the mangroves. For example, in the Brazil Northeast shrimp farming is one of the main threats to mangrove conservation. Thus, remote sensing based studies allow identifying these threats and assist to delineate conservation issues to mangrove forests, as shown by the studies of Santos *et al.* (2014), Guimarães

et al. (2009) and Medeiros (2009), in the Brazilian Northeast mangroves. In the use of medium-resolution optical imagery for mangrove studies, Brazil is following the global tendency, as found by Kuenzer *et al.* (2011), that many papers underscore the importance of medium-resolution imagery for mangrove-habitat mapping, wherein Landsat TM data have been used extensively.

3.3. Studies of Brazilian mangroves by high-resolution optical imagery

Images of optical systems of high spatial resolution (≤ 5 m) are recent products of remote sensing and sources of large-scale and detailed information about mangrove vegetation. These tools allow the discrimination and mapping of mangrove plant species or assembly of plant species, detailed characterization of the canopy structure, estimation of green biomass and leaf area index at high spatial detail (Heuman, 2011; Kuenzer *et al.*, 2011). Many of the high-detail applications that were once exclusively dependent on aerial photographs surveys can be currently developed with data obtained from high spatial resolution sensors (Novo, 2011). However, the use of these images is limited to applications that require synoptic view of large areas, because it is necessary to obtain a large number of images, which may not be available, as well as for multitemporal studies, because they are recent images which are not obtained at fixed intervals of time (Novo, 2011).

High resolution images include, for example, images of the panchromatic band from sensors as HRG (High Resolution Geometric) from SPOT-5 satellite, PRISM (Panchromatic Remote-sensing Instrument for Stereo Mapping) from ALOS satellite and HRC sensor (High Resolution Camera) from CBERS-2B satellite. Besides these, there are multi-spectral images of new very high resolution sensors such as GeoEye, RapidEye, QuickBird, Worldview-2, Worldview-3 and Ikonos. In the case of panchromatic images, its fusion with lower resolution multispectral images (pansharpening) is a suitable technique, allowing the generation of a final product in three colors bands and with the maximum resolution of the panchromatic image (e.g Santos, L.C.M., 2010; Bitencourt & Santos, 2013; Santos *et al.* 2014).

Studies that applied high-resolution images for analyzing Brazilian mangroves are still scarce (Table A in SI-I) and few use the potential offered by these images for quantitative and more detailed analysis, as for the discrimination of plant species. Images of the sensor Ikonos have been used for general mapping of mangroves and their vulnerability to oil spills (e.g., Andrade *et al.*, 2010), as well as discrimination of mangroves in regeneration, removed and preserved phases (e.g., Vasconcelos, 2009, Vasconcelos *et al.*, 2011). In the study of Andrade *et al.* (2010), it was highlighted the use of these images for mapping mangrove vulnerability to oil spills, which is essential as one of the first step in the development of an integrated coastal zone management. Vasconcelos (2009) and Vasconcelos *et al.* (2011) showed the application of Ikonos images for constant environmental monitoring, as to report the ecosystem dynamics in urban areas.

QuickBird imagery have been used to study the spatial-temporal dynamics of mangrove forests, including dynamic of gaps and identification of dominant plant species (e.g., Espinoza, 2008; Espinoza *et al.*, 2009), as well as serving as auxiliary data for mangrove mapping carried out with lower spatial resolution images (*e.g.*, Araújo, 2010). Santos, L.C.M. (2010) and Santos *et al.* (2014) fused the panchromatic image HRG/ SPOT-5 with the multispectral image of the CCD/CBERS-2B, creating a final product that provided information on a large scale, essential to map and characterize the mangroves and identify human pressures as shrimp farming. In this view, Tenório *et al.* (2015) evaluated the role of marine aquaculture in the conversion of mangrove forests into shrimp farms using HRG2/SPOT-5 and GeoEye satellite images obtained from the Google Earth PRO. Due to the high spatial resolution of these images the visual interpretation was an efficient tool for their study. Based on their results, they pointed out recommendations for the sustainable use of mangroves on the Amazon coast.

The production of high-resolution images has allowed the use of new image analysis techniques based on objects, called OBIA, Object-Based-Image-Analysis (Blaschke, 2010). Object-based methods use spatial neighborhood properties for classification while pixel-based approaches use solely the spectral information. OBIA emulates the expert knowledge applying classification rules in segments of the images. This classification considers space and geometric attributes and hierarchical relationships among neighborhood (Definiens, 2007). With the availability of high-resolution images and OBIA methods, remote sensing techniques can be very beneficial to monitor mangrove areas (Meneghetti, 2013). In the global context, remote sensing studies in mangrove areas have demonstrated the superiority of such procedure in comparison with the commonly used pixel-based supervised classification approach (Kuenzer, 2011). In Brazil, there are few studies that apply this technique (e.g., Vasconcelos *et al.*, 2011; Meneghetti, 2013; Silva *et al.*, 2013; Nascimento *et al.*, 2013; Almeida, *et al.*, 2014; Meneghetti & Kux, 2014; Arasato *et al.*, 2015a).

OBIA is a new remote sensing technique in the study of mangroves and it has been showing a great accuracy and applicability for more detailed mapping. For exam-

ple, Almeida, *et al.* (2014) used IKONOS images and OBIA, combined with structural vegetation data (measured in the field) to map different physiographic types of mangrove forests. They mapped 4 types of mangroves: fringe, basin, transition and colonization forests. Meneghetti (2013) and Meneghetti & Kux (2014) used WorldView-2 images and OBIA (data mining technique) to land cover mapping, including mangrove areas. This study found that the new spectral bands of WorldView-2 sensor (Red Edge, Near Infrared-2 and Coastal Blue) assisted in discrimination of typical targets of coastal areas such as dunes, mangroves and tidal channels, improving the classification of land cover. Among these bands, the Red Edge allowed the discrimination and separation of the mangroves from the other classes. The results and techniques developed by these authors show the application of new underexplored tools, as the Red Edge band for mangrove mapping. The maps resulted from this study will facility the decision making for the local coastal management.

Arasato *et al.* (2015a) used WorldView-2 images, OBIA and vegetation index, to generate thematic maps of land use and cover, types of mangrove (mangrove, mangrove swamp with associated species, gaps) and mangrove species. Moreover, integrating the map of types of mangrove with LIDAR data, the authors mapped the height of the mangrove forests. This study shows a good example of integrating different techniques to high detail and biomass mangrove mapping. However, many manual edits based on visual interpretation keys were required for finishing the maps. In this case, the high spatial and spectral resolution of the images facilitated the identification and visual discrimination.

3.4. Studies of Brazilian mangroves by SAR (Synthetic Aperture Radar) images

Sensors of Synthetic Aperture Radar (SAR) operate in the region for microwave, based on the transmission of long wavelengths and detecting the amount of backscattered energy (Jensen, 2009). These sensors provide images that cover a wide geographic region, providing synoptic view of vast areas for mappings at large scales of 1: 100,000 to 1: 400,000 (Jensen, 2009). Thus, SAR images are appropriate tools for mapping mangroves in large geographic regions, such as in regional to national scales. The spatial resolution SAR images is variable according to the type of sensor and can vary from low to high, in the latter case, in new SAR sensors.

SAR images also enable the extraction of information about surface roughness, dielectric properties, moisture (Jensen, 2009) and salinity of landscape targets. SAR sensors are active systems (they have own source of energy) which allow acquiring images during the day and night. Moreover, since they operate in microwave, it is possible to generate images that are not affected by cloud cover, fog and precipitation (Novo, 2011). For the study of mangroves, these features are very important, because the ecosystem is distributed in coastal areas in tropical and subtropical regions, where the cloud cover is usually intense. In the global context SAR images have been successfully used for the study of mangroves (Heuman, 2011), providing information on the extent of vegetation, structural parameters, flood limits, health, deforestation and amount of total biomass. However, these images are limited to discrimination on the level of plant species (Kuenzer *et al.*, 2011) and to identify the border between mangroves and adjacent tropical forest (Nascimento *et al.*, 2013).

Among remote sensing techniques, synthetic aperture radar is a particularly advantageous method to monitor mangroves: images are not dependent on cloud cover and can provide information from forest understory (Pereira *et al.*, 2012). These tools provide an additional and powerful source of data for the mapping of coastal land cover under conditions that are restrictive to the acquisition of optical satellite images, such as constant cloud cover and smoke from fires (Souza-Filho *et al.*, 2011).

In Brazil, Herz (1991) conducted the first study at the national level using SAR imagery to map mangroves along the Brazilian coast. Although the importance of this study as the first to document Brazilian mangroves at national scale, it should be considered with caution as database for other mappings, because this study presents failure in the discrimination of mangroves and lacks of more integration with field studies. Other studies using exclusively SAR images (Table A in SI-I) were developed in local and regional levels, mostly on the Brazil north coast. In these studies, SAR images are mainly used to map types of mangrove forests, stages of vegetation, and loss of mangrove area due to severe erosion, despite the potential of these tools to study mangrove biomass. Souza-Filho & Paradella (2003), using visual interpretation, indicated that the mapping of mangrove forests using SAR images was facilitated due to a high contrast of mangroves with water. In another approach, Souza-Filho *et al.* (2011) indicated the applicability of multipolarized SAR images, obtained from R99B sensor from the Amazon Surveillance System (SIVAM), to discrimination mangroves. This study provided important new insights into the interpretation of coastal wetlands, such as the use of multi-polarized L-band SAR to identify and discriminate distinct geomorphic targets in tropical wetlands, as mangroves. Multipolarized airborne system may be especially useful for mapping the wetlands along the Amazon coast (Souza-Filho *et al.*, 2011). Pereira (2011) and Pereira *et al.* (2012) also used multipolarized SAR images, from the sensor PALSAR (Phased Array L-band Synthetic

Aperture Radar), for mapping and to discriminate physiographic types of mangrove forests. Pereira (2011) correlated structural parameters of the mangrove forests with backscatter signals from SAR images, for mapping mangrove structure. This study highlighted that SAR data are potential tools for mapping and study the structure of mangrove forests and the L-Band SAR data was the most effective for mapping mangrove areas, and therefore it is recommended as a tool for coastal management (Pereira *et al.*, 2012).

3.5. Studies of Brazilian mangroves by the integration of SAR and optical imagery

The combination of SAR and optical sensors images generate additional results for the production of coastal environments maps, allowing an adequate visual discrimination of the extent of mangroves (Souza-Filho & Paradella, 2005; Rodrigues & Souza-Filho 2011, Nascimento *et al.*, 2013). In the global context, the integration of these images has been important to discriminate different densities of mangrove vegetation, different age groups and types of forests based on the dominant species (Kuenzer *et al.*, 2011). In Brazil, the first studies of this type was developed by Espíndola (1986a, 1986b) who used MSS/Landsat and SAR images to discriminate 13 unites of mangroves in Cananéia-Iguape (São Paulo State). More recently, the combination of SAR and optical sensors have been used for general mangrove mapping (e.g., Santos *et al*., 2009; Souza-Filho, 2000; Souza-Filho *et al.*, 2005; Teixeira & Souza-Filho, 2009; Rodrigues & Souza-Filho, 2011) as well as to assess and map mangrove vulnerability to oil spills (e.g., Souza-Filho *et al.*, 2009). This integrated approach also allows the discrimination of mangrove forest types and stages of vegetation (e.g., Souza-Filho & Paradella, 2002; 2005), analysis of spatio-temporal changes in vegetation cover (e.g., Lara *et al*., 2002, Cohen & Lara, 2003; Souza-Filho *et al*., 2006; Batista *et al.*, 2009; Costa, 2010; Dantas *et al*., 2011;. Nascimento *et al.*, 2013) and recovery analysis of vegetation in areas degraded by human impacts (e.g., Lara *et al.,* 2002; Cohen & Lara, 2003).

In this integrated approach images of Landsat optical sensors are also the most used and those of SAR imagery are from RADARSAT-1 (C-band). Some of these studies gains relevance because they merged images of optical sensors with SAR images (e.g., Souza-Filho & Paradella, 2002; Souza-Filho *et al.*, 2005, 2009; Rodrigues & Souza-Filho, 2011), generating an integrated product which gives more detailed and precise information and results for mapping and analyzing mangroves. It is interesting to highlight the study Nascimento *et al.* (2013), which used JERS-1 SAR, ALOS-PALSAR and Landsat TM in a OBIA to map mangroves in the north region, and confirmed that Brazil is the country with the largest contiguous belt of mangrove forests, located from east of the Amazon River mouth, Pará State, to the Bay of São José in Maranhão. Nevertheless, these mangroves are experiencing significant change because of the dynamic coastal environment and the influence of sedimentation from the Amazon River along the shoreline, requiring continued observations using combinations of SAR and optical data (Nascimento *et al.*, 2013).

Considering the study of mangrove vegetation, optical images recorded the spectral information of the upper layers of vegetation such as leaves and canopy, while in certain bands (L and P) of SAR images the microwave length is capable of penetrate in the lower layers of vegetation, providing information on the structure of branches and stems. This integration of different images provides additional information, especially to evaluate the total biomass of mangrove forests (Aschbacher *et al.*, 1995; Kuenzer *et al.*, 2011). Therefore, synergistic information on structure and composition derived from radar backscatter signals and the reflectance information from the optical imagery are most promising for vegetation-mapping applications (Giri & Delsol, 1993; Aschbacher, 1995; Kuenzer *et al.*, 2011).

However, as in any remote sensing study, for this approach be effective, the integration of remote sensing results with field data is essential. This can be achieved by the development of allometric models to estimate mangrove vegetation biomass, considering the diameter and height data from mangrove trees obtained in field, and parameters estimated by remote sensing data. Nevertheless, these models are site-specific and species-specific, which limits the reliability of some estimates of biomass by remote sensing to be applied in different mangrove areas. Worldwide, studies applying this approach make use of allometric models already published in the literature (e.g., Simard *et al*., 2006; 2008). In Brazil, some allometric models were developed for mangroves on the southeast coast (Soares & Schaeffer-Novelli, 2005; Arasato *et al.*, 2015b) and northeast (e.g., Silva, 1993; Santos, 2012). More recently, the study Arasato *et al.* (2015b) integrated LiDAR, WorldView-1 and field data to map and monitor mangrove structure and biomass, concluding that LiDAR data can be operationally applied in mangrove biomass estimation. Despite the potential to develop this approach for Brazilian mangroves, allometric biomass models are not available for mangroves located on the northern region, requiring field works for their generation.

3.6. Gaps in the knowledge and news perspectives

The use of remote sensing to study Brazilian mangroves are still in development and there are many new techniques and sensor images to be explored in this field of knowledge. In overall, images from medium-resolution optical imagery are the most explored, especially from

Landsat sensors (Table A in SI-I). Nevertheless, most of the studies use a qualitative approach, applying the technique of visual interpretation. The use of quantitative techniques is urgent and necessary in order to provide more reliable results, to allow comparative analysis between different areas and to provide more ecological data which is necessary to apply in management decision making. For example, vegetation index are still underexplored in the study of Brazilian mangroves (Table B in SI-I). This methodology allows to estimate green biomass of mangroves and to identify more productive mangroves, which are important information do delineate mangrove areas for conservation and fishery. Theses approaches are new perspectives which should be explored. For example, Santos (2015) and Santos *et al.* (2015, *in press*) used maps of mangrove vegetation index as input layer in a multicriteria anlaysis to map more suitable mangrove areas for fishery and conservation of the mangrove crab *Ucides cordatus*. There are many types of vegetation index indices such as Normalized Difference Vegetation Index (NDVI), Enhanced Vegetation Index (EVI), Simple Ratio (SR), which allow quantifying the vegetation density per area, mangrove canopy closure, gaps, green biomass, leaf area index and comparisons among different mangrove forests (e.g., Kovacs, 2004, 2005; Giri *et al.*, 2007, Santos & Bittencourt, 2013). In Brazil, this approach is underexplored and still lacks calibration from parameters collected in field. These are gaps of knowledge which should be filled by new studies.

Similarly, Brazilian mangroves lacks of studies using the quantitative analysis as OBIA, which is a classification technique that uses objects rather than just individual pixels for image analysis (Heuman, 2011). OBIA applied in high resolution images is a new and potential tool to mapping mangroves up to species level and is a new perspective to be explored in Brazilian mangrove remote sensing. Information and maps of mangrove species is crucial in management strategies. Worldwide, few studies have used OBIA to map the areal extent and change of mangroves as this approach is more commonly applied to species mapping (e.g., Krause *et al.*, 2004; Wang *et al.*, 2004a, 2004b), but this classification has potential for mapping mangrove species and extent, showing very high accuracy for classifying mangroves (Conchedda *et al.*, 2008; Heuman, 2011).

Studies using CBERS images for the analysis of mangroves in Brazil are still scarce (Table A in SI-I), despite the potential offered by these images. The CCD images have shown potential to map Brazilian mangroves in medium scale, especially to identify human pressures on mangroves located on the northeast coast. More recently, since January 2015 images from the new launched satellite CBERS-4 are available. This satellite has two sensors MUXCAM and PANMUX, the first producing images with 20 m of spatial resolution and the second images with 5 m (panchromatic) and 10 m of spatial resolution (multispectral), thus having application in many scales of study (INPE, 2015). All images from CBERS are freely available thus an important tool for monitoring mangroves. As new perspectives, CCD and the new images from PANMUX and MUXCAM can be used for monitoring mangroves and for the calculation of vegetation index. For local and high scale studies, the HRC and PANMUX panchromatic images with high spatial resolution (2.7 m and 5 m, respectively) can be merged with multispectral PANMUX images for better visual interpretation through color compositions and application of quantitative techniques, as supervised classification and OBIA (e.g., Santos & Bitencort, 2013; Santos *et al.*, 2014). Data fusion techniques can improve classification accuracy by drawing upon different data sources to maximize the dimensionality of available information (Heuman, 2011). For regional studies, the joint use of the images of these sensors images (CCD, HRC, PANMUX, MUXCAM) is an excellent method because it offers complementary information at different scales. Although the CBERS satellites are no longer in operation (CBERS-2 since 2009, CBERS-2B since 2010 and CBERS-4 since 2015) these images are a major source for short term multitemporal studies and detection of changes.

Another new perspective to be explored is the Landsat-8 satellite which images are recent and current freely available, produced since 2013. The Landsat-8 has a new sensor called OLI (Operational Land Imager) which is an optical sensor with nine multispectral bands, spatial resolution of 30 meters and a panchromatic band with a spatial resolution of 15 meters, generating images with 12-bit of radiometric resolution (USGS, 2015). The high spectral and radiometric resolution of this sensor increases the discriminatory power of digital quantitative analysis, as OBIA and supervised/unsupervised classifications, separating different types of mangrove forests. Another potential is the calculation of vegetation index and the fusion of the panchromatic band with multispectral bands, generating color compositions with a spatial resolution of 15m, which allows better visual discrimination of mangroves. Finally, the new ultra-blue band (0.43µm - 0.45µm) is indicated for coastal studies (USGS, 2015), and in the case mangrove would be useful to differentiate the vegetation fraction among the water fraction.

In the study of Brazilian mangroves, the exploration of spectral resolution did not show great progress in these three decades, and it is mostly used three to five sensor bands, although there are in the market hyperspectral sensors that produce numerous bands (e.g., CASI, AISA +, EO-1 Hyperion, AVIRIS, Hymap, Dedalus).

In the global context these sensors have been explored in the study of mangroves (e.g., Green *et al.*, 1998, Hirano *et al.*, 2003; Yang *et al.*, 2009; Heuman, 2011). Hyperspectral data provide new opportunities for mapping mangrove forests by providing a large number of very narrow bands (<10 nm) in the 0.38–2.5μm range (Kuenze *et al.*, 2011). This greatly increases the level of detail, because a characterization of the complete spectra of mangrove cover types is possible (Green *et al.*, 1998). These tools have not been explored in the study of Brazilian mangroves and are new perspectives to be considered.

Finally, the potential of SAR images to extract information about biomass of trunks, branches and aerial roots, salinity in the leaves, in soil and water as well as moisture from the vegetation of Brazil's mangroves, have not yet been explored and thus they are new perspectives that urge to be applied in this field of study. Worldwide these tools have been successfully applied to estimate above-ground biomass and structural parameters of mangrove vegetation, mainly using polarized images (Kuenzer *et al.*, 2011). The quantification of above-ground biomass is very important in the context of global climate changes, in order to identify mangroves that act as carbon stocks, which are important areas for conservation. Given their high biomass and productivity, there is increasing interest in the role that mangroves may play in global carbon budgets (Spalding *et al.*, 2010). In this context, JAXA (Japan Aerospace Exploration Agency) launched the ALOS-2 PALSAR which SAR images promise the possibility of estimating total above-ground biomass, due to the properties of the L band, the pixel of 10 m and 12-bit radiometric resolution. Nevertheless, this approach needs field validation in order to develop allometric models for mangrove biomass, which is site and species specific, thus requiring, for some sites and regions of Brazil, specially the North, the development of these models. This is a gap in the knowledge of Brazilian mangrove remote sensing that must to be filled in new studies.

3.7. Contributions for Integrated Coastal Management

The detection and extraction of data about the spatial distribution and extent of coastal ecosystems, such as mangroves, and anthropogenic activities that affect the ecosystem are essential information for the elaboration of coastal management plans (Santos *et al.*, 2014). Other important data are from the ecosystem conservation status, vegetation stages and species composition, productive, biomass, dynamics and risk of erosion and sea level rise. The use of remote sensing techniques and tools can provided this type of information in multiple scales of space and time. This data and information can be used in geoprocessing techniques, e.g., multicriteria evaluation analysis (MCE), to define more suitable areas for multiple uses in the decision making process of the integrated coastal management. For example, which mangrove areas are more suitable for conservation, or which mangrove area can be used for other human uses as fishery, shrimp farming, aquaculture or tourism? This can be answered by an integrated analysis of the data resulted from remote sensing studies, in geoprocessing analysis, like MCE (e.g., Santos, 2015; Santos et al. *in press*).

Resource allocation for use or conservation, a central issue in integrated coastal management, and requires the developing of analytical and operational evaluation tools for decision-making (Andalecio, 2010) which can be achieved by the analysis with GIS and remote sensing techniques (Eastman, 2012). In these cases which involve multidisciplinary knowledge bases, a geoprocessing procedure called Multi-Criteria Evaluation (MCE) is the more appropriate (Huang *et al.*, 2011) to achieve conservation and management use purposes. MCE provides a systematic methodology to combine the inputs with cost/benefit information and stakeholder views to rank project alternatives (Huang *et al.*, 2011).

In Brazil, since 1986, when the first studies using remote sensing tools were developed, they have been contributed with important information for mangrove and coastal management. For example, pioneers studies as Abdon (1986, 1988); Braga *et al.*, (1989) and Machado (1992) discriminated changes in mangrove due to anthropogenic impacts. Along the years, the evolution of remote sensing studies of Brazilian mangroves clearly demonstrates a large contribution in the context of coastal management and mangrove ecosystems, providing data and information about the ecosystem status and extent in past periods and data about natural and anthropogenic changes, which are important for designing management and land use plans in coastal zones. In addition, some studies detected the importance of the establishment of protected areas in mangroves, (e.g., Silva *et al.*, 2013) and as one of the main important, Magris & Barreto (2010) identified the need in the national scale for the implementation of protected areas mainly in the northeast of Brazil.

Here we showed various applications of remote sensing tools to study Brazilian mangroves and their applicability to aid in the ecosystem and coastal management. The usefulness of such tools depends on the quality of the data, on the expertise of the technical team and on the availability of information on the geometric accuracy. All of these aspects must be addressed and quantified in order to provide a sound scientific basis for integrated management policy formulations (Hunsaker *et al.*, 2001; Krause *et al.*, 2004). Additionally, all tools have potentialities and limitations, thus a main step is to

choose the adequate tool and technique among the diverse available. The selection of the appropriate images and techniques will primarily depend on the scale and objectives of the study as well as on the financial viability to acquire commercial satellite images. We summarized the applications and limitations of different types of remote sensing images for the study of mangroves in Brazil (Table C in SI-I), which can serve as a framework guide for those interested in applying these tools to study mangroves and to produce data and information to aid in coastal management.

4. Conclusions

In the last three decades, the use of aerial photography and TM and ETM + images, from Landsat series, in a qualitative approach, predominated in the study of Brazilian mangroves, while images of other optical sensors (e.g., CCD/CBERS, HRV/SPOT, IKONOS) and SAR images, are still expanding and gaining expression in this field of study. The use of these remote sensing tools has generated very important results for the ecological knowledge of the ecosystem and to support the planning and sustainable use of mangroves in the face of human pressures and for decision making in the integrated coastal management, in local, regional and national levels. However, there are still gaps in this research area. One is the lack of calibration of remote sensing data with field parameters for the estimation of vegetation index by optical images, and for the development of allometric models to estimate mangrove biomass by SAR images.

The remote sensing in the study of Brazilian mangrove is still in development and there are many new perspectives to be explored. From those, we emphasize the use of freely available images of new sensors as OLI/Landsat, PANMUX and MUXCAM/CBERS-4, the use of very high resolution images for species mapping, hyperspectral data, SAR images to estimate aboveground biomass, and the application of quantitative techniques as OBIA, to map mangrove species and vegetation index to estimate green biomass. With respect to spatial resolution, which has changed a lot in these three decades, with the production of high and very resolution imagery, the studies of Brazilian mangroves by these tools showed an overall small growth and did not follow the global trend. However, we must consider that the advancement and consolidation of these tools in the context of Brazil, only will occur by the availability of cheaper and accessible images and greater availability of resources for acquiring them.

Finally, the diversity of remote sensing imagery combined with the freely availability of some images, as well a high variation on the longevity of the sensors, do not allow to conclude which is the best image to be used in the study and analysis of Brazilian mangroves. Thus, the selection of the appropriate images depends primarily on the scale and objectives of the study as well as the financial viability to acquire commercial satellite images. In this process, which is the first step in management studies that use these types of tools, is important to evaluate the potentialities and limitations of each type of images. Our study gives information and shows a framework to aid in this evaluation. Here we found that remote sensing and geoprocessesing are fundamental tools to be considered in mangrove and costal management.

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Appendix

Supporting Information associated with this article is available online at http://www.aprh.pt/rgci/pdf/rgci-662_Santos_Supporting-Information.pdf

References

Abdon, M. M.; Espíndola, C. R. S.; Valeriano, D. M.; Vieira, E. G. M.; Setzer, A. W.; Santos, M. A.; Novelli, Y. S. (1986) - Avaliação das áreas de manguezal do rio Piauí (SE) através de sensoriamento remoto. In*: IV Simpósio Brasileiro de Sensoriamento Remoto*, pp. 710-715. INPE, São José dos Campos, Brazil. ISBN: 978-8517000485.

Abdon, M.M.; Vieira, E.G.M.; Espíndola, C.R.S.; Setzer, A.W. (1988) - Evaluation of the extension and degradation of mangrove areas in Sergipe state with remote sensing data. In: *ISPRS Archives*, XXVII, Part B7, pp. 32-37. Kyoto, Japan.

Almeida, P.M.M. (2010) - *Análise espaço-temporal da área ocupada por florestas de mangue em Guaratiba (Rio de Janeiro, RJ) de 1985 até 2006 e sua relação com as variações climáticas.* Dissertação de Mestrado, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ, Brasil. *Unpublished*.

Almeida, P.M.M; Schmid, K.; Cruz, C.B.M.; Soares, M.L.G. (2011) - Dinâmica de um remanescente de floresta de mangue do município do Rio de Janeiro. *XV Simpósio Brasileiro de Sensoriamento Remoto*, pp.1982-1988. INPE, São José dos Campos, Brazil. ISBN: 978-8517000560.

Almeida, P.M.M.; Soares, M.L.G.; Estrada, G.C.D.; Cruz, C.B.M.; Fernandeza, V. (2014) - Mapping physiographic types of mangrove forests through the objectbased classification method. *SouthEastern European Journal of Earth Observation and Geomatics*, Special Issue, 3:425-428.

Alongi, D.M. (2002) - Present state and future of the world's mangrove forests. *Environmental Conservation,* 29(3):331-349. DOI: 10.1017/S0376892902000231.

Alves, A.L.; Amaro V.E.; Vital, H. (2003) - Multitemporal analysis of multispectral Landsat 5 - Thematic Mapper images for monitoring and evaluation of coastal morphodynamic on the northeastern coast of Brazil. *Journal of Coastal Research,* Special Issue, 5:279-283. Available on-line at http://www.jstor.org/stable/40928772.

Andalecio, M.N. (2010) - Multi-criteria decision models for management of tropical coastal fisheries. A review. *Agronomy for Sustainable Development*, 30:57-580. DOI: 10.1051/agro/2009051

Andrade, M.M.N.; Szlafsztein, C.F.; Souza-Filho, P.W.M.; Araújo, A.D.R.; Gomes, M.K.T. (2010) - A socioeconomic and natural vulnerability index for oil spills in an Amazonian harbor: A case study using GIS and remote sensing. *Journal of Environmental Management*, 91(10):1972-1980. DOI: 10.1016/j.jenvman.2010.04.016.

Arasato, L.S.; Bentz, C.M.; Silva, R.S.B.; Guerra, J.B.; Paes, J.E. S.; Freitas, L.R.; Luiz, S. (2015a) - Uso do sensoriamento remoto ótico de alta resolução para a caracterização e monitoramento qualitativo de manguezais. *XVII Simpósio Brasileiro de Sensoriamento Remoto*, pp. 5141-5148. INPE, São José dos Campos, Brazil. ISBN: 978-851700768.

Arasato, L.S.; Bentz, C.M.; Fonseca, M.G.; Guerra, J.B.; Paes, J.E. S.; Freitas, L.R.; Costa, U.E.; Luiz, S. (2015b) - Avaliação do uso de modelos LiDAR e Worldview-1 para a caracterização e monitoramento de manguezais. In*: XVII Simpósio Brasileiro de Sensoriamento Remoto*, pp. 5050-5057. INPE, São José dos Campos, Brazil. ISBN: 978-851700768.

Araújo, C.A.S. (2010) - *Aplicações de técnicas de Sensoriamento Remoto na análise multitemporal do ecossistema manguezal na Baixada Santista, SP*. Dissertação de Mestrado, Universidade de São Paulo, São Paulo, SP, Brasil. *Unpublished*.

Armitage, D. (2002) - Socio-institutional dynamics and the political ecology of mangrove forest conservation in Central Sulawesi, Indonesia. *Global Environmental Change,* 12:203-217. DOI: 10.1016/S0959-3780(02)00023-7.

Aschbacher, J.; Ofren, R.; Delsol, J.P.; Suselo, T.B.; Vibulsresth, S.; Charrupat, T. (1995) - An integrated comparative approach to mangrove vegetation mapping using advanced remote sensing and GIS technologies: Preliminary results. *Hydrologica*, 295:285-295.

Barbier, E.B. (2000) - Valuing the environment as input: review of applications to mangrove-fishery linkages. *Ecological Economics,* 35: 47-61, special issue: The values of wetlands: landscape and institutional perspectives. DOI: 10.1016/S0921-8009(00)00167-1.

Barbier, E.B.; Hacker, S.D.; Kennedy,C.; Koch, E.W.; Stier, A.C.; Silliman, B.R. (2011) - The value of estuarine and coastal ecosystem services. *Ecological Monographs,* 81:169-193. DOI: 10.1890/10-1510.1

Batista, E.M.; Souza-Filho, P.W.M.; Silveira, O.F.M. (2009) - Avaliação de áreas deposicionais e erosivas em cabos lamosos da zona costeira amazônica através da análise multitemporal de imagens de sensores remotos. *Revista Brasileira de Geofísica*, 27(1):83-96. DOI: 10.1590/S0102-261X2009000500007.

Bernardy, R.J. (2000) - *Uso de sensoriamento remoto para análise ambiental do Parque Manguezal do Itacorubi, Florianópolis – SC*. Dissertação de Mestrado, Universidade Federal de Santa Catarina, Florianópolis, SC, Brasil. *Unpublished*.

Bonetti-Filho, J. (1996) - *Sensoriamento remoto aplicado à análise de ambientes costeiros impactados: avaliação metodológica – Baixada Santista. São Paulo*. Tese de Doutorado, Universidade de São Paulo, São Paulo, SP, Brasil. *Unpublished*.

Braga, R.A.P.; Uchoa, T.M.M.; Duarte, M.T.M.B. (1989) - Impactos ambientais sobre o manguezal de Suape - PE. *Acta Botanica Brasilica*, 3(2):9-27. DOI: 10.1590/S0102-33061989000300003.

Coelho, C.J.C. (2008) - *Lógica Fuzzy e geoprocessamento na determinação da vulnerabilidade à ocupação direta dos mangues na Bacia Hidrográfica do Anil na Ilha de São Luiz-MA*. Dissertação de Mestrado, Universidade Federal do Maranhão, Sã Luiz, MA, Brasil. *Unpublished*.

Cohen, M.C.L.; Lara, R.J. (2003) - Temporal changes of mangrove vegetation boundaries in Amazonia: Application of GIS and remote sensing techniques. *Wetlands Ecology and Management*, 11(4):223-231. DOI: 10.1023/A:1025007331075.

Conchedda, G.; Durieux, L.; Mayaux, P. (2008) - An object-based method for mapping and change analysis in mangrove ecosystems. *ISPRS Journal of Photogrammetry and Remote Sensing* 63:578-589. DOI: 10.1016/j.isprsjprs.2008.04.002

Costa, B.C.P. (2010) - *Avaliação ambiental de manguezais adjacentes aos campos petrolíferos de Macau e Serra (RN), como subsídio às medidas mitigadoras ao processo erosivo.* Dissertação de Mestrado, Universidade Federal do Rio Grande do Norte, Natal, RN, Brasil. *Unpublished*.

Cunha-Lignon, M. (2005) - *Ecologia de manguezais: Desenvolvimento espaço-temporal no sistema costeiro Cananéia-Iguapé, São Paulo, Brasil.* Tese de Doutorado, Universidade de São Paulo, São Paulo, SP, Brasil. *Unpublished*.

Cunha-Lignon, M.; Menghini, R. P.; Santos, L.C.M.; Niemeyer-Dinóla, C.; Schaeffer-Novelli, Y. (2009) - Análises espaço-temporais dos manguezais do estado de São Paulo (Brasil): subsídios à gestão costeira. *Revista Gestão Costeira Integrada,* 9(1): 79-91. DOI: 10.5894/rgci125.

Cunha-Lignon, M., Kampel, M. (2011) - Análise multitemporal de imagens Landsat para monitoramento de áreas de manguezal: subsídio à gestão costeira do litoral sul do Estado de São Paulo. In*: XV Simpósio Brasileiro de Sensoriamento Remoto*, pp. 5032-5038. INPE, São José dos Campos, Brazil. ISBN: 978-8517000560.

Cunha-Lignon, M.; Kampel, M.; Menghini, R.P; Schaeffer-Novelli, Y.; Cintrón, G.; Dahdouh-Guebas, F. (2011) - Mangrove forests submitted to depositional processes and salinity variation investigated using satellite images and vegetation structure surveys. *Journal of Coastal Research*, Special Issue 64:344-348.

Dahdouh-Guebas, F.; Zetterström, T.; Rönnbäck, P.R.;Troell, M.; Wickramasinghe, A.; Koedam, N. (2002) - Recent changes in land-use in the Pambala-Chilaw lagoon complex (Sri Lanka) investigated using remote sensing and GIS: conservation of mangroves vs. development of shrimp farming. *Environment, Development and Sustainability,* 4(2):185-200. DOI: 10.1023/A:1020887204285.

Dahdouh-Guebas, F.; Hettiarachchi, S.; Sooriyarachchi, S.; Lo Seen, D.; Batelaan, O.; Jayatissa, L.P.; Koedam, N. (2005a) - Transitions in ancient inland freshwater resource management in Sri Lanka affect biota and human populations in and around coastal lagoons. *Current Biology,* 15:579-586. DOI:10.1016/j.cub.2005.01.053.

Dahdouh-Guebas, F.; Jayatissa, L.P.; Di Nitto, D.; Bosire, J.O.; Lo Seen, D.; Koedam, N. (2005b) - How effective were mangroves as a defence against the recent tsunami? *Current Biology,* 15(12):443-447. DOI: 10.1016/j.cub.2005.06.008.

Dahdouh-Guebas, F.; Verheyden, A.; Kairo, J.; Jayatissa, L.; Koedam N. (2006) - Capacity building in tropical coastal resource monitoring in developing countries: a re-appreciation of the oldest remote sensing method. *International Journal of Sustainable Development and World Ecology*, 13:62-76. DOI: 10.1080/13504500609469662.

Dantas, S.T.P.L.; Amaro, V. E.; Costa, B.C.P. (2011) - Mangrove reforestation as a mesotidal coastal protection and clean development mechanism on Macau-Serra oil field, Potiguar Basin, Northeast Brazil. *Journal of Coastal Research*, Special Issue 64: 1268-1271.

Definiens Imaging GMBH. (2007) - *Definiens developer 7.* 195p. Definiens (The Imaging Intelligence Company), München, Germany.

Duke, N.C.; Meynecke, J.; Dittmann, A.M.; Ellison, A.M.; Anger, K.; Berger, U.; Cannicci, S.; Diele, K.; Ewel, K.C.; Field, C.D.; Koedam, N.; Lee, S.Y.; Marchand, C.; Nordhaus, I.; Daudouh-Guebas, F. (2007) - A world without mangroves? *Science,* 317:41-42. DOI: 10.1126/science.317.5834.41b.

Eastman, J. R. (2012) - *IDRISI Selva Manual*. 324p. Clark University.

Espíndola, C.R.S. (1986a) - Interpretação de dados MSS/Landsat para avaliar a distribuição física dos manguezais de Cananéia-Iguape (SP). *IV Simpósio Brasileiro de Sensoriamento Remoto*, pp. 604-614. INPE, São José dos Campos, Brazil. ISBN: 978-8517000485.

Espíndola, C.R.S. (1986b) - *Avaliação de dados MSS/LANDSAT para identificação e delimitação de manguezais na área de Cananeia-Iguape (Estado de São Paulo)*. Dissertação de Mestrado, Instituto Nacional de Pesquisas Espaciais, São José dos Campos, SP, Brasil. *Unpublished*.

Espinoza, H.C.F. (2008) - *Evolução temporal da cobertura vegetal do Rio Tavares (Florianópolis-SC) empregando sensoriamento remoto e SIG*. Dissertação de Mestrado, Universidade do Vale do Itajaí, Itajaí, SC, Brasil. *Unpublished*.

Espinoza, H.C.F.; Rosa, M.M.P.T. (2009) - Evolução Temporal da Cobertura Vegetal do Manguezal do Rio Tavares (Florianópolis-SC) Empregando Técnicas de Sensoriamento Remoto. In: *XIV Simpósio Brasileiro de Sensoriamento Remoto*, pp. 2705-2712. INPE, São José dos Campos, Brazil. ISBN: 978-8517000447.

FAO - Food and Agriculture Organization of the United Nations (2007) - *The world's mangrove 1980-2005*. 89p., FAO Forestry Paper, n. 153, Rome, Italy. ISBN: 978-9251058565.

Farnsworth, E.J.; Ellison, A.M. (1997) - The global conservation status of mangroves. *Ambio,* 26:328-334.

Feagin, R.A.; Mukherjee, N.; Shanker, K.; Baird, A.H.; Cinner, J., Kerr; A.M., Koedam, N.; Sridhar, A.; Arthur, R.; Jayatissa, L.P.; Lo Seen, D.; Menon, M.; Rodriguez, S.; Shamsuddoha, Md; Dahdouh-Guebas, F. (2010) - Shelter from the storm? Use and misuse of coastal vegetation bioshields for managing natural disasters. *Conservervation Letters* (1), 1-11. DOI: 10.1111/j.1755-263X.2009.00087.x

Florenzano, T.G. (2002) - *Imagens de satélite para estudos ambientais*. Oficina de Textos, São Paulo, Brazil. ISBN: 858623821X.

Giarrizzo, T.; Krumme, U. (2008) - Heterogeneity in intertidal fish fauna assemblages along the world's longest mangrove area in northern Brazil. *Journal of Fish Biology* 72(3):773-779. DOI: 10.1111/j.1095-8649.2007.01728.x

Giri, C.P.; Delsol, J.P. (1993) - Mangrove forest cover mapping in Phangnga Bay, Thailand, Using SPOT HRV and JERS-1 data in conjunction with GIS. *Proceedings of International Seminar on Remote Sensing for Coastal Zone and Coral Reef Applications*, Bangkok, Thailand.

Giri C.; Pengra, B.; Zhu, Z.L.; Singh, A.; Tieszen, L.L. (2007) - Monitoring mangrove forest dynamics of the Sundarbans in Bangladesh and India using multi-temporal satellite data from 1973 to 2000. *Estuarine Coastal and Shelf Science*, 73:91-100. DOI: 10.1016/j.ecss.2006.12.019

Godoy, M.D.P. 2015. *Alteração nas áreas de mangue em estuários do Estado do Ceará devido a mudanças nos usos do solo e mudanças climáticas.* Tese de Doutorado, Universidade Federal do Ceará, Fortaleza, CE, Brasil. *Unpublished*.

Green, E.P.; Clark, C.D.; Mumby, P.J.; Edwards, A.J.; Ellis, A.C. (1998) - Remote sensing techniques for mangrove mapping. *International Journal of Remote Sensing*, 19: 935-956. DOI: 10.1080/014311698215801.

Guimarães, A. S. (2007). *Análise multitemporal da superfície de manguezal do litoral norte de Pernambuco: a participação da aquicultura na conversão de áreas de mangue em viveiro.* Dissertação de Mestrado, Universidade Federal Rural de Pernambuco, Recife, PE, Brazil. *Unpublished*.

Guimarães, A.S.; Travassos, P.; Souza-Filho, P.W.M.; Gonçalves, F.D.; Costa, F. (2009) - Impact of aquaculture on mangrove areas in the northern Pernambuco Coast (Brazil) using remote sensing and geographic information system. *Aquaculture Research*, 41(6): 828-838. DOI: 10.1111/j.1365-2109.2009.02360.x

Herz, R. (1988) - *Distribuição dos padrões espectrais associados a estrutura física dos manguezais de um sistema costeiro subtropical*. Tese de Livre Docência, Instituto Oceanográfico da Universidade de São Paulo, São Paulo, SP, Brasil. *Unpublished*.

Herz, R. (1991) - *Os manguezais do Brasil*. 233p., CIRM, Instituto Oceanográfico da Universidade de São Paulo, SP, Brazil.

Heuman, B.W. (2011) - Satellite remote sensing of mangrove forests: Recent advances and future opportunities. *Progress in Physical Geography*, 35(1):87-108. DOI: 10.1177/0309133310385371.

Hirano, A.; Madden, M.; Welch, R. (2003) - Hyperspectral image data for mapping wetland vegetation. *Wetlands* 23:436-448. DOI: 10.1672/18-20

Huang, I.B.; Keisler, J.; Linkov, I. (2011) - Multi-criteria decision analysis in environmental sciences: ten years of applications and trends. *Science of the Total Environment*, 409:3578-3594. DOI: 10.1016/j.scitotenv.2011.06.022

Hunsaker, C.T.; Goodchild, M.F.; Friedl, M.A.; Case, T. J. (2001) - Spatial uncertainty in ecology-Implications for remote sensing and GIS applications. 402p. Springer-Verlag, New York. ISBN: 978-1461302094.

INPE - Instituto Nacional de Pesquisas Espaciais. (2015) - CBERS 3 and 4 Cameras. Instituto Nacional de Pesquisas Espaciais, Sào José dos Campos, Brasil. Available on-line at http://www.cbers.inpe.br/ingles/satellites/cameras_cbers3_4.php

Jensen, J.R. (2009) - *Sensoriamento Remoto do Ambiente - Uma Perspectiva em Recursos Terrestres*. 598p., Editora Parêntese, São José dos Campos, Brazil. ISBN: 978-8560507061.

Jesus, A.S. (2010) - *Alteração da paisagem na região estuarina do Rio São Francisco no período de 1987 a 2006*. Dissertação de Mestrado, Universidade Federal de Sergipe, São Cristovão, SE, Brasil. *Unpublished*.

Kampel, M.; Amaral, S.; Soares, M.L.G. (2005). Imagens CCD/CBERS e TM/Landsat para análise multi-temporal de manguezais no Nordeste brasileiro. Um estudo no litoral do Estado do Ceará. In: *XII Simpósio Brasileiro de Sensoriamento Remoto*, pp. 979-986. INPE, São José dos Campos, Brazil. ISBN: 8517000188.

Kovacs, J.M. (2000) - Perceptions of environmental change in a tropical coastal wetland. *Land Degradation & Development,* 11:209-220. DOI: 10.1002/1099-145X(200005/06)11:3<209::AID-LDR378>3.0.CO;2-Y.

Kovacs, J.M., Flores-Verdugo, F., Wang, J., Aspden, L.P. (2004) - Estimating leaf area index of a degraded mangrove forest using high spatial resolution satellite data. *Aquatic Botany* 80(1): 13-22. DOI: 10.1016/j.aquabot.2004.06.001.

Kovacs, J.M.,Wang, J.; Flores-Verdugo, F. (2005) - Mapping mangrove leaf area index at the species level using IKONOS and LAI-2000 sensors for the Agua Brava Lagoon, Mexican Pacific. *Estuarine, Coastal and Shelf Science*, 62:377-384. DOI: 10.1016/j.ecss.2004.09.027

Krause, G.; Bock, M.; Weiers, S.; Braun, G. (2004) - Mapping land-cover and mangrove structures with remote sensing techniques: a contribution to a synoptic GIS in support of coastal management in North Brazil. *Environmental Management*, 34(3):429-440. DOI: 10.1007/s00267-004-0003-3

Kuenzer, C.; Bluemel, A.; Gebhardt, S.; Quoc, T.V.; Dech, S. (2011) - Remote sensing of mangrove ecosystems: a review. *Remote Sensing*, 3:878-928. DOI: 10.3390/rs3050878

Lara, R.; Szlafsztein, C.; Cohen, M.; Berger, U.; Glaser, M. (2002) - Implications of mangrove dynamics for private land use in Bragança, North Brazil: a case study. *Journal of Coastal Conservation*, 8(1):97-102. DOI: 10.1652/1400-0350(2002)008[0097:IOMDFP]2.0.CO;2.

Lardosa, E.I. (2011) - *Mapeamento dos remanescentes de manguezal, através da interpretação de ortofotos coloridas, e análise de vetores de pressão antrópica, como subsídio ao planejamento para conservação do ecossistema no Estado do Rio de Janeiro*. Tese de Doutorado, Universidade do Estado do Rio de Janeiro, Rio de Janeiro, RJ, Brasil. *Unpublished*.

Lardosa, E.I.; Simões, M.;Soares, M.L.G. (2013) - Cartografia das áreas de ocorrência de manguezais no Estado do Rio de Janeiro através da integração de múltiplas fontes de dados. *Revista Brasileira de Cartografia*, 65(1):1-14. Available on-line at http://www.lsie.unb.br/rbc/index.php?journal=rbc&page=article&op=view&path%5B%5D=494&path%5B%5D=549

Lillesand, T.M.; Kiefer, R.W.; Chipman, J.W. (2008) - *Remote sensing and image interpretation.* 726p. John Wiley & Sons: Minnesota University. ISBN: 978-1118343289

Luchiari, A.; Kawakubo, F.S.; Morato, R.G. (2009) - Aplicações do Sensoriamento remoto na geografia. In: Venturi, L.A.B. (org.) *Praticando Geografia: técnicas de campo e laboratório em geografia e análise ambiental*. pp. 33-54, Oficina de textos, São Paulo, Brasil. ISBN: 978-8586238444.

Lugli, D.O. (2004) - *Caracterização ecológica do apicum do manguezal do Rio Tavares, Florianópolis, Santa Catarina*. Dissertação de Mestrado, Universidade do Vale do Itajaí, Itajaí, SC, Brasil. *Unpublished*.

Machado, A. L. (1992) - *Análise da cobertura vegetal de um manguezal impactado por óleo, Canal de Bertioga, Estado de São Paulo*. Dissertação de Mestrado, Universidade de São Paulo, São Paulo, SP, Brasil. *Unpublished*.

Magris, R.A.; Barreto, R. (2010) - Mapping and assessment of protection of mangrove habitats in Brazil. *Pan-American Journal of Aquatic Sciences*, 5(4):546-556. Available on-line at: http://www.panamjas.org/pdf_artigos/PANAMJAS_5(4)_546-556.pdf

Maia, L.P.; Lacerda, L.D. (2006) - *Atlas dos manguezais do nordeste brasileiro: avaliação das áreas de manguezais dos Estados do Piauí, Ceará, Rio Grande do Norte, Paraíba e Pernambuco.* 124p. SEMACE, Fortaleza, Ceará, Brasil.

Martins, P.T.A. (2008) - *Análise das intervenções antrópicas no manguezal do Rio Cachoeira, Ilhéus, Bahia.* Dissertação de Mestrado, Universidade Federal de Sergipe, São Cristóvão, SE, Brasil. *Unpublished*.

Martins, P.T.A.; Wanderley, L.L. (2009) - Dinâmica de ocupação espacial de áreas contíguas (período 1987-2008) e sua relação com tensores de origem antrópica no manguezal do Rio Cachoeira, Ilhéus, Bahia. *Sociedade & Natureza*, 21(2):77-89. Available on-line at: http://www.seer.ufu.br/index.php/sociedadenatureza/article/view/9566/5776

Medeiros, M.L. (2009) - Estudo Multitemporal da dinâmica espacial do estuário Potengui/RN, utilizando como base os dados de sensoriamento remoto. Dissertação de Mestrado, Universidade Federal do Rio Grande do Norte, Natal, RN, Brasil. *Unpublished*.

Melo, A.T. (2008) - *Aspectos ecológicos da formação de um manguezal em área de aterro hidráulico (via expressa sul, Florianópolis, SC), através de mapeamento.* Dissertação de Mestrado, Universidade Federal de Santa Catarina, Florianópolis, SC, Brasil. *Unpublished*.

Meneghetti, G.T. (2013) - Classificação da cobertura da terra do Município de Raposa (MA) com imagens WorldView2 utilizando o aplicativo INTERIMAGE e mineração de dados. Dissertação de Mestrado, Instituto Nacional de Pesquisas Espaciais, São José dos Campos, SP, Brasil. *Unpublished*.

Meneghetti, G.T.; Kux, H. J. H. (2014) - Mapeamento da cobertura da terra do município de Raposa (MA) utilizando imagens WorldView2, o aplicativo INTERIMAGE e Mineração de Dados. *Revista Brasileira de Cartografia*, 66(2): 365-377. Available on-line at http://www.lsie.unb.br/rbc/index.php?journal=rbc&page=article&op=view&path%5B%5D=547&path%5B%5D=684

Menghini, P.M. (2008). *Dinâmica da recomposição natural em bosques de mangue impactados: Ilha Barnabé (Baixada Santista), SP, Brasil*. Tese de Doutorado, Universidade de São Paulo, São Paulo, SP, Brasil. *Unpublished*.

Mukherjee, N.; Dahdouh-Guebas, F.; Kapoor, V.; Arthur, R.; Koedam, N.; Sridhar, A.; Shanker, K. (2010) - From bathymetry to bioshields: a review of post-tsunami ecological research in India and its implications for policy. *Environental Management* 46(3):329-339. DOI: 10.1007/s00267-010-9523-1.

Nagelkerken, I.; Blaber, S.J.M.; Bouillon, S.; Green, P.; Haywood, M.; Kirton, L.G.; Meynecke, J.-O.; Pawlik, J.; Penrose, H.M.; Sasekumar, A.; Somerfield, P.J. (2008) - The habitat function of mangroves for terrestrial and marine fauna: a review. Aquatic. Botany. 89(2):155-185. DOI: 10.1016/j.aquabot.2007.12.007.

Nascimento, W.R.; Souza-Filho, P.W.M.; Proisy, C.; Lucas, R.M.; Rosenqvist, A. (2013) - Mapping changes in the largest continuous Amazonian mangrove belt using object-based classification of multisensor satellite imagery. *Estuarine, Coastal and Shelf Science*, 117:83-93. DOI: 10.1016/j.ecss.2012.10.005.

Noernberg, M.A.; Lautert, L.F.C.; Araujo, A.D. (2006) - Remote sensing and GIS integration for modelling the Paranagua estuarine complex-Brazil. *Journal of Coastal Research*, Special Issue 39:1627-1631.

Novo, E.M.LM. (2011) - *Sensoriamento remoto: princípios e aplicações*. 4th edition, 387p., Blucher, São Paulo, Brazil. ISBN: 978-8521205401.

Oliveira, C.P.L. (2001) - *Evolução temporal do manguezal do Rio Tavares (Florianópolis-SC) utilizando a foto-interpretação*. Dissertação de Mestrado, Universidade Federal de Santa Catarina, Florianópolis, SC, Brasil. *Unpublished*.

Pereira, F.R.S. (2011) - *Utilização de radar de abertura sintética no estudo da tipologia e da estrutura de bosques de mangue no litoral sul de São Paulo, Brasil*. Dissertação de Mestrado, Instituto Nacional de Pesquisas Espaciais, São José dos Campos, SP, Brasil. *Unpublished*.

Pereira, F.R.S; Kampel, M.; Cunha- Lignon, M. (2012) - Mapping of mangrove forests on the southern coast of São Paulo, Brazil, using synthetic aperture radar data from ALOS/PALSAR. *Remote Sensing Letters*, 3(7):567-576, DOI: 10.1080/01431161.2011.641511.

Pires, I.O. (1992) - *Monitoramento de manguezais através de correlação de dados da fitomassa e de radiância TM/LANDSAT. Exemplo: APA-Guapimirim (RJ).* Tese de Doutorado, Universidade de São Paulo, São Paulo, SP, Brasil. *Unpublished*.

Portugal, A.M.M. (2002) - *Manguezais de Guaratiba frente à perspectiva de elevação do nível médio relativo do mar, Baía de Sepetiba, Estado do Rio de Janeiro Brasil*. Dissertação de Mestrado, Universidade de São Paulo, São Paulo, SP, Brasil. *Unpublished*.

Primavera, J.H. (2000) - Development and conservation of Philippine mangroves: institutional issues. *Ecological Economics,* 35:91-106. DOI: 10.1016/S0921-8009(00)00170-1.

Reis-Neto, A.S.; Cunha-Lignon, M.; Arruda-Reis, M.C.C.; Meireles, A.J.A. (2011) - The Ceará river mangrove's landscape (northeast Brazil): comparative analyses of 1968 and 2009. *Journal of Coastal Research*, Special Issue 64:1802-1805.

Reis-Neto, A.S.; Meireles, A.J.A; Cunha-Lignon, M. (2013) - Analyses of the mangrove's rehabilitation process in abandoned saltwork area, in the Ceará River, Northeast Brazil. *International Journal of Applied and Natural Sciences* (ISSN: 2319-4014) 2(5):27-36..

Rodrigues, S.W.P.; Souza-Filho, P.W.M. (2011) - Use of multi-sensor data to identify and map tropical coastal wetlands in the Amazon of Northern Brazil. *Wetlands*, 31(1):11-23. DOI: 10.1007/s13157-010-0135-6.

Santos, A.S.P. (2009) - *Dinâmica da paisagem na foz do rio Poxim em Aracaju - SE (1961-2003).* Dissertação de Mestrado, Universidade Federal de Sergipe, São Cristóvão, SE, Brasil. *Unpublished*.

Santos, V.F.; Polidori, L.; Da Silveira, O.F.M.; De Figueiredo, Jr., A.G. (2009) - Aplicação de dados multisensor (SAR e ETM+) no reconhecimento de padrões de uso e ocupação do solo em costas tropicais: Costa Amazônica, Amapá, Brasil. *Revista Brasileira de Geofisica*, 27(1):39-55. DOI: 10.1590/S0102-261X2009000500004.

Santos, A.L.G. (2010) - *Manguezais da Baixada Santista: alterações e permanências (1962-2009).* Dissertação de Mestrado, Universidade de São Paulo, São Paulo, SP, Brasil. *Unpublished*.

Santos, L.C.M. (2010) - *Sistema estuarino-lagunar do Rio São Francisco, zona costeira de Sergipe, Brasil: uso e cobertura da terra e diagnóstico ambiental dos manguezais*. Dissertação de Mestrado, Universidade de São Paulo, SP, Brasil. *Unpublished*.

Santos, L.C.M.; Cunha-Lignon, M.; Schaeffer-Novelli, Y.; Cintrón-Molero, G. (2012) - Long-term effects of oil pollution in mangrove forests (Baixada Santista, Southeast Brazil) detected using a GIS-based multitemporal analysis of aerial photographs. *Brazilian Journal of Oceanography*, 60(2):159-170. DOI: 10.1590/S1679-87592012000200006

Santos, L.C.M.; Bitencourt, M.D. (2013) - Imagens CBERS para o estudo de manguezais do Brasil: aplicações, potencialidades e limitações. In: *XVI Simpósio Brasileiro de Sensoriamento Remoto*, pp. 2226 - 2233. INPE, São José dos Campos, Brazil. ISBN: 978-8517000669.

Santos, L.C.M.; Matos, H.R.; Schaeffer-Novelli, Y; Cunha-Lignon, M.; Bitencourt, M.D; Koedam N.; Dahdouh-Guebas, F. (2014) - Assessment of anthropogenic pressures in the São Francisco River Estuary, (Northeast Brazil): a GIS-based analysis of CBERS and SPOT satellite images to aid local mangrove forest management. *Ocean and Coastal Management*, 89:39-50. DOI: 10.1016/j.ocecoaman.2013.12.010

Santos, L.C.M. (2015) - A pesca nos manguezais no Estuário do Rio São Francisco: uma abordagem sócio-ecológica com ênfase no caranguejo *Ucides cordatus* (Linnaeus 1763). 169p. Tese de Doutorado, Universidade de São Paulo, São Paulo, SP, Brasil. *Unpublished*.

Santos, L.C.M.; Dadouh-Guebas, F.; Bitencourt, M. D. (2015) - Multi-criteria evaluation for the conservation of the mangrove crab Ucides cordatus: a case study in the São Francisco River Estuary (Northeastern Brazil). In: *XVII Simpósio Brasileiro de Sensoriamento Remoto*, pp. 5392-5399. INPE, São José dos Campos, Brazil. ISBN: 978-851700768.

Santos, L.C.M.; Rollo, M.M.; Costa, T.M.; Pinheiro. M.A.A.; Dahdouh-Guebas, F.; Bitencourt, M.D. (*in press*) - Spatial analysis of a coastal area for conservation and fishery of mangrove edible crab (*Ucides cordatus*). *Journal of Coastal Research*, Special Issue 75.

Satyanarayana, B.; Mulder, S.; Jayatissa, L.P.; Dahdouh-Guebas F. (2013) - Are the mangroves in the Galle-Unawatuna area (Sri Lanka) at risk? A social-ecological approach involving local stakeholders for a better conservation policy. *Ocean and Coastal Management* 71:225-237. DOI: 10.1016/j.ocecoaman.2012.10.008.

Schaeffer-Novelli, Y.; Cintrón-Molero, G.; Adaime, R. R. Camargo, T.M. (1990) - Variability of mangrove ecosystems along the Brazilian Coast. *Estuaries*, 13(2):204-219. DOI: 10.2307/1351590.

Silva, J.Q. (2009) - *Estudo comparativo dos índices de reflectância da vegetação de manguezal e várzea-de-maré do litoral paraense através de sensoriamento remoto e técnicas espectrofotométricas.* Dissertação de Mestrado, Universidade Federal do Pará, Belém, PA, Brasil. *Unpublished*.

Silva, E.D.O. (2010) - *Evolução espaço-temporal do manguezal do estuário do Rio São Mateus empregando técnicas de sensoriamento remoto*. Dissertação de Mestrado, Universidade Federal do Espírito Santo, Vitória, ES, Brasil. *Unpublished*.

Silva, J.B. (2012) - *Sensoriamento remoto aplicado ao estudo do ecossistema manguezal em Pernambuco.* Tese de Doutorado, Universidade Federal de Pernambuco, Recife, PE, Brasil. *Unpublished*.

Silva, G. F.; Almeida, P. M. M.; Cardoso, P. V.; Rosário, L. S.; Cruz, C. B. M. (2013) - O uso da classificação baseada em objeto no estudo das mudanças nos manguezais da região metropolitana do Rio de Janeiro dos anos 1994/2007 - Brasil. *XVI Simpósio Brasileiro de Sensoriamento Remoto*, pp. 3047-3053. INPE, São José dos Campos, Brazil. ISBN: 978-8517000669.

Simard, M.; Zhang, K.; Rivera-Monroy, V.H.; Ross, M.; Ruiz, P.; Castaneda- Moya, E.; Rodriguez, E.; Twilley, R. (2006) - Mapping mangrove height and estimate biomass in the Everglades using SRTM elevation data. *Photogrammetric Engineering and Remote Sensing*, 72(3):299-311. Available on-line at http://eserv.asprs.org/PERS/2006journal/mar/2006_mar_299-311.pdf.

Simard, M.; Rivera-Monroy, V.H.; Mancera-Pineta, J.E.; Castañeda-Moya, E.; Twilley,R.R. (2008) - A systematic method for 3D mapping of mangrove forest based on Shuttle Radar Topography Mission elevation data, ICEsat/GLAS waveforms and field data: Application to Ciénaga Grande de Santa Marta, Colombia. *Remote Sensing of Environment,* 112:2131-2144. DOI: 10.1016/j.rse.2007.10.012

Soares, M.L.G.; Schaeffer-Novelli, Y. (2005) - Above-ground biomass of mangrove species. I. Analysis of models. *Estuarine, Coastal and Shelf Science*, 65:1-18. DOI: 10.1016/j.ecss.2005.05.001.

Souza-Filho, P.W.M. (2000) - Avaliação e aplicação de dados de sensores remotos no estudo de ambientes costeiros tropicais úmidos, Bragança, Norte do Brasil. Tese de Doutorado, Universidade Federal do Pará, Belém, PA, Brasil. *Unpublished*.

Souza-Filho, P.W.M.; Paradella W.R. (2002) - Recognition of the main geobotanical features along the Bragança mangrove coast (Brazilian Amazon Region) from Landsat TM and RADARSAT-1 data. *Wetlands Ecology and Management*, 10(2): 123-132. DOI: 10.1023/A:1016527528919.

Souza-Filho, P.W.M.; Paradella, W.R. (2003) - Use of synthetic aperture radar for recognition of coastal geomorphological features, land-use assessment and shoreline changes in Bragança coast, Para, Northern Brazil. *Anais da Academia Brasileira de Ciências*, 75(3):341-356. DOI: http://dx.doi.org/10.1590/S0001-37652003000300007.

Souza Filho, P.W.M. (2005) - Costa de manguezais de macromaré da Amazônia: cenários morfológicos, mapeamento e quantificação de áreas usando dados de sensores remotos. *Revista Brasileira de Geofisica*, 23(4):427-435. DOI: 10.1590/S0102-261X2005000400006.

Souza-Filho, P.W.M.; Paradella, W.R. (2005) - Use of RADARSAT-1 fine mode and Landsat-5 TM selective principal component analysis for geomorphological mapping in a macrotidal mangrove coast in the Amazon Region. *Canadian Journal of Remote Sensing,* 31(3):214-224. DOI: 10.5589/m05-009

Souza-Filho, P.W.M.; Gonçalves, F.D.; Beisl, C.H.; Miranda, F.P.; Almeida, E.F.; Cunha, E.R. (2005) - Sistema de observação costeira e o papel dos sensores remotos no monitoramento da costa norte brasileira, Amazônia. *Revista Brasileira de Cartografia*,

57(2):79-86. Available on-line at http://www.lsie.unb.br/rbc/index.php?journal=rbc&page=article&op=view&path%5B%5D=135&path%5B%5D=118.

Souza-Filho, P.W.M.; Farias-Martins, E.D.S.; Da Costa, F.R. (2006) - Using mangroves as a geological indicator of coastal changes in the Bragança macrotidal flat, Brazilian Amazon: a remote sensing data approach. *Ocean & Coastal Management*, 49:462-475. DOI: 10.1016/j.ocecoaman.2006.04.005

Souza-Filho, P.W.M.; Goncalves, F.D.; Rodrigues, S.W.P. (2009) - Multi-sensor data fusion for geomorphological and environmental sensitivity index mapping in the Amazonian mangrove coast, Brazil. *Journal of Coastal Research*, Special Issue 56:1592-1596.

Souza-Filho, P.W.M.; Paradella, W.R.; Rodrigues, S.W.P.; Costa, F.R.; Mura, J.C.; Gonçalves, F.D. (2011) - Discrimination of coastal wetland environments in the Amazon region based on multi-polarized L-band airborne Synthetic Aperture Radar imagery. *Estuarine, Coastal and Shelf Science*, 95(1):88-98. DOI: 10.1016/j.ecss.2011.08.011

Spalding, M.; Kainuma, M.; Collins, L. (2010) - *World atlas of mangroves*. Earthscan, London, Washington, DC. ISBN 978-1844076574.

Teixeira, S.G.; Souza-Filho, P.W.M. (2009) - Mapeamento de ambientes costeiros tropicais (Golfão Maranhense, Brasil) utilizando imagens de sensores remotos orbitais. *Revista Brasileira de Geofísica* 27(1):69-82. DOI: 10.1590/S0102-261X2009000500006.

Tenório, G.S.; Souza-Filho, P.W.M.; Ramos, E.M.L.S.; Alves, P.J.O. (2015) - Mangrove shrimp farm mapping and productivity on the Brazilian Amazon coast: Environmental and economic reasons for coastal conservation. *Ocean & Coastal Management* 104:65-77. DOI: 10.1016/j.ocecoaman.2014.12.006.

USGS - United States Geological Survey. (2015) - *Frequently Asked Questions about the Landsat Missions*. United States Geological Survey, USA. Available on-line at http://landsat.usgs.gov/band_designations_landsat_satellites.php

Vale, C. C. (1999) - *Contribuição ao estudo dos manguezais como indicadores biológicos das alterações geomórficas do Estuário do Rio Mateus (ES).* Dissertação de Mestrado, Universidade de São Paulo, São Paulo, SP, Brasil. *Unpublished*.

Vale, C. C. (2004) - Séries geomórficas costeira do Estado do Espírito Santos e os habitats para o desenvolvimento dos manguezais: uma visão sistêmica. Tese de Doutorado, Universidade de São Paulo, São Paulo, SP, Brasil. *Unpublished*.

Valiela, I.; Bowen, J.L.; York, J.K. (2001) - Mangrove forests: one of the world's threatened major tropical environments. *Bioscience,* 51(10):807-815. DOI: 10.1641/0006-3568(2001)051[0807:MFOOTW]2.0.CO;2.

Vasconcelos, A.O. (2009) - *Análise multitemporal da área de proteção ambiental de Guapimirim utilizando técnicas de segmentação e classificação orientada a objeto de imagens IKONOS II dos anos 2006 e 2008.* Dissertação de Mestrado, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ, Brasil. *Unpublished*.

Vasconcelos, A.O. ; Landau,L.; Miranda, F.P. (2011). Multitemporal analysis of a mangrove ecosystem in Southeastern Brazil using object-based classification applied to IKONOS II data. *MultiTemp, IEEE*, pp.169-172. ISBN: 978-1457712036.

Vieira, S.L. (2007) - *Transdisciplinaridade aplicada à gestão ambiental de unidade de conservação. Estudo de caso: manguezal do Itacorubí. Florianópolis/SC. Sul do Brasil.* Tese de Doutorado, Universidade Federal de Santa Catarina, Florianópolis, SC, Brasil. *Unpublished*.

Wang, L.; Souza-Filho, W.P.; Gong, P. (2004a) - Integration of object-based and pixel-based classification for mapping mangroves with IKONOS imagery. *International Journal of Remote Sensing*, 25:5655-5668. DOI: 10.1080/014311602331291215

Wang L.; Souza-Filho, W.P.; Gong P.; Biging, G.S. (2004b) - Comparison of IKONOS and QuickBird images for mapping mangrove species on the Caribbean coast of Panama. *Remote Sensing of Environment*, 91:432-440. DOI: 10.1016/j.rse.2004.04.005

Yang, C.; Everitt, J.H.; Fletcher, R.S.; Jensen, R.R.; Mausel, P.W. Evaluating AISA+ hyperspectral imagery for mapping black mangrove along the South Texas Gulf Coast. *Photogrammetric Engineering & Remote Sensing*, 75:425-435. Available on-line at http://eserv.asprs.org/PERS/2009journal/apr/2009_apr_425-435.pdf

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Temporal evolution of the contamination in the southern area of the Patos Lagoon estuary, RS, Brazil*

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ABSTRACT

The southern area of the Patos Lagoon estuary has been subjected to intense industrial and port-related activities which have not only caused meaningful changes in the landscape but also degraded aquatic resources by contaminating them with dissolved nutrients and trace metals in the last decades. This study aims at compiling data on the development that has happened in the urban and industrial occupation in Rio Grande, a city located in the south of Rio Grande do Sul, RS, Brazil, by relating it to the main results of contamination indicators in the estuarine environment regarding water, sediment, soil and atmosphere. Bibliographic data have shown an increase in domestic effluents around the city in the 1980's, mainly in more sheltered areas, such as the Saco da Mangueira, where cyanobacteria eutrophication has often occurred because of the high concentration of nutrients. The content of trace metals in the water of channel areas of the estuary was always lower than the maximum limit established by Brazilian quality criteria. However, the sediment showed higher concentrations of some trace metals (e.g. copper, lead, nickel, vanadium and zinc), the metalloid As and Hg than the maximum concentrations established by the legislation, mainly in several places around urban, industrial and port areas. The labile fraction (or potentially bioavailable) in the water and in the sediment showed that trace metals have provided significant contributions to sheltered areas, such as marinas, but have exceeded in shipyards. Trace metals in the urban soil and man-made ground of the city indicated that there were anthropogenic contributions, mainly by mercury. Anomalies in the content of lead found in the atmospheric particulate matter and acid rain were also reported. Therefore, more severe environmental policies, effective control, industrial wastewater treatment and control of atmospheric emissions must be carried out in order to maintain environmental quality and public health. The city authorities in Rio Grande need to implement the existing integrated estuary management program in a proper and practical way, involving stakeholders and local governments.

Keywords: contamination, nutrients, trace metals, estuary, environmental management

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RESUMO

Evolução temporal da contaminação na área sul do estuário da Lagoa dos Patos, RS, Brasil

A parte sul do estuário da Lagoa dos Patos apresenta intensa atividade portuária e industrial, sendo que estas propiciaram nas últimas décadas alterações significativas na paisagem e na degradação dos recursos hídricos, incluindo a contaminação por nutrientes dissolvidos e por metais traço. Este estudo visa compilar uma revisão dos impactos resultantes do desenvolvimento da ocupação urbana, industrial e naval da cidade do Rio Grande ao longo dos anos, procurando relacioná-los com os principais resultados de indicadores da contaminação do ambiente estuarino nos compartimentos água, sedimento, solo e atmosfera da região. Os dados bibliográficos indicaram um acréscimo do lançamento de efluentes domésticos ao redor da cidade nos anos de 1980, principalmente em área mais abrigadas do estuário como o Saco da Mangueira, o que vem promovendo desequilíbrios tróficos (hipertrofia das águas de margem) e frequente florações de cianobactérias, devido ao aporte de nutrientes. Os teores de metais traço na água de áreas de canal no estuário se encontram dentro dos limites estabelecidos pela legislação vigente. Entretanto, o sedimento demonstrou altas concentrações de alguns metais traço (por ex. cobre, chumbo, níquel, vanádio e zinco), o metaloide As e o Hg, acima do estabelecido pela legislação, principalmente em vários locais ao redor da área urbana, industrial e portuária da cidade. A fração lábil (ou potencialmente biodisponível) de metais traço em água e sedimento indicaram contribuições significativas em áreas abrigadas como marinas e excederam em áreas de estaleiros. Metais traço nos solos e os aterros da cidade mostraram contribuições antropogênicas, com destaque para o mercúrio. Anomalias nos teores de chumbo no material particulado atmosférico e chuva ácida foram também reportados. Urge uma política ambiental mais severa e com efetiva fiscalização, proibindo fluentes clandestinos, exigindo tratamento básico dos efluentes pelas indústrias e controle das emissões atmosféricas, que vise a manutenção da qualidade ambiental e saúde pública da população que vive na área estuarina. O poder público do município de Rio Grande deve implementar de forma apropriada e prática o existente programa de gestão integrada para o estuário, envolvendo as partes interessadas e governantes locais.

Palavras-Chave: *contaminação, metais traço, nutrientes, estuário, gestão ambiental*

1. Introduction

Estuaries hold a large number of organisms and high biological productivity. They are privileged areas not only because they favor their multiple use, regarding urban, port and industrial occupation on its shoreline, but also because their waters can be used for sailing, fishing and leisure activities (Clark, 2001). The multiple uses of the estuaries enable the input of anthropogenic elements in the aquatic environment not only through urban and industrial effluents, but also through the precipitation of industrial air emissions. Other events, such as accidental chemical release from vessels, may also affect the fauna and the flora of the estuarine environment in the short or in the long term, depending on how long the aquatic environment can stand it (Burgin & Hardiman, 2011; Law *et al*., 2003). Therefore, activities that pose risk to the quality of the estuarine water may generate conflicts concerning the use of the environment. They may also harm other sectors such as local fisheries, which often have their production decreased (Cicin-Sain & Knecht, 1998).

Assessment of the estuarine environmental quality is needed since it enables the temporal evolution of the impact of human related activities on local contamination to be followed, moreover providing diagnoses to be used as a basis of environmental management programs. In addition, it is a tool to be applied to environmental actions that are carried out by policy makers and environmental managers in order to improve the quality of the estuary. In general, studies of the estuarine environment and its surrounding area are conducted in a specific environmental compartment (water, sediment, biota, rainwater or dry atmospheric precipitations) for various years to verify the contamination level and its relation with the urban and industrial development of a region. This is the scenario of studies that have been carried out in the southern area of the Patos Lagoon estuary in the southern coast of Rio Grande do Sul, Brazil (*e.g*. Baumgartem *et al.*, 1995; Mirlean *et al.*, 2000, 2005b. 2008, 2009; Costa & Wallner-Kersanach, 2013; Guttierrez, 2013).

This estuary has been receiving higher amounts of nutrients and trace metals of anthropogenic origin in the last 15 years due to the increase in port, naval and industrial activities in the region. Therefore, this study aims at providing knowledge about the impact of human related activities, namely the development of the urban and industrial in Rio Grande, the main city located in the southern shoreline of the Patos Lagoon. For this assessment, studies of nutrients in water and trace metals in water, sediment, soil and atmosphere that have been carried out in the study area for 35 years were considered.

2. The Patos Lagoon and its estuarine area

The Patos Lagoon stretches over 10,360 km^2 on the coastal plain in the Rio Grande do Sul state. It is considered the largest choked-type coastal lagoon (Kjerfve, 1986) (Figure 1). Fluvial systems that comprise the hydrographic basin of the Guaíba system (the Jacuí, Taquarí, Caí, Sinos and Gravataí Rivers) are located in the north of the lagoon and supply 86% of its average total freshwater input. The freshwater discharge of the Guaíba River may vary from 41-22,000 $m^3 s^{-1}$ with an

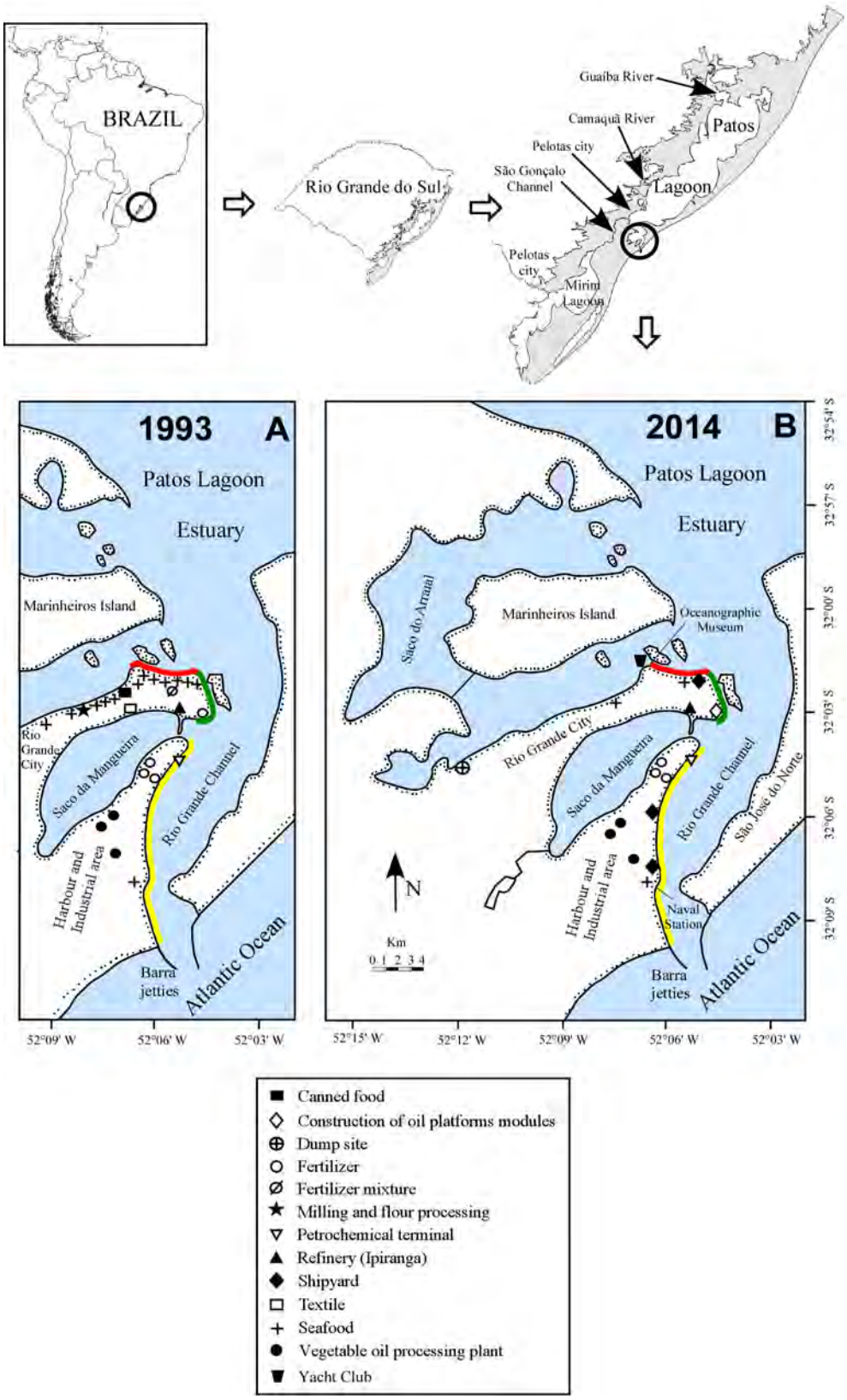

Figure 1 - The estuary of Patos Lagoon, the city of Rio Grande and the location of industrial, naval and port activities that contribute to potential contamination by wastewater and / or air emissions for the estuarine water during the years 1993 (A) and 2014 (B). Porto Velho (■), Porto Novo (■) e Super Porto (■). Figure A was adapted from Almeida *et al.* (1993).

Figura 1 - O estuário da Lagoa dos Patos, a cidade de Rio Grande e a localização das atividades indústriais, navais e portuárias que contribuem com uma potencial contaminação através de efluentes e/ou emissões atmosféricas para as águas estuarinas durante os anos de 1993 (A) e 2014 (B). Áreas portuárias: Porto Velho (■), Porto Novo (■) e Super Porto (■). Figura A foi modificada de Almeida et al. (1993).

annual mean around 1,000 $m^3 s^{-1}$. In the middle course, west of the lagoon, the Camaquã River is an important fluvial system because of its inflow contribution to the lagoon reaching 5,000 $m^3 s^{-1}$ during flood periods (Möller & Castaing, 1999). The São Gonçalo Channel, whose aquatic contribution comes from the Mirim Lagoon, is located in the low course of the lagoon.

These rivers represent the major transport pathway of nutrients and suspended matter to the estuary. Because the Patos Lagoon is over 250 km long, the time that water takes to travel from Guaíba River (Figure 1) to the estuarine region is about 20 days (Herz, 1977). Therefore, nutrients originated from rivers have a high residence time within the lagoon before reaching the estuarine region, where biogeochemical processes may result in their consumption (Nienscheski *et al.*, 1999).

The estuarine area of the Patos Lagoon stretches over the southern portion of the lagoon, where seawater entrance reaches its average limit in Ponta da Feitoria, close to Pelotas city (Möller & Castaing, 1999). Even though the estuary has high hydrodynamic rate, mainly conditioned by the wind strength and direction, the tidal effect (0.4 m) is minor. Its narrow channel communicates with the Atlantic Ocean and enables high outflow of lagoon waters, which may reach 25,000 $m^3 s^{-1}$ in low tide (Herz, 1977). During winter (June-August) and El Niño events the high freshwater discharge practically replaces salt water and occupies the entire lagoon system (Pasquini *et al.*, 2012) and the calculated freshwater residence time is *c*. 5 months (Windom *et al.*, 1999).

The lagoon has high primary productivity which supports nurseries of several species of mollusks, crustaceans and fish that use this environment in their whole or partial life cycle (Odebrecht *et al*., 2010). Many species, such as the shrimp *Penaeus paulensis*, have commercial interest within the estuarine area. Since there are in this area activities related to the port, fishery, navigation, leisure, moreover transportation and vessel repair in this area, their impact can be seen in the vicinity of the estuary.

The estuarine area has been a receptor of several urban, industrial and agricultural effluents, especially from the cities of Rio Grande, Pelotas and São José do Norte (Odebrecht *et al*., 2010).

Several studies carried out in this estuary have shown that there is considerable contamination by trace elements pollutants in different environmental compartments (soil, sediment, water, biota) in the Rio Grande area (Garcia *et al.*, 2010; Mirlean *et al.*, 2005a, 2008; 2009). The chemical elements that stand out as subjects of concern because of their harmful effects on the environment and public health are Pb, Hg and As.

To understand the cause of this contamination by trace metals in the Rio Grande area is necessary to understand the history of the urban and industrial development of the city. The development of the city is related with the creation and expansion of the port area, which is divided in Porto Velho, Porto Novo and Super Porto (Text A in SI-I, see Supporting Information).

This development triggered the need to update the study conducted by Almeida et al (1993) as shown in Figure 1A, because Rio Grande only collects and treats about 33% of its sewage currently. Its treatment system has recently been expanded but, most peripheral areas do not have any sewage treatment yet. Therefore, a new assessment started in 2014 in the Saco da Mangueira, an inlet whose waters are receptors of a significant anthropogenic contribution from the south of the city (Aguiar *et al*., 2014). This study identified 49 effluents whose origin was anthropogenic and 2 pluvial ones. Taking into account that only 22 effluents had been identified in this inlet in 1993, there has been an increase in the input of contaminants.

These effluents were qualitatively analyzed to identify their level of contamination represented by the phosphorus concentrations. Phosphorus is one of the main constituents of the organic matter and can be found in significant amounts in domestic wastewater, food and fertilizer industries. A predetermined volume of reagent (10% of the sample volume), previously prepared according to Baumgarten *et al*. (2010), was added to every effluent sample. The blue shades of the sample were compared to one of the six blue shades of a table, in which each blue shade was related to one different contamination level (Pinheiro *et al*., 2010).

Since there is no recommended limit for phosphorus effluent under Brazilian law Resolution 357 (CONAMA, 2005), the distinction between contaminated or uncontaminated samples was based on the concentrations reported in this legislation to freshwater Classes 2 and 3, which allow maximum values of 0.05 and 0.15 mg L^{-1}. Concentrations up to 2 mg L^{-1} corresponded to very weak and weak contamination (Figure 2 Levels B and C), whereas concentrations of 3, 6 and 12 mg L^{-1} represented respectively a medium, strong and very strong contamination, respectively (Figure 2, levels D, E and F) (Pinheiro *et al*., 2010).

This mapping qualitatively identified the most contaminated effluents in terms of anthropogenic organic matter, thus showing which effluents will need to be monitored later in quantitative terms of their compositions and compared to the current legislation.

3. Main contamination sources throughout urban and industrial development

Urban development and the fishing industry expansion in the 1980's led to the assessment of water quality which determined the organic contamination of the wa-

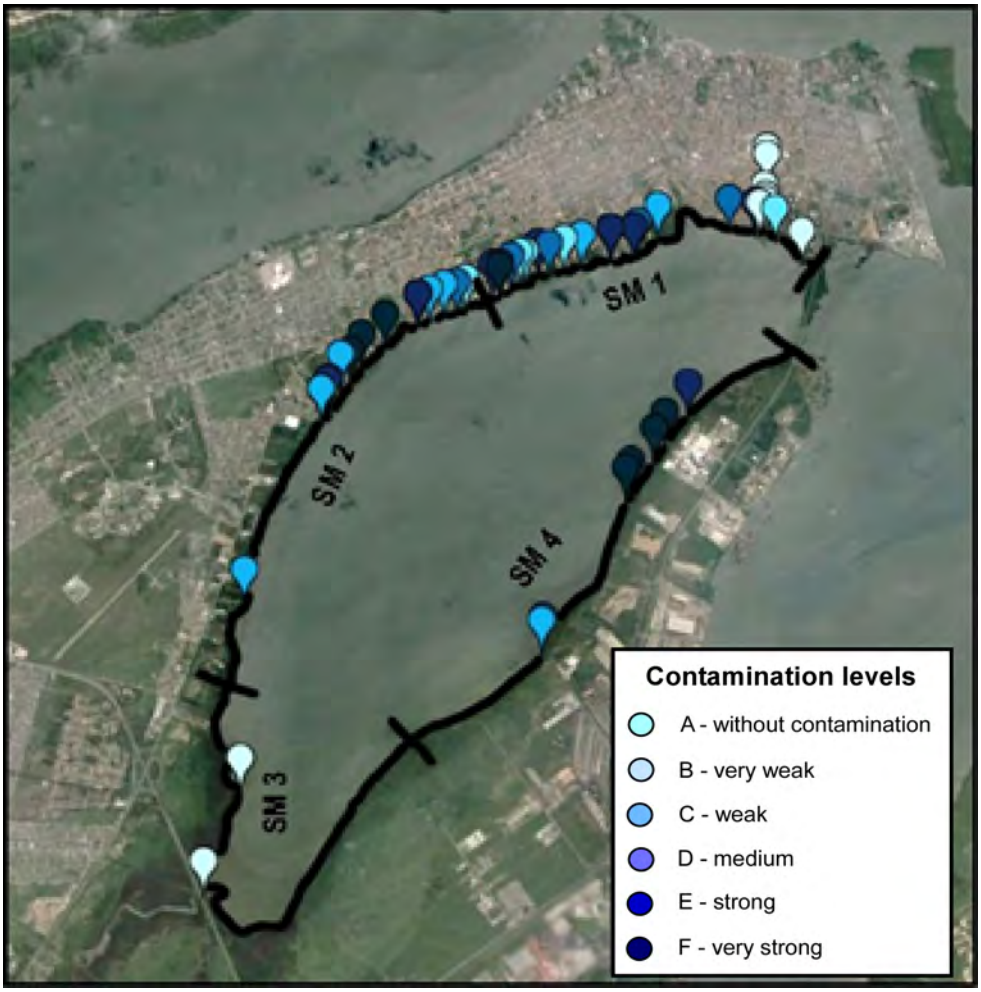

Figure 2 - The Saco da Mangueira, south of Rio Grande, indicating the sites of liquid effluent discharge and distinguished by the qualitative level of organic matter contamination according to Aguiar *et al.* (2014). The image is located between the latitude of 32º02' S and 32º08'S and the longitude of 52º04' W and 52º10'W.

Figura 2 - O Saco da Mangueira, ao sul da cidade do Rio Grande indicando os locais de lançamento de efluentes líquidos e diferenciados pelo nível qualitativo de contaminação por matéria orgânica de acordo com Aguiar et al. (2014). A imagem encontra-se entre a latitude de 32º02 'S e 32º08'S e a longitude de 52º04' W e 52º10'W.

ter around the city. After the change in the industrial profile of the city, most studies carried out in the second half of the 1990's focused on the port area, before the recent port expansion in the beginning of 2000. The studies had mainly on long-term objectives regarding the monitoring of the constituents of the water column and sediment in the Rio Grande Channel which flows into the estuary. These studies were carried out in the context of environmental assessments in Rio Grande. However, few of them have analyzed the anthropogenic contribution in terms of atmospheric contamination.

More recent studies (Bento *et al*., 2013; Costa & Wallner-Kersanach, 2013; Aguiar *et al.*, 2014;) have been carried out along the coastline of the city and the three port areas (Figure 1) to identify potential spots of contamination inputs. In order to better understand the evolution of the contamination studies in relation to the development that is going on in this region, they were organized in terms of environmental compartments, and focused on nutrients and trace metals, since these compounds are the most significant contributions to the environment.

3.1. Water compartment

3.1.1. Nutrients

Industrial development in the 1980's, mainly fishing industries and fertilizer plants, resulted in several changes in the estuarine water quality. The contamination observed at that time was related with oil and grease (Kantin *et al.*, 1980), anionic detergents (Kantin *et al*., 1981) and dissolved ammonium, nitrate, nitrite and phosphate (Costa *et al*., 1982). The excess of those nutrients used to cause euthrophication in the waters along the coastline of the city, mainly in the Saco da Mangueira inlet and in the port area (Kantin *et al.*, 1981; Almeida *et al.*, 1984).

This environmental problem was mostly caused by the excessive content of nitrogenous compounds resulting from effluents rich in organic matter. These effluents

have domestic origin or are discharged by fishing industries and vegetable grain processing units. In addition, phosphorus compounds originated from chemical fertilizer plants and domestic effluents were also reported.

Throphic unbalance in the estuary has been followed over the years (Baumgarten *et al*., 1995; Baumgarten, 2010; Odebrecht *et al*., 2010). Its result is the generation of euthrophication in the waters around Rio Grande (Baumgarten and Paixão, 2013), with cyanobacteria *Microcystis aerruginosa* blooms, which found favorable conditions to develop in the estuary (Yunes *et al.*, 1995), moreover intense proliferation of cyanobacteria *Aphanothec* sp (Baumgarten, 2010). When the water quality of the Saco da Mangueira was compared with another estuarine inlet, farther from the city, Persich *et al*. (1996) observed that the former had larger phytoplankton biomass than the latter and, as a result, higher rates of euthrophication because it received more organic matter than it was able to depurate. This process was observed for ammonium and phosphate in the Saco da Mangueira, mainly associated to the Industrial District, where high values of Biochemical Oxygen Demand (BOD_5 were measured (Baumgarten, 2010).

High contribution of nutrients in the shallow waters was also observed at the northern area of the city where the municipal dumpsite is located. However, this high concentration was no further observed in the waters away from the shoreline (Sprengler *et al*., 2007) (Figure 1B).

Temporal assessments of concentrations of dissolved inorganic nitrogen (ammonium, nitrate, nitrite), dissolved inorganic phosphate and silicate in the Patos Lagoon estuarine waters, based on weekly data collected from 1983 to 1990 and on monthly data collected from 1993 to 2007, showed that there was high variation of the dissolved inorganic nutrients in water. Even though the concentration of phosphate and the sum of nitrite and nitrate had gradually increased from 1999 to 2001, they decreased significantly in 2002 and in 2003 when the El Nino effect led to higher freshwater discharge from the lagoon. In general, the lagoon hydrology is greatly affected by factors such as wind, rainfall and evaporation; thus, there is no distribution pattern of constituents which can be indicatives of organic contamination in the water column, mainly during extreme events (Abreu *et al.*, 2010). It happens not only because the study areas are located in areas where there is high water circulation but also because such constituents do not persist in the water column. This process is suggested since nutrient removals occur with salinity zero to c. 5-7 and the organic matter mineralization could be a dominant process mainly in areas with salinity up to 25-27 in the Patos Lagoon (Window *et al*., 1999).

In the estuary channel, nutrients did not show any seasonal pattern because of the complex hydrographic of the Patos Lagoon by comparison with the inlets (Niencheski *et al.*, 1999).

3.1.2. Trace metals

Trace metals, which are natural elements in the geological composition, contribute to aquatic environments, such as the Patos Lagoon, in dissolved and/or particulate forms. Their anthropogenic contributions to the southern estuarine area result mainly from the urban and industrial development of the Rio Grande city.

The impact caused by the municipal dump site of Rio Grande City in the salt marsh area and in the shore of the Saco do Martins (Figure 1B) was evident. The stream which receives the leachate indicated high Pb concentrations ranging from 0.93 to 1.60 mg L^{-1}, by comparison with the maximum limits established by the legislation (CONAMA, 2005) of 0.5 mg L^{-1} for effluent launching (Sprengler *et al*., 2007).

However, the high outflow of the lagoon waters during low tide (Herz, 1977), along with extreme events or dredging activities in the port area have affected the concentrations of trace elements, both in water and in sediment. The monitoring of the total fractions of metals in water carried out in port areas located in the Porto Velho, the Porto Novo and the Super Porto from 1996 to 2001 showed significant decrease in the concentrations of copper, lead and zinc in the water. According to Barbosa *et al.* (2012), the average concentrations of Pb, Cu and Zn were 3.86 µg L^{-1}, 26.85 µg L^{-1} and 23.43 µg L^{-1}, respectively, in 1997. There was a decrease in mean concentrations of 1.66 µg L^{-1} for Pb, 5.25 µg $L^{-1}$for Cu and 10.94 µg L^{-1} in 2000. This process is attributed to the El Niño, which was one of the most powerful events during June/1997 and July/1998 and favored high discharge and the maintenance of freshwater in the estuary (Barbosa *et al.*, 2012). In addition, the decrease in trace metals in both water and sediment observed in 2000 and in 2001 may have been also affected by the intense dredging activities carried out in the estuary.

Studies of water monitoring in port areas were conducted annually until 2012 (www.portoriogrande.com.br) and showed that the higher concentrations of metals (Cr, Cu, Fe, Pb and Zn) in the water column usually occurs in bottom waters with the sediment resuspension. Likewise, trace metal increases in the water have also been observed during the dredging activities while the sediment is resuspended in the estuary. However, 30 minutes after the end of the dredging process, some metal contents show almost the initial levels of concentration again (Table A in Supporting Information II) for Cr and Pb (Corradi *et al.*, 2007). This may be likely explained by the low metal concentrations in water and the high hydrodynamic of the estuary causing dilution and dispersion of the elements.

Studies of water quality have focused on the channel areas in the estuary over the years. Because of the low metal concentrations verified in the water column, currently, the main concern is the quality of the shallow *waters* along the coastline due to the industrial intensification process, including the naval one.

In the Patos Lagoon estuary, there are studies, which show the association of the metals, in dissolved and in the particulate fractions (Windom *et al.*, 1999; Niencheski & Baumgarten, 2000). The model of the behavior of dissolved trace elements in the Patos Lagoon estuary proposed by Window *et al.* (1999) suggests that, around salinity 5-7, there is an increase in cobalt and nickel in the water due to cation exchanges and/or their desorption from particles due to the mix between freshwater and seawater. When salinity is around 25-27, there is an increase in most metals in the water because of the remineralization of organic matter and the remobilization of bottom sediment.

Even though the behavior of the total dissolved fraction of mercury and other trace metals/metalloids has been known for some time now, the potentially bioavailable fraction (the labile one) of metals in the water column was only known recently in this environment.

3.1.3. Speciation of trace metals in water

Recent studies in port areas of the Patos Lagoon estuary have applied analytical techniques to study speciation of trace metals, which analyze the labile or potentially bioavailable metal fraction in water or sediment. The estimation of this fraction, which may be incorporated more easily into the tissues of organisms, is more likely to represent a bioavailable fraction than the total metal (Leeuwen *et al.*, 2005).

A technique that quantifies metal in its labile fraction was recently used with *in situ* passive samplers, the diffusive gradients in thin films (DGT), which integrates metal concentrations found in the environment through time, even in high hydrodynamic waters, such as estuaries. Moreover, this technique enables comparisons among geographically different areas (Davison & Zhang, 1994).

The DGT technique started to be used in the Patos Lagoon estuary in 2003; the first time this technique was applied to estuaries in Brazil. It has still been used in the water to check the evolution of labile concentrations of some metals in the areas around the city. Taking into account the elements under analysis (Cd, Co, Cu, Mn, Ni, Pb and Zn), Cd, Cu and Pb showed higher bioavailability in the water of two locations in the marinas north of the city, when compared with the less urbanized site, the Marinheiros Island (Wallner-Kersanach *et al.*, 2009).

Due to the gradual release of trace metals from antifouling paints in vessels, marinas and ports were investigated in 2006 regarding the concentration of labile Cu, which is found in high concentrations in these paints. Its variation was 0.11-0.45 µg L^{-1} in the marinas located in the Naval Station, the Porto Novo, the Oceanographic Museum and the Yacht Club whereas concentrations of 0.10-0.15 µg L^{-1} were found in the Porto Novo and the Super Porto (Petrobrás Terminal) (Figure 1). Concentrations of Cu were higher at the marinas since they are more sheltered and may be compared to areas with marinas in Australian estuaries which are densely populated with leisure boats (Dunn *et al.*, 2004; Warnken *et al.*, 2004).

After this contamination was detected, new studies were carried out in 2009 and 2010 to investigate the labile Cu and Zn in the estuary because of the high concentration found in antifouling paints used in that estuarine area. Two old shipyards, the marina of the Yacht Club and the Porto Novo were assessed. The Gustavo Fernandes Filho shipyard at the Porto Velho area and the Santos shipyard at the Super Porto showed the highest concentrations over the period of study. Labile Cu concentrations were approximately 0.45 µg L^{-1} whereas labile Zn was close to 10 µg L^{-1} (Costa & Wallner-Kersanach, 2013).

These studies showed that not only domestic and industrial effluents contribute to the contamination of estuarine waters. Navigation activities have been a potential source of trace metals from antifouling paints which are potentially avaliable to all organisms.

3.2. Sediment compartment

The assessment of trace metals in water reflects instantaneous contaminant concentration, but the sediment better depicts the long-term inputs. Therefore, studies with sediment in the Patos Lagoon estuary, especially on the channel areas, show contamination evidence, mainly by arsenic (As) and mercury (Hg) (Mirlean *et al.* 2003a and b). The latter has been more investigated than the former in several studies, therefore, Hg will be presented in more detail in section 4.4.

The distribution and contamination of sediments by As in the Patos Lagoon estuarine area was first studied by Mirlean *et al.* (2003b). Studies of the sediment quality and of the monitoring of the dredging at the Rio Grande Port were conducted from 2002 to 2005 (www.portoriogrande.com.br). The highest concentration of As in the estuarine system (up to 50 mg kg^{-1}) was found in the sediment at Porto Novo, Super Porto and adjacent channels (Figure 1B).

In the estuarine region, total levels of As had a strong increase: they were tenfold or twentyfold the values (2.5 and 7.7 mg kg^{-1}) found in the sediment on the limnic region of the Patos Lagoon. In addition, the mobile (labile) form of As in the sediment found of the estuarine region at the Porto Novo also increases to 80%

of the total value and 65% on average, whereas it increases to 63% of the total levels and 39% on average in the channels (Mirlean *et al.*, 2003b). The mobile fraction is considered to be potentially bioavailable (Salomons and Förstner, 1984); thus, it shows the fraction that is capable of harming to the biota.

The study carried out by Mirlean *et al.* (2003b) shows that levels of As in most sediment at the Porto Novo (Figure 1) exceed the PEL (probable effect level) of 17 mg kg^{-1} that represents the value above which the biota may be affected (Long *et al.*, 1995). Some sediment samples exceed the SEL (severe effect level) of 33 mg kg^{-1}, which indicates that the biota will be severely affected. Some of these values were used to establish the legislation regarding the quality of the sediment that is used for dredging Brazilian jurisdictional areas (CONAMA, 2012). The Brazilian Sediment Quality Criteria for As are 19 mg kg^{-1} (Level 1 - threshold below the probability of a possible adverse effect to the biota) and 70 mg kg^{-1} (Level 2 - threshold above a possible deleterious effect to the biota).

Natural raw phosphorites and activities carried out by fertilizer plants are the main sources of sediment contamination by As in estuarine areas (Shumilin *et al.*, 2001; Mirlean *et al.*, 2003b). Elevated As concentrations higher than 300 mg kg^{-1} were found in the raw material and products used in this industrial sector. Analyses show that the content of As in phosphorite is 100 mg kg^{-1} and that superphosphates have 390 mg.kg^{-1}, mainly in its mobile form (Mirlean *et al.*, 2003b).

The content of As varies considerably depending on the area in the estuary and time. However, other factors, such as granulometry, the organic content of the sediment (Förstner & Wittman, 1981), physicochemical and geochemical conditions in the estuary and the frequency of dredging control As content in the bottom sediment (Urban *et al*., 2010).

Despite variability, higher values of As are usually found in the sediment at the Porto Novo and its surroundings, i. e., the Rio Grande Channel and other channels along the mouth of the Saco da Mangueira (Figure 1). In the Porto Novo region, As content tends to decrease along the Super Porto Channel up to the channel between the jetties. Sources from an old fertilizer plant located at the southern area of the Porto Novo (Figure 1A) and favorable conditions for sedimentation and accumulation of sediment in this region are factors that favor As enrichment.

Environmental studies conducted to assess the quality of superficial and sub-superficial sediments provide evidence of the previous observations. When the whole estuarine system is analyzed, i. e., considering all sandy and clayish sediments, the most usual variation ranges between 2 and 40 mg kg^{-1} of As. However, maximum values may exceed the level of 19 mg kg^{-1} of As established by the legislation (CONAMA, 2012), and recommended by Level 1.

The metals Pb, Cd, Zn, Cu and Cr in superficial sediments of the estuary have a very similar distribution pattern. The highest values are found in more shallow waters which are adjacent to the main industrial, urban and port effluents (Baisch, et al., 1988; Asmus, 2008). Deeper zones, mainly in navigation channels, in general, have lower values of trace metals. These channels are constantly dredged and have high velocities of water flux reaching 1.7-1.9 m s^{-1} after prolonged periods of heavy rain, while the maximum velocities of the current in the lagoon are approximately 0.3 m s^{-1} (Garcia, 1998). Dredged sediments are later deposited in a marine site. Usually, from 2 to 3 million tons of sediment are dredged every 2 or 3 years in order to maintain or deepen the channels and harbors areas (www.portoriogrande.com.br). Every dredging operation removes at least 0.5 to 1 m of superficial sediment from the navigation channels. However, dredging may resuspend the sediment and may cause dispersion of possible metals accumulated in the sediment.

3.2.1 Speciation of trace metals in the sediment

There have been some studies of metal speciation in the Patos Lagoon estuary (Baisch et al., 1988; Baisch, 1994). Oxy-hydroxides and, secondarily, sulphides and organic matter are the most important metal carriers in sediments of the Patos Lagoon estuary. On the other hand, Mirlean *et al.* (2003b, 2009) applied partial extractions for sediment samples and showed that As usually takes its labile form, while Hg does not.

Metal speciation and bioavailability of particulate sediment matter were assessed in urban and industrial effluents from the Patos Lagoon estuary. The domestic effluent, whose contamination was the result of untreated sewage, had high total concentrations in the effluent solid phase.

Sequential extractions in particulate matter from the effluents (Figure 3) revealed high values of Cd in the labile fraction (∑ exchangeable + carbonate + reducible + organic), mainly related to exchangeable fraction. There was a high percentage of Pb in the labile fraction, but it is linked mainly to oxy-hydroxides and the organic fraction. Cu and Zn were also associated with the labile fraction in the domestic effluent at higher levels, while Ni, Cr showed lower values in the labile fractions in the industrial, domestic and mixt effluents. More than 50% of the amount of Cd, Mn, Pb and Zn was associated with the labile fraction and domestic effluent, that is the most dangerous in terms of contamination risk to the local biota.Assessment of labile trace metals (direct extraction with 0.1 M HCl) in the areas which were more affected –

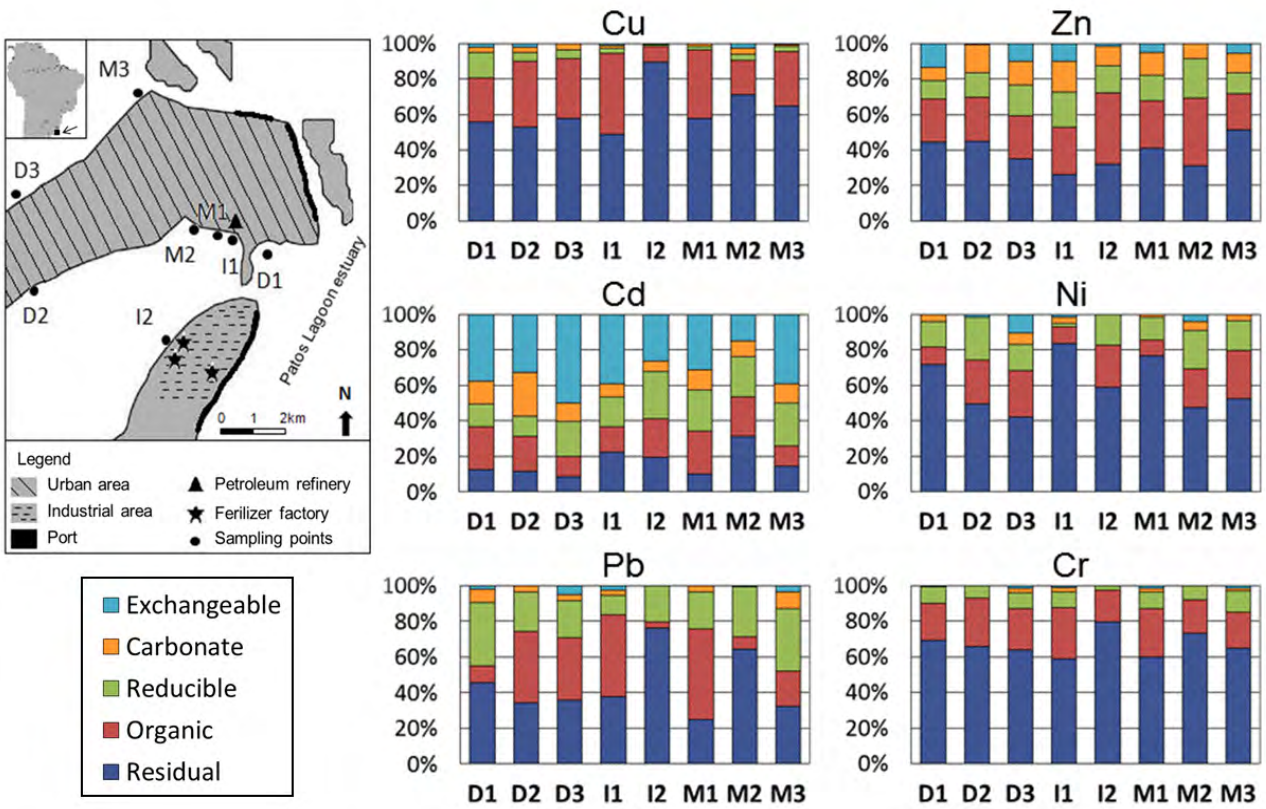

Figure 3 - Metal sequential extractions of particulate sediment matter from urban (D), industrial (I) and mixt (M) effluents from the Patos Lagoon estuary (adapted from Bento et al., 2013).

Figura 3 - Extração sequencial de metais do material particulado em suspensão de efluentes urbanos (D), industriais (I) e mistos (M) do estuário da Lagoa dos Patos (adaptado de Bento et al., 2013).

shipyard, marina and port shorelines waters – regarding the fine fractions of the sediment (<0.63 µm) on a dry weight basis was recently carried out (Costa, 2012). Concentrations range from 3 to768 mg kg^{-1} for Cu, 16 to 578 mg kg^{-1} for Zn, 6 to 178 mg kg^{-1} for Pb, 0.86 to 3 mg kg^{-1} for Cr and 1 to 7 mg kg^{-1} for Ni were found. Most maximum concentrations exceed the typical values for continental crust (Taylor, 1964), with exception of Cr and Ni. According to the Federal Resolution (CONAMA, 2012) on dredged sediment, concentrations of Cu, Zn and Pb at the Irmão Fernandes Shipyard (which has operated for more than 100 years in the Porto Velho) exceeded Level 2, a fact that shows there may be adverse effect on the biota. However, Cu concentrations at the Santos Shipyard (which has operated for more than 20 years in the Super Porto) exceeded only Level 1, which is considered the attention level since there might be some adverse effects on the biota.

The extended El Niño effect on the region for six months caused a decrease in concentrations of labile metals in the sediment due to intense freshwater discharge. With the restoration of normal climatic conditions, water pH and salinity were found to be the main factors controlling the lability of metals in sediment (Costa, 2012).

3.3. Atmosphere and soil compartments

Garcia *et al*. (2010) observed that he influence of atmospheric emissions from the oil refinery in Rio Grande city (Figure 1) shows that the metal Ni and V have a strong relationship in the soil and therefore they are efficient markers of the chronic impact of these emissions on the estuarine region. Other elements under analysis (Cd, Cu, Pb and Zn) did not have any relation with refining activities but resulted from other sources found in the urban, industrial and port complex in Rio Grande.

The As contamination in sediment and soil in the Patos Lagoon estuary was analyzed by studies carried out from 2003 to 2005 (Mirlean *et al.*, 2003b; Mirlean & Roisenberg, 2006) and by several environmental monitoring reports (www.portoriogrande.com.br). Other studies show the contamination by lead (122 – 19,256 mg kg^{-1}) (Mirlean et al., 2005b) and Hg (0.01 – 14 mg kg^{-1}) in soil in Rio Grande (Conceição, 2005).

Atmospheric pollution caused by the presence of Pb and other trace metals (Cd, Cr, Ni, Cu, Zn) in the atmospheric particulate matter smaller than 2.5 µm ($PM_{2.5}$) was the theme of some studies, such as the ones published by Vanz (2000), Vanz *et al*. (2003), Mirlean

et al. (2005b) and Gutierrez (2013). Pb (PM_{100}) anomalous content was identified in solid atmospheric precipitation above 1000 µg m^{-3} (Vanz *et al.*, 2003) (Figure 4). These studies showed that these urbanized regions in Rio Grande may be exposured to Pb concentrations, which exceed the established legal limits from USA (1,5 µg m^{-3}) and East Europe (0.7 µg m^{-3}) for PM_{10}.

The main sources of atmospheric Pb are attributed not only to the fusion of Pb in the preparation of fishing apparatus and to the availability of residues on the soil but also to the use of paints with high content of Pb (Pb oxide) on houses of poorer populations (Mirlean et al., 2005b).

In a study carried out by Mirlean & Roiserberg (2006) in Rio Grande, the fertilizer plants and their activities were recognized as atmospheric sources of Cd and As. Moreover, this industrial sector had previously been known as the main responsible one for acid rains in Rio Grande, since 62% of the annual rainwater indicated pH values lower than 5.0 (Mirlean *et al.*, 2000). The analysis of rainwater showed that Cd in the soluble form precipitates close to emission source, whereas As is transported farther and also in the soluble form precipitates at a greater distance. The pH controls the distribution of cadmium and arsenic in rain and groundwater. Concentration of soluble cadmium along the impact line increases with reduction of pH and arsenic, contrary to the increase in pH. Concentrations of Cd and As in surface soil correlate well among themselves near to emission point (Mirlean & Roiserberg, 2006).

Therefore, contributions given by atmospheric and soil contamination in Rio Grande must be taken into account when environmental assessment of water quality is carried out due to the potential anthropogenic input to the Patos Lagoon estuary. However, it is important to take into consideration the whole set of compartments in order to better assess the origin of an element, as was achieved by studies of Hg in the region (Mirlean *et al.*, 2003a; Mirlean & Oliveira, 2006; Mirlean *et al.*,2008).

3.4. Mercury contamination: case study

The first information on mercury pollution in the Patos Lagoon estuary was obtained in 1998 when the Chem Oil Company tanker with 12000 t concentrated sulphuric acid had an accident and discharged part of the acid into their waters. Acid attack on the estuarine sediments led to metal redeposition along the trajectory of the acid effluent. Mercury anomaly with metal concentration of about 5 mg kg^{-1} in the sediment was found during the study of the accident (Mirlean *et al.*, 2001).

The mercury content in sediments following the accident was much higher than the metal amount found in the sulphuric acid, making researchers look for the source of mercury pollution on the coast. The study of mercury distribution in the city effluents showed high values in particulate suspended matter. The highest Hg concentration (up to 21.1 mg kg^{-1}) was found in domestic and mixed (domestic + runoff) effluents. It was evident that local industry effluents were not responsible for mercury pollution in the estuary (Mirlean *et al.*, 2003a). However, the origin of the high mercury concentration in urban effluents was not revealed.

The existence of highly mercury polluted soil covers was reported in Rio Grande (Mirlean & Oliveira, 2006). It was also found that, in historical buildings in the city, the concentrations of mercury reach up to 25 mg kg^{-1}. Moreover, mercury contamination was detected in man-made ground (MG) deposits on all coastal reclamation sites of the city (Figure 5). It was observed that the older the MG, the higher the level of pollution. In the deposits dating from the beginning of the 18th century (the very first coastal reclamation fill), mercury concentration are the highest registered value, i.e., almost 25 mg kg^{-1}. In the MG dating from the first half of the 19th century, mercury concentration was almost twofold lower. Mercury concentration increases in MG's dating from the middle of the 20th century: that are mainly composed of city garbage. Nevertheless, mercury concentration in deposits dating from the 20th century concedes that the oldest ones have both the highest registered concentration and the highest average value (Mirlean & Oliveira, 2006).

Plausible sources of mercury in the 18th century could be technological processes applied for felt production known as "carotting" which, at that time, included skin processing in mercury nitrate solutions. Absence of the neutralization of the used solutions, and any organized system of recycling of city garbage in general is the reason of a high level of pollution by mercury of environment that accordingly redounded to the high concentration of mercury in MG deposits of that time. However, a hundred years later, MG deposits were still highly polluted with mercury. The felt industry, initially represented by small workshops that joined into a large factory later, had been considerably developed by the end of the 19th century. It may be confidently identified as the main source of mercury at that time. In the first half of the 20th century, fast industrial growth demanded intensification of coastal reclamation. The MGs'were filled mainly by sand dune, lagoon sediments dredged during the deepening of the navigation channel and coal ash. The city garbage was a lot less used by comparison with earlier days. It explains the decrease in mercury concentration in MG material in the first half of the 20th century. Moreover the coastal reclamation planned and controlled by the Municipality, the city area also grew because of unregulated reclamation in its peripheral portion. Homeowners, whose backyards abutted on the coast, filled up shoal, thus, increasing their private areas. At such sites, any solid material and, more often, city garbage mixed up with beach sand were used.

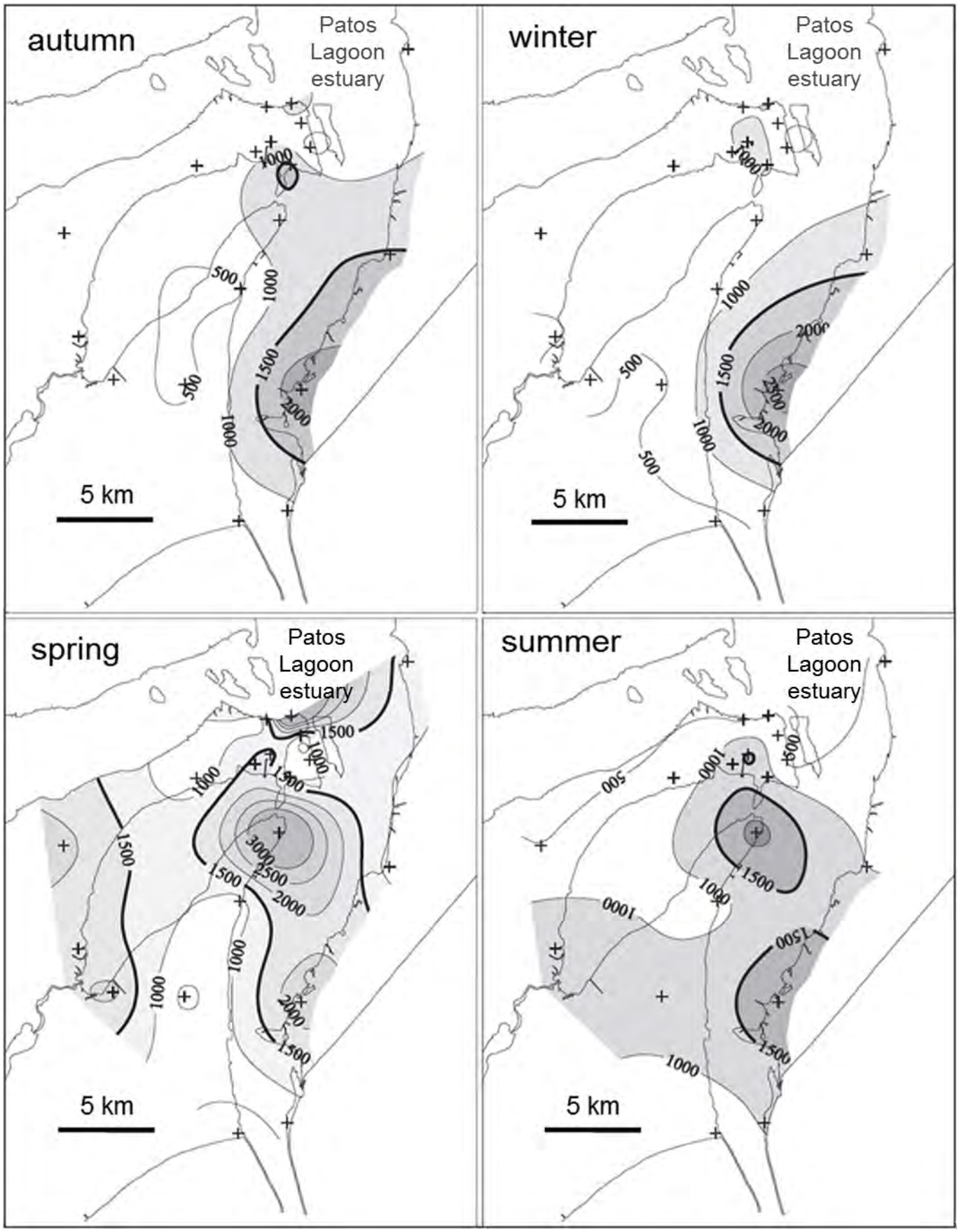

Figure 4 - Spatial distribution of Pb (mg kg^{-1}) in atmospheric particulate matter in four seasons in the estuary of the Patos Lagoon. (+) Sampling sites (Vanz et al., 2003).

Figure 4 - Distribuição especial de Pb (mg kg^{-1}) em material particulado atmosférico nas quatro estações sazonais no estuário da Lagoa dos Patos. (+) Locais de amostragem (Vanz et al., 2003).

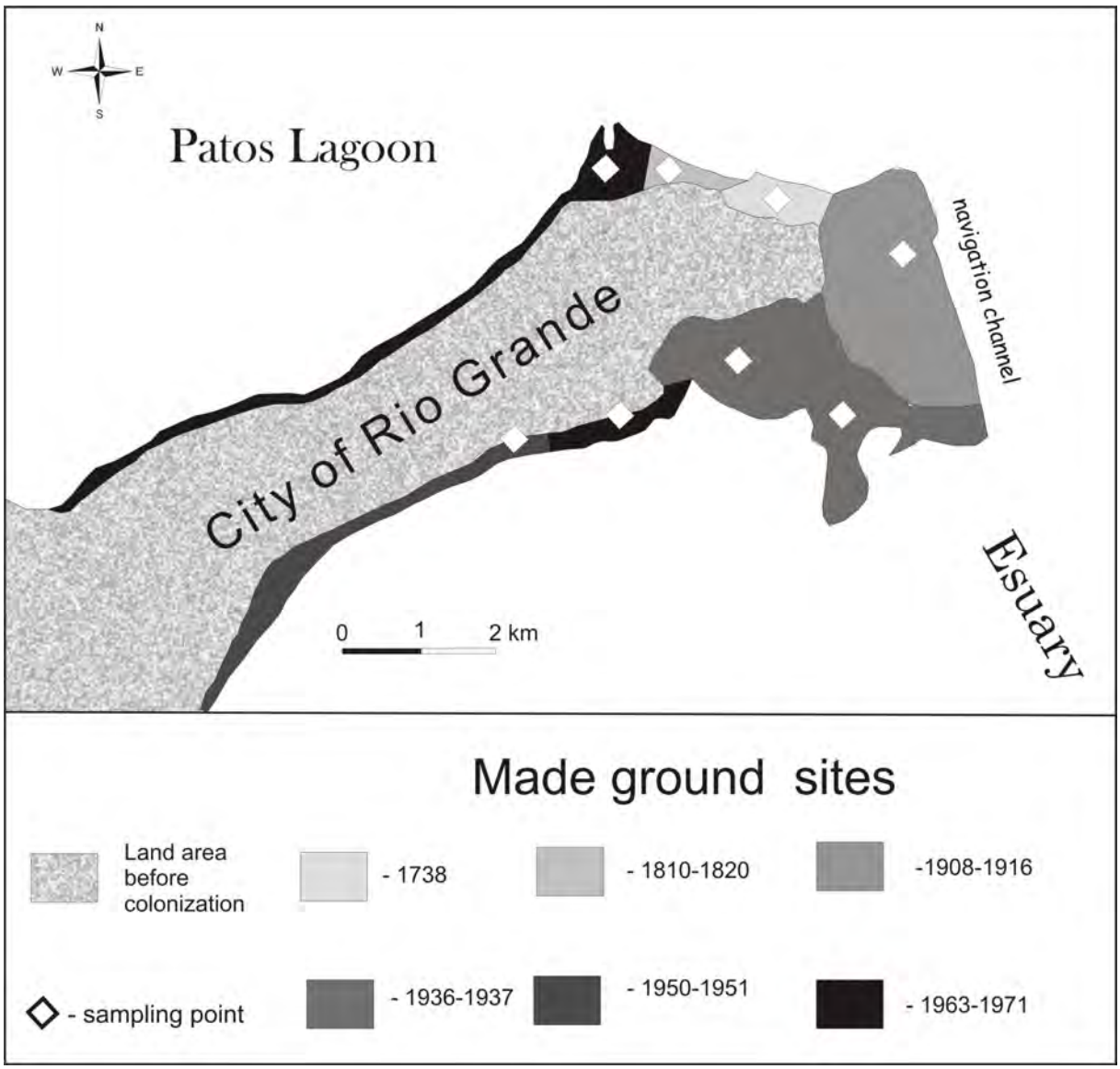

Figure 5 - Man-made ground sites of Rio Grande according to Mirlean & Oliveira (2006).

Figure 5 - Locais de aterro na cidade do Rio Grande de acordo com Mirlean & Oliveira (2006).

The MG' pollution provides explanation for mercury distribution in the whole environment in the region of Rio Grande city. The high concentration of particulate mercury in drainage effluents is most likely caused by small particles washed out from polluted MG'. Sediment of shoals near city coasts contains the highest amount of mercury (17 mg kg^{-1}) in areas adjacent to the most polluted MG' (Mirlean *et al.,* 2003a).

Mercury dispersion from soil and industrial emissions affects the large area around the city and enables Hg accumulation in fish (Mirlean *et al.,* 2005a). It was demonstrated that mercury precipitation on lakes around the city increased closer to downtown and to industrial sources. Metal in fish tissue generally increased along the same gradient, but also varied with trophic level and preferred depth zone. Atmospheric mercury deposition on these closed lakes may be directly linked to concentrations in fish, with surface-feeding piscivorous species attaining the highest concentrations, which, in some cases, approximated and exceeded the threshold level of 0.5 mg kg^{-1} of total Hg.

From 1998 to 2008, the distribution of mercury in the sediments of the Patos Lagoon estuary and nearby coastal marine deposits was monitored. Polluted urban soils and coastal reclamation fills were confirmed as the main sources of high mercury concentrations in shallow estuarine sediments which enter the navigation channel close to the urban area and are transported into the ocean. Hg concentration in sediments in the navigation channel has considerably increased since 2004 due to the intense reconstruction activity in the urban area (Mirlean *et al.*, 2009). Periodic dredging of the channel strengthens the preconditions for coastal marine sediment contamination by mercury. However, it does not occur because the resuspended dredged sediments are significantly diluted by natural suspended particulate

matter. This fact can be explained by a disproportionate volume of sediments being resuspended during dredging and sedimentary load being naturally deposited from the plume in the coastal zone. According to Calliari et al. (2007), approximately $30 \times 10^6 m^3$ of sediment has been dredged (an annual average of $1.5 \times 10^6 m^3$), and about $64 \times 10^6 m^3$ deposited naturally (an annual average of $3.2 \times 10^6 m^3$) during the last 20 years. Assuming that even up to 5% of the total dredge volume ($1.5 \times 10^3 m^3$) is suspended in estuarine water, this amount is a small part (1/40) of the total volume of mud input in the coastal area by natural influence in the last 20 years.

Mercury pollution of soil in Rio Grande, which firstly occurred downtown in the 18th century and expanded in the 19th and in the 20th centuries, still impacts all compartments (soil, sediments, water, air and biota) of the surrounding environment.

4. Current areas under impact in the estuary

Studies carried out over the last 35 years in the estuary of the Patos Lagoon showed that there was an increase in the anthropogenic contributions of trace metals in several compartments of the environment. Even though the estuary is a quite dynamic environment, more sheltered areas, such as the Saco da Mangueira and other estuarine nearshore areas, have indicated water contamination because the inputs of potentially hazardous substances and sediment pollution as the inputs have been causing harmful effects. The low carrying capacity of the sheltered areas is attributed to their low hydrodynamics and little water renovation, moreover effluent directly discharged into them. Consequently, these areas close to the shore in the estuary can neither depurate nor restore, thus, generating an increase in environmental liabilities.

In order to summarize data provided by several studies carried out over many years, areas endangered by organic loads and trace metals around the city urban and industrial areas, including the three port areas, were mapped (Figure 6).

Most effluents that flow into the estuarine environment are clandestine, both urban and industrial. Strict environmental policies are needed to improve environmental estuarine quality, mainly in the Saco da Mangueira inlet. More control is needed to trigger, at least, basic effluent treatment which must be carried out by existing industries, residential condominiums and commercial buildings that are setting up in the region (Baumgarten, 2010).

The government must find a solution to the soils contaminated by the trace metals in Rio Grande municipality. Decrease in atmospheric particulate and in their acidity, mainly from fertilizer plants, must be aimed at.

5. Environmental management measures

The development of the Rio Grande city in the Patos Lagoon estuary has yielded conflicts of its resources use over the years and misappropriation of the city's shoreline areas has occurred as well. In general, the poor institutionalization of coastal management has been observed (Tagliani *et al.*, 2003, 2007). In environmental terms, there has been a decrease in the diversity of benthic organisms in most impacted areas of the Saco da Mangueira (Bemvenuti and Angonesi, 2011) and the degradation of coastal habitats, such as dunes, inlets and salt marshes (Seeliger & Costa, 1998). On large scale, there has been significant decline in fishery in the estuary since the end of the 1980's, a fact that has affected thousands of fishermen involved in the traditional activity (Reis & D'Incao, 2000; Tagliani *et al.*, 2003).

Such conflicts regarding the resources use and disposal of clandestine effluents from urban and industrial areas have produced a continued environmental degradation and affected the carrying capacity of the aquatic environment.

Measures are needed in order to inhibit discharge of clandestine and illegal industrial, domestic and naval effluents, which are rich in organic matter and trace metals, in the nearshore waters of the estuary, mainly in the inlets. If the increase input of nutrients into the estuarine waters is not controlled, dissemination and growth of opportunistic blooms may happen to an intolerable level for public health, mainly in the Saco da Mangueira (Baumgarten, & Paixão, 2013). The uncontrolled contribution of trace metals to the water and their accumulation in sediment showed that some areas have been impacted, indicating a demand on the environmental control. This is evident due to labile metal concentrations that were found, since they can be potentially avaliable to all organisms. The atmospheric and soil contamination in Rio Grande must also be taken into account when environmental assessment of water quality is carried out, as a result of the potential anthropogenic input to the Patos Lagoon estuary. Particular attention should be paid to the element Hg, because of its toxicity and its higher concentration in man-made ground of the city.

The peninsular shape of the city and the poor city control enables clandestine discharge of effluents to be connected to the city pluvial system, which flows into the estuary. The expansion of this system must be implemented and new systems must be designed in areas where industries have been built. Likewise, industries located in areas where there is no sewage collection, such as the industrial district and several condominiums on the nearshore waters of the estuary, should be requested to implement private sewage treatment systems.

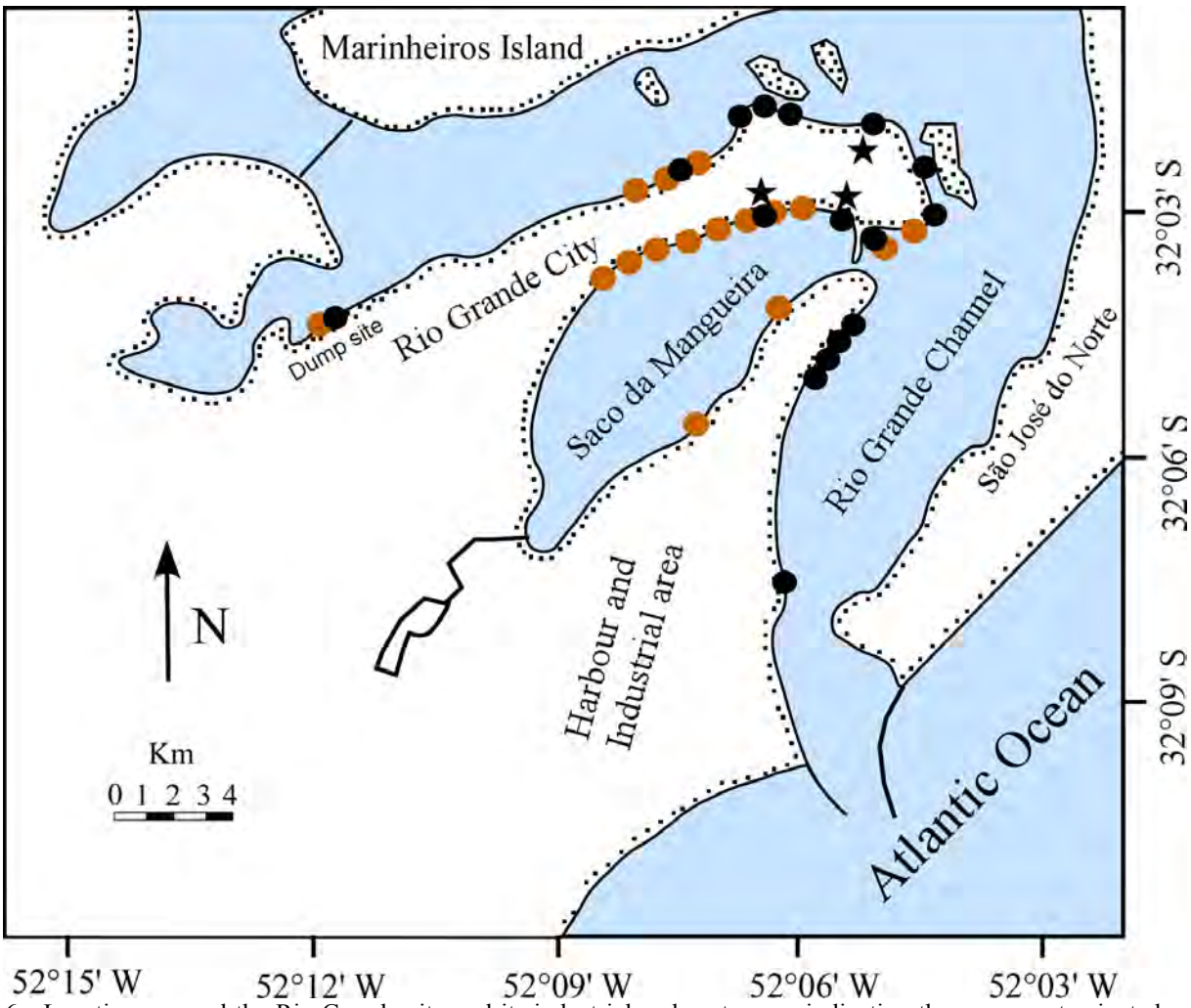

Figure 6 - Locations around the Rio Grande city and its industrial and port areas, indicating the more contaminated areas by organic matter in the water (●) and trace metals in the sediment (●) and soil (★). Water data according to Aguiar & Baumgarten (2014) and Sprengler *et al*. (2007); sediment data according to Mirlean *et al.* (2003a and b, 2009) and Costa *et al.* (unpublished data) and soil data according to Mirlean, *et al.(*2005b, 2006, 2008) and Mirlean & Roiserberg (2006).

Figura 6 - Locais ao redor da cidade de Rio Grande e sua área industrial e portuária, indicando as áreas mais contaminadas por matéria orgânica na água (●), metais traço no sedimento (●) e em solos (★). Dados em água segundo Aguiar & Baumgarten (2014) e Sprengler et al. (2007); dados em sedimento segundo Mirlean et al. (2003a e b, 2009) e Costa et al. (dados não publicados) e dados em solos de acordo com Mirlean, et al. (2005b, 2006, 2008) e Mirlean & Roiserberg (2006).

The Municipal Plan of Basic Sanitation became official in 2013; it has an overview of environmental problems faced by the whole city as well as political and structural solutions that the city hall must implement. Therefore, it must be implemented as soon as possible to improve environmental quality.

The increase trends in environmental liabilities around the city demands the mitigations of the socio-environmental conflict (Tagliani *et al.*, 2007). Therefore, regulations issued by the Municipality of Rio Grande resulted in the Southern Coast Program, which is part of the Rio Grande Municipal Environmental Plan that focuses on environmental management (Tagliani & Polette, 2011). It included the Local Harbor Agenda, which establishes an environmental program for all the three harbors. Based on these local resolutions and according to Anello & Koehler (2011), neither liquid effluents nor atmospheric emissions are, in many cases, within the limits established by local legislation.

Although several initiatives and advances have been achieved under the Southern Coast Program, the consolidation of an integrated management program for the Patos Lagoon estuary requires the development of several activities based on a clear action strategy (Tagliani *et al.*, 2011). However, the institutional structure and fragility of the country perhaps becomes the bigger challenge for the implementation of an effective integrated coastal management program for this area as pointed out by Tagliani *et al.* (2003).

The city government must implement an integrated management program for the estuary in a real and practical way, involving stakeholders and local governments

as suggested by USEPA's Community-Based Environmental Protection (Brown *et al*., 2002). The studies under analyses in this paper clearly show the temporal evolution of environmental impacts on several areas of the estuary. An environmental policy based on the mapping of the biodiversity and the liabilities should be set to in the long term. The state environmental agency must also act more effectively to supervise industrial liquid effluents and atmospheric emissions. If this set of actions is not quickly and adequately implemented, it may endanger the environment and the population's life quality in the southern region of the estuarine system.

Appendix

Supporting Information associated with this article is available online at http://www.aprh.pt/rgci/pdf/rgci-596_Wallner-Kersanach_Supporting-Information.pdf

References

Abreu, P.C.; Odebrecht, C.; Niencheski, L.F. (2010) - Nutrientes dissolvidos. *In:* Ulrich Seeliger; Clarisse Odebrecht (org.), *O estuário da Lagoa dos Patos*, pp.43-48, Editora FURG, Rio Grande, RS, Brasil. ISBN: 978-8575661444.

Aguiar, V.F.; Baumgarten, M.G.Z.; Rodrigues, H. (2014) - Identificação e diagnóstico dos locais de lançamento de efluentes nas margens da enseada estuarina Saco da mangueira (Rio Grande, RS). *Anais do Congresso Brasileiro de Oceanografia* (ISBN: 978-85-66184-03-7), pp. 1793-1792, Itajaí, Brazil. Available on line at http://www.aoceano.org.br/site/images/pdf/livro_de_resumos_cbo2014.pdf

Almeida, M.T.A.; Baumgarten, M.G.Z.; Kinas, P.G.; Kantin, R. (1984) - Estudo da poluição orgânica das águas das imediações da cidade do Rio Grande (RS, Brasil). *Revista Atlântica* (ISSN 2236-7586), 7:15-24, Editora FURG, Rio Grande, RS, Brasil.

Almeida, M.T.A.; Baumgarten, M.G.Z.; Rodrigues, R.M.O. (1993) - *Identificação das possíveis fontes de contaminação das águas que margeiam a cidade do Rio Grande-RS*. 36p., Série Documentos Técnicos em Oceanografia No. 6, Editora FURG, Rio Grande, RS, Brazil.

Anello, L.F.; Koehler, P.H.W. (2011) - Integração do sistema de gestão ambiental do Complexo Portuário – Industrial. *In:* Paulo Tagliani, Milton Asmus. (Org.), *Manejo Integrado do Estuário da Lagoa dos Patos*, pp.61-72, Editora da FURG, Rio Grande, RS, Brazil. ISBN: 978-8575662069.

Asmus, M.; Baisch, P.; Baugarten, M. G.Z.; Bemvenuti, C. E.; Filmann, G.; Niencheski, L. F.; Taglianni, P.; Wallner, M. (2008) - Programa de monitoramento ambiental do Porto de Rio Grande. *III Simpósio de Dragagens Portuárias do Brasil - Engenharia, Tecnologia e Meio Ambiente*, MCT, 1:114-135, Curitiba, Brasil.

Baisch, P.; Niencheski, F.; Lacerda, L. (1988) - Trace metals distribution of Patos Lagoon estuary. *In:* Ulrich Seeliger, Luis Drude de Lacerda; Sambasiva Rao Patchineelam (org.), *Metals in Coastal Environments of Latin America*, pp.59-64, Springer-Verlag. Berlin, Germany. ISBN: 978-3642714856.

Baisch, P. (1994) - *Les oligo-éléments métalliques du système fluvio-lagunaire dos Patos, Flux et Dévenir (Brésil)*. 345p., Thèse de Doctorat, Université de Bourdeaux I, Bourdeaux, France. *Unpublished*.

Barbosa, F.G.; Wallner-Kersanach, M.; Baumgarten, M.G.Z. (2012) - Metais traço nas águas portuárias do estuário da Lagoa dos Patos, RS. *Brazilian* Journal of *Aquatic Science* and *Technology* (ISSN: 1808-7035), 16(2):27-36, Itajaí, Brasil. Available on-line at http://siaiweb06.univali.br/seer/index.php/bjast/article/view/3401/2435

Baumgarten, M.G.Z.; Niencheski, L.F.; Kuroshima, K. N. (1995) - Qualidade das águas estuarinas que margeiam o município do Rio Grande (RS): Nutrientes dissolvidos. *Revista Atlântica*, (ISSN: 2236-7586), 17(1):17-34, Editora FURG, Rio Grande, RS, Brasil.

Baumgarten, M.G.Z. (2010) - A eutrofização das águas de uma enseada do estuário da Lagoa dos Patos (RS) protegida pela legislação ambiental. *Fepam em Revista* (ISSN 1982-2162), 3(2):34-42, Porto Alegre, Brasil. Available on-line at http://www.fepam.rs.gov.br/fepamemrevista/downloads/Revista_V3N2%20-%202010%20-%20LEVE.pdf

Baumgarten, M.G.Z.; Wallner-Kersanach, M.; Niencheski, L.F.H. (2010) - *Manual de Análises em Oceanografia Química*. 172p., Editora FURG, Rio Grande, Brasil. ISBN: 978-8575661413.

Baumgarten, M.G.Z.; Paixão, B.E.G. (2013) - Uso do índice do estado trófico para avaliar a qualidade das águas do estuário da Lagoa dos Patos (RS). *Revista Atlântica* (ISSN: 2236-7586), 35(1):5-22, Rio Grande, Brasil. Available online at http://www.seer.furg.br/atlantica/article/view/2965/2996.

Bento D.M.; Mirlean, N.; Baisch, P. (2013) - Metal speciation in urban-industrial effluents: impact assessment for an estuary in southern Brazil. *Fresenius Environmental Bulletin* (ISSN: 1018-4619), 22(4a):1-8, Technische Universität München, München, Germany.

Bemvenuti, C.E.; Angonesi, L.G. (2011) – A qualidade ambiental da enseada estuarina Saco da Mangueira: Estrutura da Comunidade Bentônica. *In:* Paulo Tagliani; Milton Asmus. (org.), *Manejo Integrado do Estuário da Lagoa dos Patos*, pp.201-206, Editora da FURG, Rio Grande, RS, Brasil. ISBN: 978-8575662069.

Brown, B.S.; Munns Jr, W.R.; Pau, J.F. (2002) - An approach to integrated ecological assessment of resource condition: the Mid-Atlantic estuaries as a case study. *Journal of Environmental Management*, 66:411-427. DOI: 10.1006/jema.2002.0598

Burgin, S.; Hardiman, N. (2011) - The direct physical, chemical and biotic impacts on Australian coastal waters due to recreational boating. *Biodiversity and Conservation*, 20 (4):683-701. DOI: 10.1007/s10531-011-0003-6

Calliari, L.J.; Holland, K.T.; Pereira, P.S.; Guedes, R.M.C.; Espírito Santo, R. (2007) - The influence of mud on the inner shelf, shoreface, beach and surf-zone morphodynamics-Cassino, Southern Brazil. *Proceedings of 7th Conference on Coastal Sediments*, 2:1455–1465, New Orleans, U.S.A. Available online at http://www.praia.log.furg.br/Publicacoes/2007/2007b.pdf

Cicin-Sain, B.; Knecht, R.W. (1998) - *Integrated Coastal and Ocean Management: concepts and practices*. 517p., Island Press, Washington, United States of America. ISBN: 1559636041.

Clark, R. B. (2001) - *Marine Pollution*. 161p., Oxford University Press, Oxford, Great Britain. ISBN: 0198792921.

CONAMA (2012) - Conselho Nacional do Meio Ambiente. Resolução n°454. 01 de Novembro de 2012. DOU de 08 de Novembro de 2012. Revoga a Resolução CONAMA n° 344 de 2004 e 421 de 2010. Available online at http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=693

Conceição, C.O. (2005) - *Contaminação dos aterros urbanos por metais pesados no município - Rio Grande (RS)*. 115p, Dissertação de Mestrado, Universidade Federal do Rio Grande, Rio Grande, RS, Brasil. Unpublished.

Corradi, C.E.; Braumgarten, M.G.Z.; Niencheski, L.F.H.; Wallner-Kersanach, M. (2007) - Monitoramento hidroquímico da área do Porto do Rio Grande (RS) submetida a atividades de dragagem. *In:* Eliane Bêe Boldrini; Carlos Alberto Soares; Eduardo Vedro de Paula (org.), *Dragagens Portuárias no Brasil – Licenciamento e Monitoramento Ambiental*, pp.77-78, Ministério de Ciência e Tecnologia, Brasília, Brasil.

Costa, N.R.; Kantin, R.; Niencheski, L. F.; Batista, J.R.; Braumgarten, M.G.Z. (1982) - Estudo da poluição orgânica nas águas que rodeiam a cidade de Rio Grande. *Engenharia Sanitária e Ambiental* (ISSN: 1413-4152), 21(2):222-231, ABES – Associação Brasileira de Engenharia Sanitária e Ambiental, Rio de Janeiro, RJ, Brasil.

Costa, L.D.F. (2012) - *Avaliação de metais na forma lábil no sedimento e na água de marinas e áreas portuárias de Rio Grande, RS, na Lagoa dos Patos sob influência do uso de tintas anti-incrustantes em embarcações*. 110p., Dissertação de doutorado Universidade Federal do Rio Grande, Rio Grande, RS, Brasil. *Unpublished*.

Costa, L.D.F; Wallner-Kersanach, M. (2013) - Assessment of labile fraction of copper and zinc in marinas and port areas in southerm Brasil. *Environmental Monitoring and Assessment*, 185:6767-6781. DOI: 10.1007/s10661-013-3063-0

Davison,W.; Zhang, H. (1994) - In situ speciation measurement of trace components in natural waters using thin-film gels. *Nature*, 367: 546-548. DOI: 10.1038/367546a0

Domingues, M.V. de la R.; Carvalho, D.S.; Carvalho, A.B. (2013) - O Polo Naval e Offshore e o desenvolvimento regional da metade sul do Rio Grande do Sul. *Ensaios FEE* (ISSN: 1980-2668), 34:933-954, Porto Alegre, Brasil. Available on-line at http://revistas.fee.tche.br/index.php/ensaios/article/view/3053/3201.

Dunn, R.J.K.; Teasdale, P.R.; Warnken, J.; Schleich, R.R.; (2003) - Evaluation of the diffusive gradient in a thin film technique for monitoring trace metal concentrations in estuarine waters. *Environmental Science and Technology*, 37: 2794-2800. DOI: 10.1016/j.envpol.2006.10.027

Förstner, U.; Wittman G. (1981) - *Metal Pollution in the Aquatic Environment*. Springer. 486 p., Berlin, Heidelberg, Germany. ISBN: 978-3540128564.

Garcia, C.A.E. (1998) - Características hidrográficas. *In:* Ulrich Seeliger; Clarisse Odebrecht; Jorge P. Castello (org.), *Os Ecossistemas Costeiros e Marinhos do Extremo Sul do Brasil*, pp. 219-226, Editora Ecoscientia, Rio Grande, RS, Brasil. ISBN: 354061365x.

Garcia, F.A.P.; Mirlean, N.; Baisch, P.R. (2010) - Marcadores metálicos como avaliação de impacto crônico de emissões petroquímicas em zona urbana. *Química Nova* (*ISSN* 1678-7064), 33(3):716-720, São Paulo, Brasil. Available on-line at http://quimicanova.sbq.org.br/imagebank/pdf/Vol33No3_716_39-NT09017.pdf

Gutierrez, F.B. (2013) - *Estudo do material particulado atmosférico (MP 2,5) em áreas adjacentes a Laguna dos Patos em Rio Grande, RS- Rio Grande (RS)*. 138 p., Dissertação de Mestrado, Universidade Federal do Rio Grande, Rio Grande, RS, Brasil. *Unpublished*.

Herz, R. (1977) - *Circulação das aguas superficiais da Lagoa dos Patos*. 217 p., Dissertação de Doutorado, Universidade de São Paulo, São Paulo, SP, Brasil. *Unpublished*.

Kantin, R.; Costa, N.R.; Baptista, J.R.; Philomena, A.L.; Giesta, S.M.; Niencheski, L.F. (1980) - Contaminação das águas ao redor da cidade do Rio grande: óleos e graxas. *Ciência e Cultura* (ISSN: 2317-6660), 33(2):236-239, Campinas, Brasil.

Kantin, R.; Baumgarten, M.G.Z.; Cabeda, M.; Beaumond, A.C;, Almeida, T.L. (1981) - Concentration of anionic detergents in Rio Grande water (South of Brasil). *Marine Pollution Bulletin*, 12:50-53. DOI: 10.1016/0025-326X(81)90259-9

Kjerfve, B. (1986) - Comparative oceanography of coastal lagoons. *In:* Douglas A. Wolfe (org.), *Estuarine Variability*, pp.63-81, N.Y. Academic Press., Orlando, FL, U. S. A. ISBN: 0127618902.

Law, R.J.; Kelly, C.; Matthiessen, P.; Aldridge, J. (2003) - The loss of the chemical tanker Ievoli Sun in the English Channel, October 2000. *Marine Pollution Bulletin*, 46(2):254-257. DOI: 10.1016/S0025-326X(02)00222-9

Leeuwen, H.P.V.; Town, R.M.; Buffle, J.; Cleven, R.F.M.J.; Davison, W.; Puy, J.; Riemsdijk, W.H.V.; Sigg, L. (2005) - Dynamic speciation analysis an biovailability of metals in aquatic system. *Environmental Science and Technology*, 22: 8545-8556. DOI: 10.1021/es050404x

Long, E.R.; Macdonald, D.D.; Smith, S.L.; Calder, F.D. (1995) - Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environmental Management (ISSN: 1432-1009), 19(1):81-97. Available online at http://link.springer.com/journal/267/19/1

Mirlean, N.; Vanz, A.; Baisch, P. (2000) - Níveis e origem da acidificação das chuvas na região de Rio Grande, RS. *Química Nova* (ISSN: 1678), 23(5):590-593. Available on-line at http://quimicanova.sbq.org.br/imagebank/pdf/Vol23No5_590_03.pdf

Mirlean, N.; Baraj, B.; Niencheski, L. F.; Baisch, P.; Robinson, D. (2001) - The effect of accidental sulphuric acid leaking on metal distributions in estuarine sediment of Patos Lagoon. *Marine Pollution Bulletin*, 42(11):1114-1117. DOI: 10.1016/S0025-326X(01)00099-6

Mirlean, N.; Andrus, V.; Baisch, P. (2003a) - Mercury pollution sources in sediments of Patos Lagoon Estuary, Southern Brazil. Marine Pollution Bulletin, 46(3):331–334. DOI: 10.1016/S0025-326X(02)00404-6

Mirlean,N.; Andrus, V.E.; Baisch, P.;Griep, G.; Casartelli, M.R. (2003b) - Arsenic pollution in Patos Lagoon estuarine sediments. Marine Pollution Bulletin, 46(11):1480-1484. DOI: 10.1016/S0025-326X(03)00257-1

Mirlean, N.;Larned, S.; Nikora, V.; Kutter, V. (2005a) - Mercury in lakes and lake fishes on a conservation-industry gradient in Brazil. *Chemosphere*, 60(2): 226-236. DOI: 10.1016/j.chemosphere.2004.12.047

Mirlean, N.; Robinson, D.; Kawashita, K.; Vignol, M. L.; Conceição, R; Chemale, F. (2005b) - Identification of local sources of lead in atmospheric deposits in an urban area in Southern Brazil using stable lead isotope ratios. *Atmospheric Environment*, 39(33):6204-6212**.** DOI**:** 10.1016/j.atmosenv.2005.07.002

Mirlean, N.; Oliveira, C. (2006) - Mercury in coastal reclamation fills in southernmost Brazil: Historical and environmental facets. *Journal of Coastal Research*, 22(6):1573-1576. DOI: 10.2112/04-0352.1

Mirlean, N.; Roisenberg, A. (2006) -The effect of emissions of fertilizer production on the environment contamination by cadmium and arsenic in southern Brazil. *Environmental Pollution*, 143(2):335-340. DOI: 10.1016/j.envpol.2005.11.022

Mirlean, N.; Calliari, L.J.;Baisch, P.; Loitzanbauer, E.; Shumilin, E. (2009) - Urban activity and mercury contamination in estuarine and marine sediments (Southern Brazil). *Environmental Monitoring and Assessment*, 157(1):583-590. DOI: 10.1007/s10661-008-0558-1

Möller, O.O.; Castaing, P. (1999) – Hydrological characteristics of the estuarine area of Patos Lagoon (30ºS, Brazil). *In:* Gerardo M.E. Perillo; María Cintia Piccolo; Mario Pino-Quivira (org.), *Estuaries of South America: their geomorphology and dynamics*, pp.83-100, Springer-Verlag, Berlin, Germany.

Niencheski, L.F.H.; Baumgarten, M.G.Z.; Fillmann, G.; Window, H. L. (1999) - Nutrients and suspended matter behaviour in the Patos Lagoon Estuary (Brazil). *In:* Gerardo M.E. Perillo; María Cintia Piccolo; Mario Pino-Quivira (org.), *Estuaries of South America: their geomorphology and dynamics*, pp.67-81, Springer-Verlag, Berlin, Germany.

Niencheski, L.F.H.; Baumgarten, M.G.Z. (2000) - Distribution of particulate trace metal in Southern Part of the Patos Lagoon Estuary. *Aquatic Ecosystem Health and Management*, 3(4):515-520. DOI: 10.1016/S1463-4988(00)00041-5

Odebrecht, C; Abreu,P.C.; Bemvenuti, C.E.; Copertino, M.; José H. Muelbert, J.H.; Vieira, J.P.; Seeliger, U. (2010) - The Patos Lagoon Estuary, Southern Brazil - Biotic Responses to Natural and Anthropogenic Impacts in the Last Decades (1979–2008). *In:* Michael J. Kennish, Hans W. Paerl (org.), *Coastal Lagoons: Critical Habits of Environmental Change*, pp. 434-455, CRC Press, Boca Raton, FL, U.S.A.. ISBN: 978-1420088311.

Pasquini, A.I.; Niencheski, L.F.H.; Depetris, P.J. (2012) -Yhe ENSO signature and other hydrological characteristics in Patos and adjacente coastal lagoons, South-eastern Brazil. *Estuarine, Coastal and Shelf Science*, 111:139-146. DOI: 10.1016/j.ecss.2012.07.004

Persich, G.R.; Odebrecht, C.; Bergesch, M.; Abreu, P.C. (1996) - Eutrofização e fitoplâncton: comparação: comparação entre duas enseadas rasas do estuário da Lagoa dos Patos. *Revista Atlântica*, (ISSN on line: 2236-7586 / ISSN print: 0102-165635), 18:27-41, Rio Grande, RS, Brasil. Available on-line at http://www.seer.furg.br/atlantica.

Pinheiro Junior, E.M.; Baumgarten, M.G.Z.; Souza, M.L. (2010) - A poluição das águas por matéria orgânica: uma abordagem didática para o ensino fundamental. *In:* Raquel Pereira Quadrado, Maria Teresa O. Nunes, Cláudia Andréa Z. Rizzi, Paula Regina C. Ribeiro (org.), *Ecos do Sul: conhecer os ecossistemas costeiros é tri legal*. pp.210-229, Editora da FURG, Rio Grande, RS, Brasil . ISBN: 978-8575661475.

Reis, E.G.; D'incao, F. (2000) - The present status of artisanal fisheries of extreme southern Brazil: an effort towards community based management. *Ocean & Coastal Management*, 43(7):585-595. DOI: 10.1016/S0964-5691(00)00048-X

Salomons, W.; Förstner, U. (1984) - *Metals in the hydrocycle*. 349 p., Springer-Verlag. Berlin, Heidelberg, Germany. ISBN: 3540127550.

Seeliger, U.; Costa, C.S.B. (1998) – Impactos Naturais e Humanos. *In:* Ulrich Seeliger; Clarisse Odebrecht; Jorge P. Castello (org.), *Os Ecossistemas Costeiros e Marinhos do Extremo Sul do Brasil*, pp.219-226. Editora Ecoscientia, Rio Grande, RS, Brazil. ISBN: 354061365x

Shumilin, E.; Paez-osuna, F.; Green-ruiz, C.; Sapozhnikov, D.; Guadalupe, D.; Rodrıguez-meza, G.D.; Godrınez-orta, L. (2001) - Arsenic, antimony, selenium and other trace elements in sediments of the La Paz Lagoon, Peninsula of Baja, California, Mexico. *Marine Pollution Bulletin*, 42(3):174-178, Great Britain. DOI: 10.1016/S0025-326X(00)00123-5

Souza, P.R.S. (2011) - *Áreas urbanas desfavorecidas do município de Rio Grande/RS*. 118p., Dissertação de Mestrado em Geografia, Universidade Federal do Rio Grande, Rio Grande, RS, Brasil.. *Unpublished*.

Spengler, A.; Wallner-Kersanach, M.; Baumgarten, M.G.Z. (2007) – Rio Grande Municipal dump site impact in the estuary of the Patos Lagoon (RS, Brazil). *Acta Liminologica Brasilensia*, (ISSN 2179-975x), 19(2):197-210, Rio Claro, Brasil. Available on-line at http://www.ablimno.org.br/acta/pdf/acta19_vol2_07.pdf

Tagliani, P.R.A.; Landazurib, H.; Reis, E.G.; Tagliani, C.R.; Asmus, M.L.; Sánchez-Arcilla, A. (2003) - Integrated coastal zone management in the Patos Lagoon estuary: perspectives in context of developing country. *Ocean & Coastal Management*, 46(9-10):807–822. DOI: 10.1016/S0964-5691(03)00063-2

Tagliani, P.R.A.; Asmus; M.L.; Tagliani, C. R. A.; Polette, M.; Costa, C. S. B.; Salas, E. (2007) - Integrated Coastal zone mangement in the Patos Lagoon Estuary (south Brazil): State of art. *In:* C. A. Brebbia; A. Kungolos (org.). *Water Resources Management IV*, pp. 679-686, Wit Press, Southampton, UK. ISBN: 978-1845640743.

Tagliani, P.R.A.; Kitzmann, D.; Asmus, M.L. (2011) - As forças e as debilidades, as opportunidades e as ameaças no manejo integrado no estuário da Lagoa dos Patos. *In:* Paulo Tagliani; Milton Asmus. (org.), *Manejo Integrado do Estuário da Lagoa dos Patos*, pp. 219-232, Editora da FURG, Rio Grande, RS, Brasil. ISBN: 978-8575662069.

Tagliani, P.R.; Polette, M. (2011) - O sistema municipal de Monitoramento . *In:* Paulo Tagliani; Milton Asmus. (org.), *Manejo Integrado do Estuário da Lagoa dos Patos*, pp. 191-199, Editora da FURG, Rio Grande, RS, Brasil. ISBN: 978-8575662069.

Torres, L.H. (2008) - Cronologia básica da história da cidade do Rio Grande (1737-1947). *Biblos*, (ISSN: 0102-4388), 22(2):9-18, Rio Grande, RS, Brasil. Available online at http://www.seer.furg.br/biblos/article/view/957/424

Urban, S.R.; Corrêa, A.X.R.; Schettini, C.A.F.; Schwingel, P.R.; Sperb, R.P.; Radetski, C.M. (2010) - Physicochemical and ecotoxicological evaluation of estuarine water quality during a dredging operation. *Journal of Soil Sediments*, 10(1):65–76. DOI: 10.1007/s11368-009-0156-z

Vanz, A. (2000) - *Estudo Geoquímico das Precipitações Sólidas Atmosféricas na Região do Rio Grande*. 119p., Dissertação de Mestrado, Fundação Universidade Federal do Rio Grande, Rio Grande, RS, Brasil. *Unpublished*.

Vanz, A.; Baisch, P.; Mirlean, N. (2003) - Avaliação de poluição do ar por chumbo particulado através de uma abordagem geoquímica. *Química Nova*, 26(1):25-31, São Paulo, Brasil. Available on-line at http://quimicanova.sbq.org.br/imagebank/pdf/Vol26No1_25_05.pdf

Wallner-Kersanach, M.; Andrade, C.F.F.; Milani, M.R.; Niencheski, L.F.H. (2009) - In situ measurement of trace metals in estuarine waters of the Patos Lagoon using the diffusive gradient in thin film (DGT). Journal of Brazilian Chemical Society, 20,(2):333-340. DOI: 10.1590/S0103-50532009000200019

Warnken, J.; Dunn, R.J.K.; Teasdale, P.R. (2004) - Investigation of recreational boats as a source of copper at anchorage sites using time-integrated diffusive gradients in thin film and sediment measurements. Marine Pollution Bulletin, 49(9-10):833-843. DOI: 10.1016/j.marpolbul.2004.06.012

Windom, H. L.; Niencheski, L. F.; Smith, R. G. Jr. (1999) - Biogeochemistry of Nutrients and Trace Metals in the Estuarine Region of the Patos Lagoon (Brazil). Estuarine, Coastal and Shelf Science, 48(1):113-123. DOI: 10.1006/ecss.1998.0410

Yunes, J.S.; Salomon, P.S.; Matthiensen, A.; Beattie, K.A.; Raggett, S.L.; Codd, G.A. (1995) – Toxic blooms of cyanobacteria in the Patos Lagoon Estuary, southern Brazil. *Journal of Aquatic Ecosystem Health*, 5(4):223-229. DOI: 10.1007/BF00662183

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Plastic fragments as a major component of marine litter: a case study in Salvador, Bahia, Brazil*

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ABSTRACT

Urban areas are hotspots for marine litter. Plastic materials are the most common type of beach litter and can fragment into even smaller pieces. A total of 24 sampling stations were distributed along the coast of Salvador, Brazil, from which every litter item > 2 cm was sampled. A total of 17,089 items were sampled from the beaches of Salvador in two different survey seasons (10,416 during the winter and 6,673 during the summer). Plastic represented 87.45% of all materials sampled during the winter and 85.24%, during the summer. In both seasons, the majority of the sampled beaches were classified as extremely dirty according to the Clean-Coast Index. Plastic fragments were found in every sampling station in both field surveys, representing 45.7% of the overall plastic items sampled. Tourism/recreation activities appeared to be important sources of litter to the area.

Keywords: plastic pollution; plastic fragments; coastal management; urban beaches; coastal currents.

RESUMO

Fragmentos plásticos como um componente principal do lixo marinho: estudo de caso de Salvador, Bahia, Brasil

Áreas urbanas concentram lixo marinho. Materiais plásticos são o tipo mais comum de lixo de praia e podem sofrer fragmentação tornando-se cada vez menores. Um total de 24 pontos de amostragem foi definido ao longo da costa de Salvador, Brasil, nos quais todo item de lixo > 2 cm foi amostrado. A maioria das praias em Salvador está cobertas por lixo – tanto fragmentos quanto itens inteiros. Um total de 17.089 itens foi coletado das praias de Salvador durante duas campanhas (10.416 durante o inverno e 6.673 durante o verão). Plástico representou 87,45% de todo o material amostrado durante o inverno e 85,24% durante o verão. Em ambas as estações a maioria das praias amostradas foram classificadas como extremamente sujas de acordo com o Clean-Coast Index. Fragmentos plásticos foram encontrados em todos os pontos de amostragem em ambas as campanhas, representando 45,7% de todo o plástico encontrado. Atividades de turismo/recreação se mostraram fontes importantes para o lixo na área.

Palavras-chave: poluição por plásticos; fragmentos plásticos; gerenciamento costeiro; praias urbanas; correntes costeiras.

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1. Introduction

Litter can be found on beaches all over the world, originated from both local and distant terrestrial sources or brought ashore by the sea (marine source). According to Storrier *et al.* (2007) and Spengler & Costa (2008), sandy beaches, estuaries and the seafloor are the preferential areas for litter accumulation. Regarding beaches, marine debris can be deposited in the backshore in various situations, such as during spring high tides and events of equinoctial meteorological tides.

Longshore currents associated with swash transport of sandy particles and winds are the main agents responsible for longshore drift. In turn, the longshore drift controls sediment flow and budget (Komar 1976; Dominguez *et al.* 1983; Fontoura 2004). Analogously to the transportation of sediment particles, these currents can also transport litter, which can be deposited or redeposited, depending on factors such as seasonality, intensity of currents and litter density, in areas far from where they were originated.

Marine litter can be found in higher concentrations in the surrounding areas of great urban centers (Moore & Allen 2000; Leite *et al.* 2014). The proximity to urban centers is a determinant factor to its occurrence (Backhurst & Cole 2000).

Marine litter poses a clear threat to human well-being and various marine organisms. There are numerous reports of ingestion of marine litter by different species (*e.g.,* Colabuono *et al.* 2009; Provencher *et al.* 2010; Tourinho *et al.* 2010; Rebolledo *et al.* 2013; Buxton *et al.* 2013), which can cause their death and/or lead to the inclusion of the most minute particles of litter into food webs (Farrell & Nelson 2013), as well as cause entanglement (Gregory 2009). Marine litter also presents potential as a means for chemical pollution dispersion, due to the affinity of plastics in particular to different chemical compounds present in seawater (Ogata *et al.* 2009). Moreover, marine litter can also favor the occurrence of invasive species, which can use floating debris for dispersion (Barnes 2002).

An important component that is often overlooked in marine litter assessments are the plastic fragments, which represent a significant portion among the samples of beach litter monitoring surveys (Sobral *et al.* 2011). These fragments originate mostly from the abrasion of larger plastic items that were exposed to weathering in the marine and coastal environment (Sul & Costa 2014).

While whole items of marine litter allow surveys to narrow down potential inputs of these solid residues to the marine and coastal environment, fragments make source identification harder. For example, while cotton buds can be associated with sewage discharges, a non-descriptive piece of plastic does not tell such a simple story.

The general objective of the present study was to evaluate the occurrence and distribution of marine litter along the coastline of Salvador, state of Bahia, Brazil (Figure 1), emphasizing the contribution of plastic fragments as a major component of marine litter in order to understand the magnitude of the problem and optimize management efforts to address it.

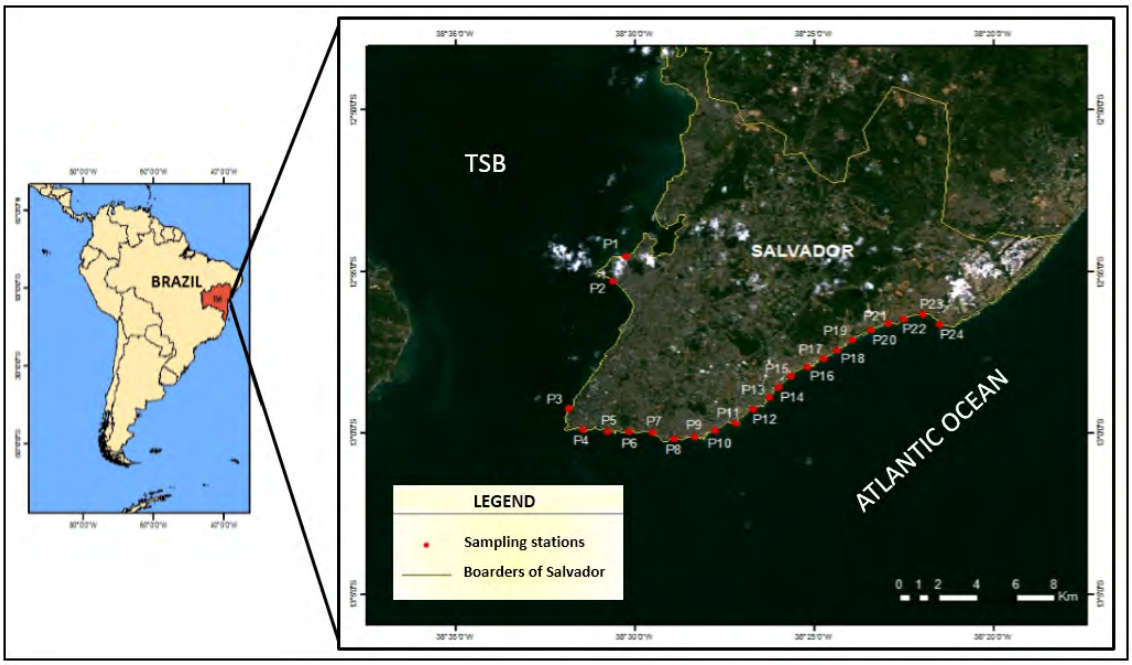

Figure 1 - Sampling stations along the coastline of Salvador, Brazil. TSB = Todos os Santos Bay.

Figura 1 - Pontos de amostragem ao longo da costa de Salvador, Brasil. TSB = Baía de Todos os Santos.

2. Study Site

With a growing population of over 2.6 million inhabitants, Salvador is one of the largest metropolises in the country (IBGE, 2010). The beaches of the municipality are also greatly sought out by tourists throughout the year, who visit them attracted by their natural beauty and the historical and cultural relevance of the city.

Along the coast of the state of Bahia, trade winds approach mainly from NE and E during the spring and summer, while during the autumn and winter, from SE and S (Bittencourt *et al.* 2008). During the autumn-winter period, SSE winds associated with the episodic approach of cold fronts reinforce SE trade winds. This atmospheric circulation system is responsible for the general pattern of wave fronts that approach the coast (Dominguez *et al.* 1992; Martin *et al.* 1998) and is also the main driver for the sediment dispersion pattern in this area. Geomorphological features indicate that this pattern respects the general NE - SW orientation of the net longshore drift in this area (Dominguez *et al.* 1992; Bittencourt *et al.* 2005).

However, locally, the direction of the general drift can be altered by the presence of promontories and rocky outcrops, generating local drift cells which do not necessarily respect the preferential direction of the net longshore drift. The area presents semidiurnal tides, with mean amplitude of 2.5 m reaching up to 2.8 m during spring tides.

3. Materials and methods

Two field surveys were performed during the winter of 2012 (from June to August – rainy season) and summer of 2013 (February – dry season), to investigate possible seasonality in the distribution and input of marine litter.

A total of 24 sampling stations were determined. Twenty-two stations were distributed every 1 km along the oceanic coastline of Salvador, from the Porto da Barra beach (P3), close to the mouth of the Todos os Santos Bay (TSB), up to the Itapuã Lighthouse (P24). The remaining 2 stations (P1 and P2) were located within the Todos os Santos Bay (TSB) (Figure 1).

A 10 m-wide transect was delimitated from the highest high water line to the end of the backshore, when encountering the first obstacle (*e.g.,* vegetation, frontal dune, wall, construction), in each sampling station (Figure 2). All litter (> 2 cm) was collected and stored in duly identified plastic bags. Pieces smaller than 2 cm are relatively difficult to be systematically sampled without using any equipment and are not sampled at this time. Sampling occurred early in the morning to avoid possible direct interferences of municipal cleaning activities.

Figure 2 - Representation of the transect delimited for sampling station P10.

Figura 2 - Representação do transecto delimitado para o ponto de amostragem P10.

Plastic items that were a fraction equal to 50% or less of the original object were counted as a fragment. Thus, the term "plastic fragment" in the present study is regardless to its size and should not be misinterpreted as "microplastic".

Litter was sorted and classified according to its composition (plastic, metal, glass, wood, cloth, others) and type of object (*e.g.,* plastic bag, beverage cans, barbecue wooden sticks, plastic fragments, etc.) in order to help in the identification of their potential sources (domestic/sewage/urban drainage, tourism/recreation, fisheries/boating activities, medical waste, indeterminate). The "indeterminate" source category encompasses not only items that can have multiple sources (such as plastic bags, for example, which can reach the beach through sewage/urban drainage or be dumped on the sand by a beach user, etc.), but also items which do not have a clear indication of potential source.

Until recently there was no global index to classify beach contamination by marine debris. Alkalay *et al.* (2007) proposed the Clean Coast Index (CCI) in order to classify beaches according to the amount of plastic on their sand since plastic is commonly the most abundant class of marine litter (Cheshire *et al.* 2009). Thus, to determine the CCI of each beach, first the density of plastics (*Dp*) was calculated as:

$$\mathrm{Dp} = \frac{\textit{No. of plastic items}}{X\,(m) \times 10\,(m)} \qquad (1)$$

where X is the width of the transect.

In possession of this information, the CCI could be calculated using the equation:

$$CCI = Dp \times K \qquad (2)$$

where K is the correction coefficient (K = 20), used for statistical reasons and convenience, according to Alkalay *et al.* (2007).

The CCI results were then classified according to the pollution degree, from "very clean" (0 – 2), "clean" (2 – 5) , "moderate" (5 – 10) and "dirty" (10 – 20) to "extremely dirty" (> 20).

Density of plastic fragments (*Dpf*) was also calculated separately. This allowed for a better assessment of their occurrence and representativeness:

$$Dpf = \frac{\textit{No. of plastic fragments}}{X\,(m) \times 10\,(m)} \qquad (3)$$

where X is the width of the transect.

The Kruskal-Wallis test was used to asses significant differences between them amount of marine litter samples during each season.

4. Results

A total of 17,089 items were sampled. From these, 10,416 were sampled during the winter, and 6,673 during the summer. There was no significant difference ($p > 0.05$) between the number of marine litter items sampled during winter and summer.

During the winter, P5 (Figure 1) presented the highest density (31.50 items/m²) and P24, the lowest (0.19 item/m²). In turn, during the summer, P12 presented the greatest density (18.80 items/m²), and P24, once again, the lowest (0.33 item/m²).

The high occurrence of plastics (> 85% in both seasons) is in accordance to the numbers found in the literature (Cheshire *et al.* 2009), and guarantees the applicability of plastic as a proxy for the CCI. During the winter, the plastic category of materials was followed by metal (4.25%), while during the summer, by wood (4.87%).

During the winter, 87.5% of the beaches (21 stations) were classified as extremely dirty according to the CCI. The three remaining sampling stations were classified as dirty, moderate and clean, each representing 4.17% of the total. During the summer, extremely dirty beaches were also the majority (79.17%, 19 stations), followed by beaches classified as dirty (12.5%, 3 stations) and then moderate and clean (4.17%, 1 station each) (Supporting Information I).

The CCI values were commonly high above the number that indicates the highest category (CCI ≥ 20). During the winter, CCI values as high as 622 (P5) and 569 (P11) were found, while during summer the highest values were 350 (P12) and 280 (P8) (Table 1 in SI-I). This indicates the extreme degree of contamination of the beaches of the municipality which, in many occasions, are vastly covered by plastic items (Supporting Information II).

Regarding the potential sources of litter, during both seasons, all beaches presented greater representativeness of the category "indeterminate". This is the case of plastic fragments which, alone, represented a major portion of the samples (39.48% from the overall sampled material from both campaigns) and generally do not allow the identification of potential sources.

If the category "indeterminate" was not considered, during the winter, 23 (95.83%) out of the 24 sampled beaches had "tourism/recreation activities" as the main potential litter source. Still regarding the winter, only one sampling station had "domestic/sewage drainage" as the most representative class. In turn, excluding the category "indeterminate" in the summer campaign, 91.67% of the litter found on the beaches during this season was attributed to the category "tourism/recreation activities" and the remaining 8.33% to "domestic/sewage drainage".

Plastic fragments were found in every sampling station in both field surveys, with a mean of 185 fragments/sampling station (Table 1 in SI-I). During the winter, 4,446 fragments were sampled, while during the summer there were 2,302. Plastic fragments represented 45.7% of the 25 types of plastic items that were identified. This category was followed by polystyrene fragments (9.6%), cotton bud/lollipop sticks (9.4%), PET bottle caps (8.8%), cigarette butts (8.3%) and plastic cutlery/straws (6.4%).

During the winter the accumulation of plastic fragments was significantly higher. Peaks in plastic fragment abundance occurred in areas near rainwater drainages and sewage runoffs, such as in stations P1, P5, P7, P8, P10, P11 and P12 (Figures 1 and Supporting Information III).

5. Discussion

The greatest occurrence and density of marine litter were found during the winter. Because winter is the rainy season in this area, the number of tourists and general users of the beach is lower. However, the volume of water that can effectively runoff to the beaches, carrying litter, increases.

On the other hand, during the summer the use of the beaches in Salvador is greater and so is the effort of cleaning actions by local authorities. However, these activities are ineffective, especially regarding the removal of smaller plastic fragments, which usually escape the most common cleaning methods (raking) (Fernandino *et al.* 2015). In some cases, as reported by Leite *et al.* (2014), the frequency of cleaning efforts on the beaches of Salvador can significantly reduce the amount of litter on beaches, such is the case of Porto da Barra beach (P03), which is cleaned twice a day. Despite this effort, the beach in question was classified in the present study as extremely dirty with CCI = 28 at the moment of sampling. This indicates that the constant input to and fragmentation of marine litter at the adjacent marine and coastal environment is greater than the remediation actions. Thus, fighting the sources directly is necessary through sanitation, sewage treatment, municipal waste collection, and environmental education programs.

In many cases, the category "indeterminate" represented more than 80% of all sampled items. This reflects the difficulty in identifying the sources of contamination of the beaches in Salvador by marine litter. One reason for this finding is because the occurrence and characteristics of plastic fragments, as previously mentioned, do not allow for a more accurate identification of sources.

Sewage and rainwater drainages can be considered as important potential sources for plastic and plastic fragments to the beaches in the municipality considering the proximity of fragment concentration peaks to these areas.

The high concentrations of plastic fragments observed in stations P10, P11, P12, P23 and P24 may have resulted from a response to wave convergence zones (WCZ), as inferred by Fernandino (2014) who considered this factor as one of the responsible agents for plastic pellet concentrations along the same coastline. According to the same author, these WCZ are generated by wave fronts from SSE, SE and S, and are capable of casting small particles towards the continent, thus favoring their accumulation in the backshore.

As highlighted by Corcoran *et al.* (2009), the combination of particle transportation, both sediment and plastic, and flood tides result in the deposition of plastic particles along high water strandlines. However, this accumulation is temporary, because with the next high tide, marine litter previously brought and deposited, can be remobilized and deposited on a new strandline or float back on the surface of the sea. Thus, the usually more stable character of non-eroded backshores (i.e., presence of vegetation, primary dunes, etc.) can provide conditions that are more favorable for deposition and accumulation of particles, which was not a common condition observed in Salvador.

Litter found on the beaches of Salvador presents high mobility, since most of the sampling stations presented walls and other man-made structures constructed on the backshore within the range of spring tide high waters and meteorological tides, reducing the sand area where litter could be deposited for longer periods.

The great number of plastic fragments suggests long exposure of the plastic litter to weathering and mechanical agents. As reported by Sul & Costa (2014), the tendency that items in these conditions will fragment even more, originating microplastic, threatening various organisms which can ingest them either directly or indirectly, ultimately affecting top predators, such as human. It is clear that plastic, especially small fragments, have the potential of integrating the sediment matrix of sandy beaches, becoming an anthropogenic component of the sediment.

6. Conclusions

No evidence was found indicating that marine litter concentration was oriented according to the longshore drift. This could be explained by the constant presence of obstacles along the shore, which alter local coastal processes. However, WCZ and sewage and rainwater drainages seemed to influence areas of greater concentration of plastic fragments.

The coastline of Salvador, as a whole, was found to be polluted by marine litter, either in a greater or lower degree. Most of the beaches were classified as extremely dirty, despite the public cleaning activities that occurs

along the beaches of the municipality. The CCI presented levels well above the minimum limit of the classification of extremely dirty (> 20) with values higher than 600. Such fact reflects the ineffectiveness of the current cleaning methods used by municipal cleaning agents.

Tourism/recreation activities were important sources of litter to the area. This finding suggests that measures and actions towards environmental education and awareness should be encouraged in order to change the behavior of the various beach users regarding marine litter production. The presence of items from domestic sources illustrates a lack of adequate sewage treatment and suggests the importance of an improvement in this sector in order to prevent its input and, consequently, improve both public and marine ecosystem health.

Analyzing the composition, size and characteristics of plastic fragments is important to understand its significance in the environment and, consequently, the threats posed by its presence.

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Appendix

Supporting Information associated with this article is available online at **http://www.aprh.pt/rgci/pdf/rgci-649_Fernandino_Supporting-Information.pdf**

References

Alkalay, R.; Pasternak, G.; Alon, Z. (2007) - Clean-coast index – a new approach for beach cleanliness assessment. *Ocean & Coastal Management*, 50(5-6):352-362. DOI: 10.1016/j.ocecoaman.2006.10.002.

Backhurst, M.K.; Cole, R.G. (2000) - Subtidal benthic marine litter at Kawau Island, north-eastern New Zealand. *Journal of Environmental Management*, 60(3):227-237. DOI: 10.1006/jema.2000.0381.

Barnes, D.K.A. (2002) - Invasions by marine life on plastic debris. *Nature*, 412(6883): 808–809. DOI: 10.1038/416808a.

Bittencourt, A.C.S.P.; Dominguez, J.M.L.; Martin, L.; Silva, I.R. (2005) - Longshore transport on the northeastern Brazilian coast and implications to the location of large scale accumulative and erosive zones: an overview. *Marine Geology*, 219(4):219-234. DOI: 10.1016/j.margeo.2005.06.006.

Bittencourt, A.C.S.P.; Dominguez, J.M.L.; Medeiros, K.O.P.; Guimarães, J.K.; Dutra, F.R.L.S. (2008) - Severe coastal erosion hotspots in the city of Salvador, Bahia, Brazil. *Shore & Beach*, 16:8-14.

Buxton, R.T.; Currey, C.A.; Lyver, P.O'B.; Jones, C.J. (2013) - Incidence of plastic fragments among burrow-nesting seabird colonies on offshore islands in northern New Zealand. *Marine Pollution Bulletin*, 74(1):420-424. DOI: 10.1016/j.marpolbul.2013.07.011.

Cheshire, A.; Adler, E.; Barbiere, J.; Cohen, Y.; Evans, S.; Jarayabhand, S.; Jeftic, L.; Jung, R.; Kinsey, S.; Kusui, T.; Lavine, I.; Manyara, P.; Ooesterbaan, L.; Pereira, M.; Sheavly, S.; Tkalin, A.; Varadarajan, S.; Wenneker, B.; Wesrphalen, G. (2009) - *UNEP/IOC Guidelines on Survey and Monitoring of Marine Litter.* 120p,, UNEP Regional Seas Reports and Studies. Available online at http://www.unep.org/regionalseas/marinelitter/publications/docs/Marine_Litter_Survey_and_Monitoring_Guidelines.pdf

Colabuono, F.I.; Barquete, V.; Domingues, B.S.; Montone, R.C. (2009) - Plastic ingestion by Procellariiformes in Southern Brazil. *Marine Pollution Bulletin*, 58(1):93-96. DOI: 10.1016/j.marpolbul.2008.08.020.

Corcoran, P.L.; Biesinger, M.C.; Grifi, M. (2009) - Plastics and beaches: a degrading relationship *Marine Pollution Bulletin*, 58(1):80-84. DOI: 10.1016/j.marpolbul.2008.08.022.

Dominguez, J.M.L.; Bittencourt, A.C.S.P.; Martin, L. (1983) - O papel da deriva litorânea de sedimentos arenosos na construção das planícies costeiras associadas às desembocaduras dos rios São Francisco (SE – AL), Jequitinhonha (BA), Doce (ES) e Paraíba do Sul (RJ). *Revista Brasileira de Geociências* (ISSN 0375-7536), 13(2):98-105, São Paulo, SP, Brasil. Available online at http://www.oceanografia.ufba.br/ftp/Sedimentologia/Bibliografia/Dominguez_etal_Papel%20da%20deria%20litoranea%20na%20construcao%20dos%20deltas%20brasileiros_RBrasGeoc_1983.pdf.

Dominguez, J.M.L.; Bittencourt, A.C.S.P.; Martin, L. (1992) - Controls on Quaternary coastal evolution of the east-northeastern coast of Brazil: roles of sea-level history, trade winds and climate. *Sedimentary Geology*, 80(3-4):213-232. DOI: 10.1016/0037-0738(92)90042-P.

Farrell, P.; Nelson, K. (2013) - Trophic level transfer of microplastic: Mytilus edulis (L.) to Carcinus maenas (L.). *Environmental Pollution*, 177:1-3. DOI: 10.1016/j.envpol.2013.01.046.

Fernandino, G. (2014) - *Ocorrência, distribuição e grau de poluição por pellets, lixo de praia e lixo bentônico nas praias do município de Salvador, Bahia, Brasil*. 114p., Master Dissertation Universidade Federal da Bahia, Salvador, BA, Brazil. *Unpublished*.

Fernandino, G.; Elliff, C.I.; Silva, I.R.; Bittencourt, A.C.S.P. (2015) - How many pellets are too many? The pellet pollution index as a tool to assess beach pollution by plastic resin pellets in Salvador, Bahia, Brazil. *Revista de Gestão Costeira Integrada / Journal of Integrated Coastal Zone Management*, 15(3):325-332. DOI: 10.5894/rgci566.

Fontoura, J.A.S. (2004) - *Hidrodinâmica costeira e quantificação do transporte longitudinal de sedimentos não coesivos na zona de surfe das praias adjacentes aos molhes da barra do Rio Grande, RS (aplicação às praias do Cassino, Mar Grosso e adjacências dos Molhes Leste e Oeste da embocadura do estuário da Lagoa dos Patos)*. 281p., PhD Thesis, Universidade Federal do Rio Grande do Sul, RS, Brazil.

Gregory, M.R. (2009) - Environmental implications of plastic debris in marine settings – entanglement, ingestion, smothering, hangers-on, hitch-hiking and alien invasions. *Philosophical Transactions of the Royal Society B*, 364(1526):2013–2025. DOI: 10.1098/rstb.2008.0265.

IBGE (2010) - *Censo demográfico – Salvador*. Instituto Brasileiro de Geografia e Estatística [web site]. Avalaible on-line at http://cidades.ibge.gov.br/xtras/perfil.php?codmun=292740

Komar, P.D. (1976) - *Beach processes and sedimentation*. 429p., Prentice Hall, New Jersey, Nj, USA.

Leite, A.S.; Santos, L.L.; Costa, Y.; Hatje, V. (2014) - Influence of proximity to an urban Center in the pattern of contamination by marine debris. *Marine Pollution Bulletin*, 81(1):242 – 247. DOI: 10.1016/j.marpolbul.2014.01.032.

Martin, L.; Dominguez, J.M.L.; Bittencourt, A.C.S.P. (1998) - Climate control of coastal erosion during a sea-level fall episode. *Anais da Academia Brasileira de Ciências* (ISSN 0001-3765), 70(2):249-266, São Paulo, SP, Brazil.

Moore, S.L.; Allen, M.J. (2000) - Distribution of anthropogenic and natural debris on the mainland shelf of the Southern California Bight. *Marine Pollution Bulletin*, 40(1):83–88. DOI: 10.1016/S0025-326X(99)00175-7.

Ogata, Y.; Takada, H.; Mizukawa, K.; Hirai, H.; Iwasa, S.; Endo, S.; Mato, Y.; Saha, M.; Okuda, K.; Nakashima, A.; Murakami, M.; Zurcher, N.; Booyatumanondo, R.; Zakaria, M.P.; Dung, L.Q.; Gordon, M.; Miguez, C.; Suzuki, S.; Moore, C.; Karapanagioti, H.K.; Weerts, S.; McClurg, T.; Burres, E.; Smith, W.; Van Velkenburg, M.; Lang, J.S.; Lang, R.C.M.; Laursen, D.; Danner, B.; Stewardson, N.; Thompson, R.C. (2009) - International pellet watch: global monitoring of persistent organic pollutants (POPs) in coastal waters. 1. Initial phase data on PCBs, DDTs and HCHs. *Marine Pollution Bulletin*, 58(10):1437-1446. DOI: 10.1016/j.marpolbul.2009.06.014.

Provencher, J.F.; Gaston, A.J.; Mallory, M.L.; O'Hara, P.D.; Gilchrist, H.G. (2010) - Ingested plastic in a diving seabird, the thick-billed murre (Uria lomvia), in the eastern Canadian Arctic. *Marine Pollution Bulletin*, 60(9):1406-1411. DOI: 10.1016/j.marpolbul.2010.05.017.

Rebolledo, E.L.B.; Van Franeker, J.A.; Jansen, O.E.; Brasseur, S.M.J.M. (2013) - Plastic ingestion by harbour seals (Phoca vitulina) in The Netherlands. *Marine Pollution Bulletin*, 67(1-2):200–202. DOI: 10.1016/j.marpolbul.2012.11.035.

Sobral, P.; Frias, J.; Martins, J. (2011) - Microplástico nos Oceanos – Um problema sem fim à vista. *Ecologi@* (ISSN: 1647-2829), 3:12-21, Lisboa, Portugal. Available on-line at http://speco.fc.ul.pt/revistaecologia_3_art_3_3.html

Spengler, A.; Costa, M.F. (2008) - Methods applied in studies of benthic marine debris. *Marine Pollution Bulletin*, 56(2):226-230. DOI: 10.1016/j.marpolbul.2007.09.040.

Storrier, K.L.; McGlashan, D.J.; Bonellie, S.; Velander, K. (2007) - Beach litter deposition at a selection of beaches in the Firth of Forth, Scotland. *Journal of Coastal Research*, 23(4):813-822. DOI: 10.2112/04-0251.1.

Sul, J.A Ivar do; Costa, M.F. (2014) - The present and future of microplastic pollution in the marine environment. *Environmental Pollution*, 185:352 – 364. DOI: 10.1016/j.envpol.2013.10.036.

Tourinho, P.S.; Ivar-Do-Sul, J.A.; Fillmann, G. (2010) - Is marine debris ingestion still a problem for the coastal marine biota of southern Brazil? *Marine Pollution Bulletin*, 60(3):396-401. DOI: 10.1016/j.marpolbul.2009.10.013.

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Evaluation of metals availability in sediments of the Bertioga Channel (Santos Estuarine Complex - SP - Brazil): A tool for chemical pollution monitoring*

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ABSTRACT

The Bertioga Channel (SE Brazilian coast) is part of the Santos Estuarine Complex, situated at the Baixada Santista. The Baixada Santista is a very important economic region of Brazil which, due to its intensive economic development, has been experiencing several interventions on its coastal environment. Both the largest harbor, located on the city of Santos, and the Cubatão industrial complex, which presents large chemical, petrochemical and steel industries, are found near the Bertioga Channel. As a consequence, this socially and environmentally relevant channel is exposed to various sources of pollution that can increase the content of contaminating metals in sediments. For these reasons, the main objective of this study was to analyze the availability of potentially toxic elements (Cd, Cr, Cu, Ni, Pb and Zn) in sediment cores sampled along the Bertioga Channel. In this study, the term availability refers to the possibility of metal remobilization in sediments. By applying the chemical procedure of sequential extraction of metals, it was determined the contents of the elements of interest associated with the sediments' main components, enabling the assessment of the mobile fraction and the behavior of the elements regarding their remobilization. Therefore, this study can serve as a management tool for monitoring chemical pollution in the region. In order to evaluate the chemical contamination in sediments, the elements' available levels (excepting Ni) were compared to Canadian quality guidelines (ISQG and PEL). Due to the absence of comparative values of Ni for this guide, this element was compared to values described on the CONAMA 454/2012 resolution for dredging material from the Brazilian Ministry of Environment. For the environment risk assessment, the Risk Assessment Code - RAC - was employed toward a better understanding of the risk concerning the elements' remobilization. The maximum available levels, estimated from the sum of all mobile fraction, were 22.06 mg kg^{-1} for Cr, 5.57 mg kg^{-1} for Cu, 11.53 mg kg^{-1} for Ni, 36.43 mg kg^{-1} for Pb and 57.53 mg kg^{-1}

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for Zn. Cd presented levels below its quantification limit for all samples. It was observed that, excepting Cd, there is potential for the remobilization of all those elements, even though they exist in very low concentration and are not associated, mainly, to the acid-soluble fraction (considered the most environmentally relevant one due to its mobility level). Changes on local conditions can induce the remobilization of those metals and, thus, allow them to become available to the environment. However, even when released possibly they should not be hazardous to the biota as a result of their low contents in the sediments. Despite the low concentrations of Cr, Cu, Ni, Pb and Zn and considering that the observations made in this study were based on their available contents, the results highlight an anthropic contribution of those metals for the region, the potential for their accumulation and showing the importance of such monitoring for the future protection of the local communities.

Keywords: SE Brazilian coast, potentially toxic elements, sequential extraction, Risk Assessment Code (RAC).

RESUMO

Avaliação da disponibilidade de metais em sedimentos do Canal de Bertioga (Complexo Estuarino Santista – SP - Brasil): uma ferramenta para o monitoramento da poluição química

O Canal de Bertioga é um dos canais que constitui o complexo estuarino de Santos, localizado na costa sudeste brasileira. A Baixada Santista é uma região economicamente importante do Brasil que, em razão do seu intenso desenvolvimento econômico, tem sofrido intervenções no seu ambiente costeiro. Nas imediações do Canal de Bertioga encontra-se o maior porto do país, localizado na cidade de Santos, e o complexo industrial de Cubatão que comporta indústrias de grande porte dos segmentos químico, petroquímico e siderúrgico. Como consequência, esse Canal de importância social e econômica, está exposto a diversas fontes de poluição com potencial para aumentar o teor de contaminantes metálicos nos sedimentos. Diante desse cenário, o principal objetivo desse trabalho foi analisar a disponibilidade de elementos potencialmente tóxicos em sedimentos de testemunhos coletados ao longo do Canal de Bertioga. O termo disponibilidade aqui empregado refere-se à possibilidade de remobilização dos metais presentes nos sedimentos. Aplicando-se procedimento químico de extração sequencial de metais, determinou-se o teor de Cd, Cr, Cu, Ni, Pb e Zn associado aos principais componentes dos sedimentos. Esses dados possibilitaram estimar o teor disponível e o comportamento destes elementos quanto à remobilização, tornando esse estudo uma ferramenta gerencial em termos de monitoramento da poluição química da região. O teor máximo disponível, estimado a partir da soma das frações móveis, foi 22,06 mg kg^{-1} para Cr; 5,57 mg kg^{-1} para Cu; 11,53 mg kg^{-1} para Ni; 36,43 mg kg^{-1} para Pb e 57,53 mg kg^{-1} para Zn. O Cd apresentou teor inferior ao seu limite de quantificação em todas as amostras. Com exceção do Cd, verificou-se que há potencial para remobilização desses elementos, ainda que estejam em baixa concentração nos sedimentos. Alterações das condições ambientais poderão causar a remobilização desses metais e, consequentemente, deixá-los disponíveis. Entretanto, se remobilizados, em razão do baixo teor, estima-se que não representariam perigo à biota. Contudo, considerando-se que esse estudo baseou-se no teor disponível, ainda que as concentrações de Cr, Cu, Ni, Pb e Zn sejam baixas, pode-se inferir que esses resultados são indicativos de uma contribuição antrópica desses elementos na região e do potencial para acumulação de metais, mostrando a importância do monitoramento de elementos potencialmente tóxicos para proteção futura das comunidades bióticas.

***Palavras-chave**: costa sudeste brasileira, elementos potencialmente tóxicos, extração sequencial, Risk Assessment Code (RAC)*

1. Introduction

Environmental pollution by chemical contaminants is a current and persistent issue, usually associated with the industrial and economic growth of a region. In recent decades, environmental studies focusing on metals availability have become an effective tool in the difficult challenge of integrated coastal management, assisting both in environmental impact diagnosis as in action plan that favors environmental preservation.

In aquatic environments, sediments are an important compartment, in which potentially toxic metals occupy a prominent position when contamination is considered. Although the accumulation of heavy metals in sediments provide temporary improvement in the quality of overlying water, polluted sediments can be seen as "time bombs" (Kelderman & Osman, 2007), since the contaminants are not necessarily fixed permanently in them (Förstner 1979; Calmano *et al*., 1996; Zoumis *et al*., 2001). A change in physicochemical conditions can result in their remobilization, which would make it available to biotic communities. In this scenario, sediments are considered both a reservoir of chemical species and an active aquatic compartment, which plays an important role in the redistribution of these species (Cotta *et al*., 2006; Cuong & Obbard, 2006).

The mobility, transport and fractionation of heavy metals are a function of the element chemical form, which in turn is controlled by the physicochemical and biological characteristics of the system (Sakan *et al.*, 2009).

In the mobilization of heavy metals from sediments the redox potential and pH are considered the main variables (Calmano *et al.*, 1993). Among the factors that could cause these redox changes are: (1) the increase in nutrients (Förstner, 1979), (2) the oxidation-reduction cycle that varies seasonally, especially in summer, when the concentration of oxygen in the water-sediment interface tends to decrease (El-Azim & El-Moselhy, 2005) and (3) the daily tidal currents that cause periodic changes in the redox potential of coastal

and estuarine sediments (Calmano *et al.*, 1993). Oxygen deficiency in the sediments leads to an initial dissolution of hidrated manganese oxide, followed by that of iron compounds, leading to partial remobilization of any co-precipitated with metallic coatings (Förstner, 1979). In turn, reduction of pH leads to carbonates and hydroxides dissolution, as well as increase in metallic cations desorption due to competition with H^+ ions (Förstner, 1981). Several investigations have shown that pH decreases during sediment oxidation, being significant at metal remobilization (Förstner, 2004).

A procedure commonly used for a detailed investigation into the behavior of metals in soils and sediments is sequential extraction. The method developed and optimized by the European Community Bureau of Reference (BCR), currently Standards, Measurements and Testing (SM&T), is considered one of the most popular (Abollino *et al.*, 2011), and establishes three distinct stages in which the elements are sequentially extracted: (1) exchangeable metals and those associated with carbonates, (2) metals associated with Fe and Mn oxides, (3) metals associated with organic matter and sulfides. Considering that in unpolluted soils and sediments the metals are associated mainly to silicates and primary minerals, which forms species relatively immobile (Rauret, 1998), it can be inferred that the metal content extracted from these fractions represents an indicative of anthropogenic influence and thus demonstrates environmental pollution.

In this context, the aim of this study was to analyze the availability of Cd, Cr, Cu, Ni, Pb and Zn in sediment cores collected along the Bertioga Channel, inserted into the Santista estuarine complex and located between latitudes 23º 51' S and 23º 57' S and longitudes 46º 08' W and 46º19'W (Figure 1).

The Bertioga Channel presents economic and social importance, including recreational and fishing activities (Silva *et al.*, 2011). The length of the Canal is of approximately 25 km, with depths up to 15 m in the region of Barra de Bertioga and some depressions to the Largo do Candinho, which observed the greatest widths; the water inflow is carried by rivers with relatively small discharges, with only the river Itapanhaú presenting a higher importance (Bernardes & Miranda, 2001).

The Baixada Santista is an economically important region of Brazil, which, because of its significance, has undergone several alterations on its coastal environment. In the vicinity of the Bertioga Channel, in the City of Santos, is located the largest port in the country, as well as the industrial complex of Cubatão, which includes large petrochemicals, chemical and steel segment industries.

As a result, this Channel is exposed to various sources of pollution that may increase the potential metal accumulation in sediments. Given this concern, several studies related to metals have been developed in the region (*e.g.*, Siqueira *et al.*, 2005; Oliveira *et al.*, 2007; Silva *et al.*, 2011; Gonçalves *et al.*, 2013.). However, available information are generally based on results from total or partial metals, making important an evaluation on the availability of potentially toxic elements in the region in order to estimate the risk of remobilization. The relevance of this kind of information is clear, both in combination with studies on the biota, as constituting an

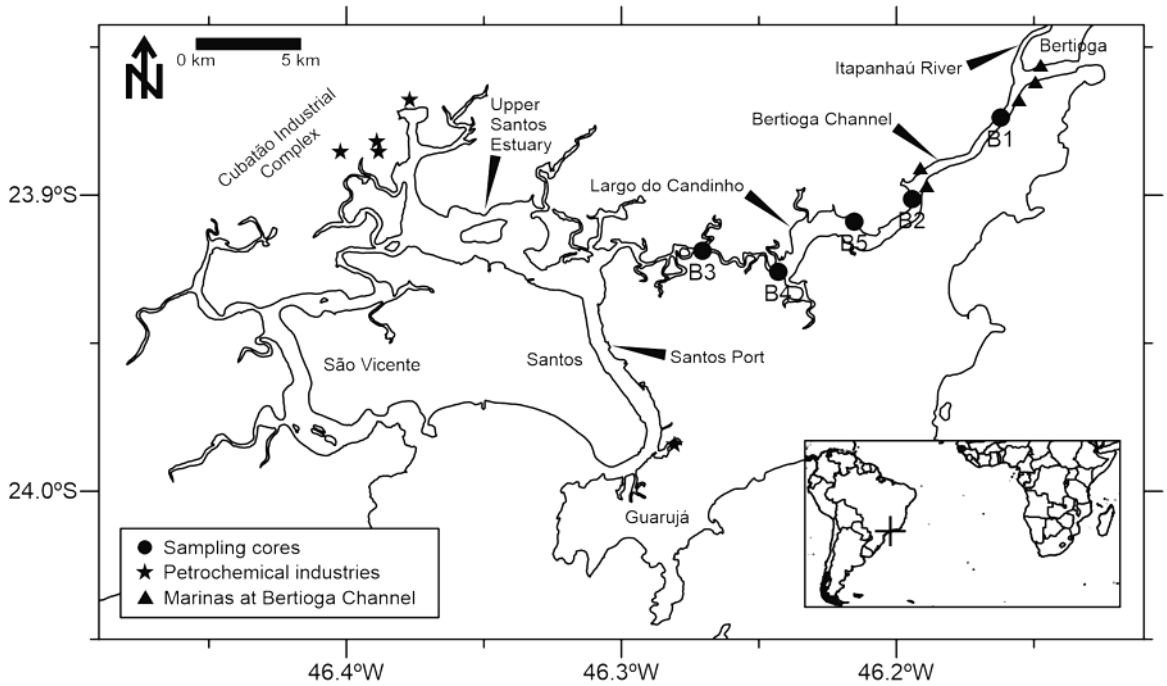

Figure 1 - Location of the sampled cores (B1, B2, B3, B4 e B5) along the Bertioga Channel.

Figura 1 - Localização dos testemunhos (B1, B2, B3, B4 e B5) coletados ao longo do Canal de Bertioga.

important coastal management tool for the monitoring of chemical pollution in the region. It is appropriate to clarify that the term "availability" used here is related to the possibility of remobilization of metals in the environment and does not reflect their bioavailability.

2. Materials and methods

2.1 Sampling and sample preparation

In February 2010 five sediment cores (B1, B2, B3, B4 and B5) were collected along the Bertioga Channel (Figure 1) using a Rossfelder VT-1 vibracorer. These sediment cores were fractionated into 2 cm thick slices and freeze-dried, after what five samples of each core (depth ranging between 0 and 10 cm) were selected, totaling 25 sediment samples that were subjected to sequential extraction. The selection of the first 10 cm layer was due to the greater biological activity and sediment-water interaction in this fraction.

2.2 Sequential extraction of metals

To determine the availability of Cd, Cr, Cu, Ni, Pb and Zn in Bertioga Channel the sequential extraction procedure was used. This method is based on the protocol developed and optimized by the European Community Bureau of Reference (BCR), currently Standards, Measurements and Testing (SM&T), described in Pueyo *et al.* (2001). The method provides three separate stages in which the metals are sequentially extracted by the chemical action of specific reagents for each of these steps. Details are included in Supporting Information.

The quantitative analysis of selected elements was performed through ICP-OES (inductively coupled plasma-optical emission spectrometry) technique (Varian analyzer, model MPX 710-ES). The quantification limits (QL) were 0.64 mg kg^{-1} for Cd; 1.00 mg kg^{-1} for Cr; 0.72 mg kg^{-1} for Cu; 0.53 mg kg^{-1} for Ni; 1.35 mg kg^{-1} for Pb and 1.56 mg kg^{-1} for Zn.

2.3 Environmental Chemical Analysis

The available content of Cd, Cr, Cu, Ni, Pb and Zn in the analyzed sediments was estimated from the sum of the concentration of these elements in the three fractions operationally defined by the BCR (F1 + F2 + F3). It is assumed that the metal associated with these fractions can be released if changes in environmental conditions occur (Calmano *et al.*, 1993; Marin *et al.*, 1997). For the composition of these sums only values higher than QL determined for each element were considered. The available content of Cr, Cu, Pb and Zn was compared with the quality standards established by the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life for marine sediment (CCME, 2001). Based on the effects of the elements on the biota are set two limits, the lowest limit, ISQG (Interim Sediment Quality Guideline) and the higher limit, PEL (Probable Effect Level). Due to the lack of reference values for Ni in this guide, results for this element were compared with the predicted values for dredging material in the Brazilian Ministry of Environment Resolution N°. 454, of 2012 (CONAMA, 2012), in which quality criteria are established from N1 levels (threshold below which there is less likelihood of adverse effects to biota) to N2 (threshold above which there is a greater likelihood of adverse effects to biota). Reference values set out in those documents are shown in Table 1.

For the analysis of environmental risk were applied the Risk Assessment Code (RAC) methodology, used in several studies as a tool for better understanding of the environmental risk in relation to remobilization of metals (eg. Jain, 2004; Singh *et al.*, 2005; Ghrefat & Yusuf, 2006; Passos *et al.*, 2010). This risk assessment criteria

Table 1 - Reference values (ISQG, PEL, N1 e N2) and range of metal available content (F1 + F2 + F3), in mg kg^{-1}, in each of the sediment core.

*Tabela 1 -Valores de referência (ISQG, PEL, N1 e N2) e variação do teor disponível de metais (*F1 + F2 + F3*), em mg kg^{-1}, em cada testemunho.*

Metal	Canadian values (CCME, 2001)[a]		Resolution nº 454/2012 (CONAMA, 2012)[b]		B1	B2	B3	B4	B5
	ISQG	PEL	N1	N2					
Ni	-	-	20.9	51.6	6.64 – 9.30	1.77 – 3.69	8.89 – 11.53	7.57 – 10.66	9,82 – 11,09
Cd	0.7	4.2			< QL	< QL	< QL	< QL	< QL
Cr	52.3	160			17.1 – 22.06	2.7 – 6.50	14.96 – 19.01	15.58 – 18.83	16.61 – 19.42
Cu	18.7	108			4.48 – 5.57	0.84 – 1.72	2.93 – 4.76	2.04 – 2.86	3.56 – 5.02
Pb	30.2	112			16.39 – 36.43	1.93 – 13.16	11.45 – 16.57	12.49 – 20.96	16.11 – 23.77
Zn	124	271			25.26 – 42.31	11.35 – 19.66	24.23 – 39.48	30.73 – 35.60	40.42 – 57.53

[a]marine sediments; [b]salt/brackish water; QL-quantification limit

is based on the content of exchangeable metals and those associated with carbonates, as this fraction elements are weakly bound to the sediments and therefore at greater risk of remobilization in the aquatic system (Passos *et al.*, 2010). In this work, the RAC criterion was applied based on the percentage of the element in the acid-soluble fraction (F1). As presented by previous works, when the metal percentage in this fraction is less than 1%, according to the RAC, there is no risk to the water system; between 1 and 10% a low risk is presented; between 11 and 30% there is medium risk; between 31 and 50% a high risk is predicted and, if greater than 50%, there is highest risk (Jain, 2004; Passos *et al*., 2010; Zakir & Shikazono, 2011).

2.4 Statistical analysis

For the statistical analysis, sediment cores were considered as replicates and concentration as the variable of interest, while depth, chemical element and fraction corresponded to the three evaluated factors. Considering this type of design, multifactorial analysis of variance (three-way ANOVA), followed by Tukey HSD test, was the procedure used to identify differences between the average concentration values among different levels of the factors (i.e., sampling depth: 0, 2, 4, 6 and 8 cm; chemical element: Cr, Cu, Ni, Pb, Zn; fraction: F1, F2, F3), also testing the interaction between these (Zar, 2010). As the original data did not meet assumptions of normality and homoscedasticity, prior to testing these were log transformed (natural logarithm (value + 1)). In summary, the purpose of this statistical analysis was to assess whether the concentration in a given location was influenced by the depth of the sediment, chemical element or the fraction considered, which is the direct indication of their availability. Only data related to Cd were not included in the analysis since its concentration presented values below QL for all samples.

3. Results and discussion

The maximum available content (F1+ F2 + F3) for Cr (22.06 mg kg^{-1}), Cu (5.57 mg kg^{-1}) and Zn (57.53 mg kg^{-1}) was below their respective ISQG. As for Pb, the maximum level (36.43 mg kg^{-1}) estimated for the depth 0-2 cm of the sediment core B1, slightly exceeded its ISQG, but this was due to a single sample, featuring a specific situation. In the other B1 samples and the other analyzed sediment cores, Pb available content was less than its ISQG. The maximum Ni content (11.53 mg kg^{-1}) was smaller than those indicated in N1. Cd content was lower than its QL on the three fractions of all samples from sediment cores. These results suggest that if there is remobilization, these elements probably do not represent a danger to biota, because of their low content. Gonçalves *et al.* (2013) also determined the levels of Cr, Cu, Ni, Pb and Zn in the sedimentary column of the same sediment cores and the results indicated that the sediments collected along the Bertioga Channel are non-toxic and not harmful for marine biota. Salaroli (2013) analyzed the levels of these elements in surface sediment samples collected along this Channel and Itapanhaú river, and compared to the reference values established by the Canadian Agency, verifying that all levels were below the PEL and, in most samples, also below TEL (Threshold Effect Level).

Considering the sediment cores, it was observed that B2 presented the set of samples with lower content of available metals and this may be due to their remote location in relation to the main sources of pollution in the region. In the other sediment cores (B1, B3, B4 and B5) the evaluated elements, in general, showed relatively similar behavior in their potential for accumulation in the sediments. These sediment cores are located near potential sources of pollution and/or in regions where oceanographic conditions favor the accumulation of metals (Figure 1). B1 is closer to the city of Bertioga and marina area, B3 is near the Santista estuary, while B4 and B5 are near the region of Largo do Candinho. In this region, there is a predominance of fine sediments (Salaroli, 2013), in which occurs the enrichment of the most active components present on the sediment surface (Förstner, 2004). The Largo do Candinho is the central region of the channel in which two tidal streams meet (Rodrigues *et al.*, 2003), favoring the deposition of fine sediments. Table 1 presents the variation of available contents for Cr, Cu, Ni, Pb and Zn in sediment cores, as well as the reference values for these elements.

Observed concentration values were not influenced by sampling depth, but were by the chemical element considered (Cu < Ni < Cr = Pb < Zn – $p < 0.03$ for all comparisons) and the analyzed fraction (F1 < F2 < F3 - $p < 0.0001$ for all comparisons), with these two factors having a significant interaction (Table 2). This result can be attributed to the particular differences between the concentrations of specific elements and their association with each of the fractions. Overall, considering the first fraction, all elements showed similar levels except Zn, which presented a higher concentration ($p < 0.0001$ for all comparisons - Figure 2). In the second fraction the only similarity in terms of concentration was observed between Pb and Cr ($p < 0.05$ for the other comparisons). In the third fraction Cr, Pb and Zn showed similar levels that, in general, were higher than those of the other elements. However, a similarity in terms of concentration was observed between Pb and Ni, which due to its intermediate concentration between Pb and Cu did not differ from these two elements.

As for the available metal content and their association with each of the fractions, it was found that Cr was associated with F2 and F3 (F1 x F2 and F1 x F3 – $p < 0.001$). In F2 the metal is bonded to Fe and Mn oxides, and in F3 to organic matter and sulfides. In general, the bind-

Table 2 - Effect of the fraction (F1, F2, F3), element (Cr, Cu, Ni, Pb, Zn) and sediment depth in the core (0, 2, 4, 6, 8 cm) on the observed concentrations. Significant results for HSD Tukey test are presented in the text.

Tabela 2 - Efeito da fração (F1, F2, F3), elemento químico (Cr, Cu, Ni, Pb, Zn) e profundidade de amostragem (0, 2, 4, 6 e 8 cm) sobre a concentração observada.

	DF	MS	F	P
Intercept	1	603.03	2005.39	< 0.0001
Metal	4	26.40	87.80	< 0.0001
Fraction	2	88.94	295.78	< 0.0001
Depth	4	0.25	0.82	0.51
Metal X Fraction	8	5.08	16.91	< 0.0001
Metal X Depth	16	0.11	0.36	0.99
Fraction X Depth	8	0.24	0.79	0.62
Metal X Fraction X Depth	32	0.11	0.35	0.99
Error	300	0.30		

DF=degrees of freedom; MS=mean square; F=observed value relating to F distribution; p=probability associated to the F value considering DF.

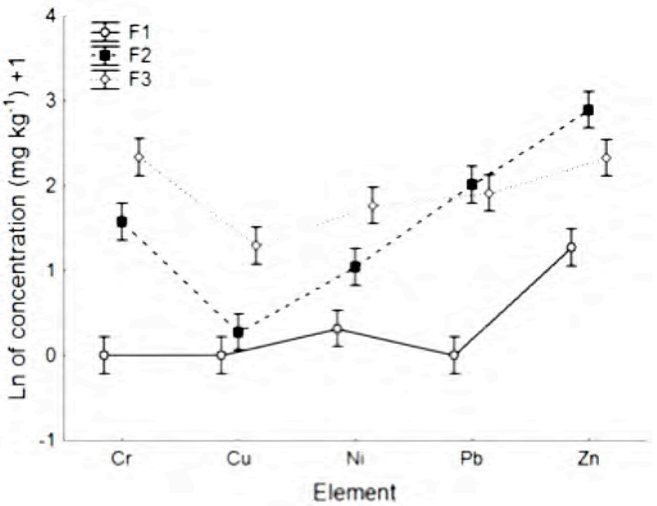

Figure 2 - Effect of the element and fraction on the observed concentration. Significant results for HSD Tukey test are presented in the text.

Figura 2 - Efeito do elemento químico e da fração sobre a concentração observada.

ing of Cr to F3 was predominant in the samples (F2 x F3 - $p < 0.001$), especially in sediment cores B1, B2 and B4.

Cu was mainly associated to F3 ($p < 0.0001$ for all comparisons), in which it is bounded to organic matter and sulfides. Only in samples of B3 and B5 sediment cores, this element was associated to F2. As reported by Morillo *et al.* (2004), it is known that Cu can easily form complexes with organic matter, because of the high stability constant of organic Cu compounds.

Ni was associated to the three phases, but especially to F3 (F1 x F3 and F2 x F3 – $p < 0.001$). The association to F1, in which the metal may be adsorbed on the surface of the sediment and, associated with carbonates, was less representative (F1 x F2 – $p < 0.001$), occurring in just a few samples of B1, B3 and B5 sediment cores. Pb presented associations with only F2 and F3 fractions (F1 x F2 and F1 x F3 – $p < 0.0001$). In sediment cores B1, B2 and B5 the association of this metal to F2 was predominant, while in B3 and B4 cores, Pb was associated mainly with F3.

Zn presented itself associated with all three fractions in all sediment cores, despite their bond with F2 being predominant (F1 x F2 and F2 x F3 – $p < 0.03$). However, comparatively to the other studied elements, Zn showed higher incidence of association to F1, even in low concentrations ($p < 0.0001$ for all comparisons – Figure 2) .

Considering these results, it can be inferred that Cr, Cu and Ni are mainly associated to the organic matter and sulfides (F3), while Zn is to Fe and Mn oxides (F2), and Pb to all these components (F2 and F3). Changes in local environmental conditions may favor the release of these elements. When these are associated with F1 they may be released by changes in the ionic composition or pH reduction; if associated to F2, by changes in redox potential, and when associated with F3, they may be released under oxidizing conditions (Marin *et al.*, 1997).

Figure 3 shows the content of available elements (F1 + F2 + F3), as well as the content associated with each of the fractions. The absence of the content by one or more fractions, means that the concentration was below the QL of the element.

For a better understanding of a metal remobilization risk, it was applied the Risk Assessment Code (RAC), based on the element contents in the F1 fraction (%). Considering that Cd, Cr, Cu and Pb in all samples showed lower content in this fraction in relation to their QL, the methodology could be applied only to Ni and Zn. As a reference of total content were used the results of pseudo-total contents of Ni and Zn in these sediment cores, already published in Gonçalves *et al.* (2013).

According to the RAC criterion, Ni, in general, showed low risk (RAC < 10%) to the environment in sediment cores B1, B3 and B5. In other cores (B2 and B4), Ni content in F1 was below its QL in all samples. Generally, Zn presented low environmental risk (RAC < 10%) in the sediment cores B1, B3, B4 and B5. However, in core B2, RAC criteria indicated medium risk remobilization (RAC < 30%) in all samples. However, remembering that this methodology considers F1 concentration in relation to the total content, and reaffirming that Zn content associated with this fraction was less than its ISQG limit, if the remobilization of this element oc-

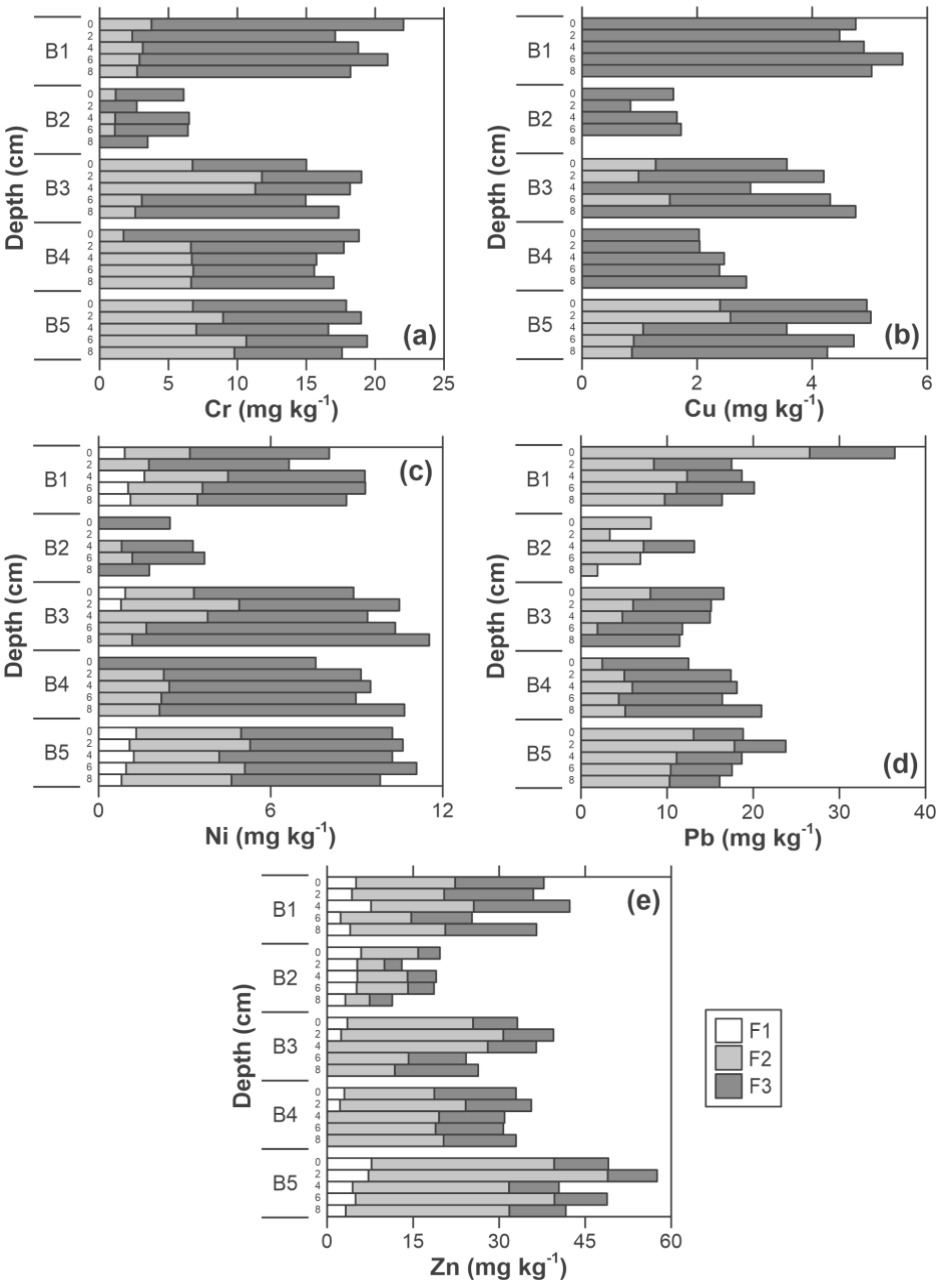

Figure 3 - Available contents of Cr (a), Cu (b), Ni (c), Pb (d) and Zn (e) (in mg kg^{-1}) and association to the mobile fractions in sediment cores of the Bertioga Channel.

Figura 3 - Teor disponível de Cr (a), Cu (b), Ni (c), Pb (d) and Zn (e) (em mg kg^{-1}) e em associação às frações móveis em sedimento de testemunhos do Canal de Bertioga.

curred, probably, it would not represent danger to the biotic communities.

In this study, the RAC criterion proved to be a complementary tool in assessing the remobilization of metals, allowing the quantification of the environmental risk. However, as reported by Ishikawa *et al.* (2009), the numerical scale RAC alone is insufficient to assess this risk, also being necessary to consider reference values of the evaluated elements, to adopt it as an efficient and reliable indicator.

Figure 4 shows the results for Ni and Zn RAC in the sediment cores. The absence of the RAC in some samples are due to their content associated with F1 being lower than the QL for the element.

4. Conclusions

The results showed that there is potential for remobilization of Cr, Cu, Ni, Pb and Zn in Bertioga Channel sediments, even though these elements were not mainly associated to the acid-soluble fraction, environmentally considered the most important due to their higher mobility. Cr, Cu and Ni were associated mainly to the organic matter and sulfides, Zn to Fe and Mn oxides and, Pb, to these four components. Changes in local envi-

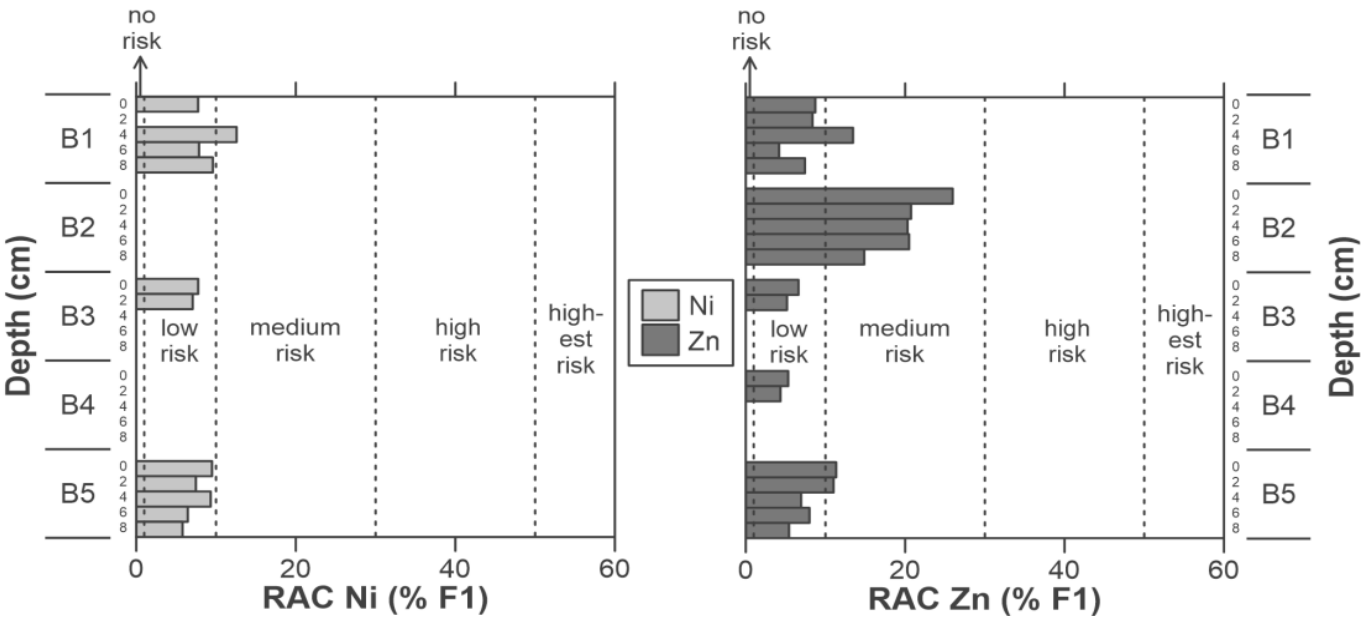

Figure 4 - Risk Assessment Code (RAC) for Ni and Zn in the cores from Bertioga Channel.

Figura 4 - Risk Assessment Code *(RAC) para Ni e Zn nos testemunhos do Canal de Bertioga.*

ronmental conditions, specifically in redox potential or those that lead to oxidizing conditions, may cause the remobilization of the evaluated metals and, consequently, leave them available in the environment. However, even if released, due to their low content in the sediments, it is estimated that they would not represent a danger to the biota.

RAC criterion, based on the metal content associated with the acid-soluble fraction (F1) was applied to Ni and Zn and generally indicated low risk of remobilization of these metals in the environment. Even in samples with medium risk, the content of these elements was lower than their reference values.

However, even though Cr, Cu, Ni, Pb and Zn concentrations in the sediments are low, suggesting the preservation of the region with respect to chemical contamination, considering that this study was based on the mobile fractions, it can be inferred that these results are an indicative of the possible anthropogenic contribution of these elements in the region, as well as of their potential for accumulation in sediment, showing the importance of the monitoring of potentially toxic elements for future protection of biotic communities. Continuous monitoring of chemical pollution in the region will allow the dimensioning of the possible impacts, thus contributing to the action plan in the scope of integrated coastal management.

The results presented in this study provide information about the behavior and mobility of Cr, Cu, Ni, Pb and Zn in Bertioga Channel sediments, representing a database that could assist in coastal and environmental management processes in the region.

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Appendix

Supporting Information associated with this article is available online at http://www.aprh.pt/rgci/pdf/rgci-670_Tramonte_Supporting-Information.pdf

References

Abollino, O.; Malandrino, M.; Giacomino, A.; Mentasti, E. (2011) - The role of chemometrics in single and sequential extraction assays: A review Part I. Extraction procedures, uni- and bivariate techniques and multivariate variable reduction techniques for pattern recognition. *Analytica Chimica Acta*, 688:104-121. DOI: 10.1016/j.aca.2010.12.020

Bernardes, M.E.C.; Miranda, L.B. (2001) - Circulação estacionária e estratificação de sal em canais estuarinos: simulação com modelos analíticos. *Revista Brasileira de Oceanografia*, 49(1/2):115-132. DOI: 10.1590/S1413-77392001000100010

Calmano, W.; Hong, J.; Förstner, U. (1993) - Binding and mobilization of heavy metals in contaminated sediments affected by pH and redox potential. *Water Science & Technology* (ISSN: 0273-1223), 28(8-9): 223-235.

Calmano, W.; Ahlf, W.; Förstner, U. (1996) - Sediment quality assessment: chemical and biological approaches. In: Calmano, W.; Förstner, U. (eds.), Sediments and toxic substances, pp. 1-35, Springer-Verlag Berlin Heidelberg. ISBN: 978-3-642-79892-4.

CCME (2001) - Canadian sediment quality guidelines for the protection of aquatic life: Summary tables. Updated. *In: Canadian Environmental Quality Guidelines*, 1999, Canadian Council of Ministers of the Environment (CCME), Winnipeg, MB, Canada.

ISBN: 1896997341. Available on-line at https://www.elaw.org/system/files/sediment_summary_table.pdf

CONAMA (2012) - *Resolução CONAMA nº 454 de 01 de novembro de 2012. Estabelece as diretrizes gerais e os procedimentos referenciais para o gerenciamento do material a ser dragado em águas sob jurisdição nacional*. Conselho Nacional do Meio Ambiente (CONAMA). DOU (Diário Oficial da República Federativa do Brasil): publicação: 08/11/2012, 1:66, Brasilia, DF, Brazil. Available on-line at http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=693

Cotta, J.A.O.; Rezende, M.O.O.; Piovani, M.R. (2006) - Avaliação do teor de metais em sedimento do Rio Betari no parque estadual turístico do Alto Ribeira - Petar, São Paulo, Brasil. *Química Nova*, 29(1):40-45. DOI: 10.1590/S0100-40422006000100009

Cuong, D.T.; Obbard, J.P. (2006) - Metal speciation in coastal marine sediments from Singapore using a modified BCR - sequential extraction procedure. *Applied Geochemistry*, 21:1335-1346. DOI: 10.1016/j.apgeochem.2006.05.001

El-Azim, H.A.; El-Moselhy, Kh.M. (2005) - Determination and partitioning of metals in sediments along the Suez Canal by sequential extraction. *Journal of Marine Systems*, 56:363-374. DOI: 10.1016/j.jmarsys.2004.12.001

Förstner, U. (1979) - Sources and sediment associations of heavy metals in polluted coastal regions. *In:* L.H. Ahrens & G. Protas (eds.), *Origin and distribution of the elements. Physics and Chemistry of the Earth*, 11, pp.849-866, Pergamon Press, Oxford, U.K. ISBN: 0080229476.

Förstner, U. (1981) - Metal transfer between solid and aqueous phases. *In:* U. Förstner & G.T.W. Wittmann (eds.), *Metal Pollution in the Aquatic Environment,* pp.197-270, Springer – Verlag, Berlin / Heidelberg, Germany. ISBN: 978-3540128564.

Förstner, U. (2004) - Traceability of sediment analysis. Trends in *Analytical Chemistry*, 23(3):217-236. DOI: 10.1016/S0165-9936(04)00312-7

Ghrefat, H; Yusuf, N. (2006) - Assessing Mn, Fe, Cu, Zn, and Cd pollution in bottom sediments of Wadi Al-Arab Dam, Jordan. *Chemosphere*, 65:2114-2121. DOI: 10.1016/j.chemosphere.2006.06.043

Gonçalves, C.; Figueira, R.C.L.; Sartoretto, J.R.; Salaroli, A.B.; Ribeiro, A.P.; Ferreira, P.A.L.; Mahiques, M.M. (2013) - Reconstruction of historical trends in potentially toxic elements from sediment cores collected in Bertioga Channel, southeastern Brazil. *Brazilian Journal of Oceanography*, 61(2):149-160. DOI: 10.1590/S1679-87592013000200007.

Ishikawa, D.N.; Noale, R.Z.; Ohe, T.H.K.; Souza, E.B.R.; Scarmínio, I.S.; Barreto, W.J.; Barreto, S.R.G. (2009) - Avaliação do risco ambiental em sedimento dos lagos do Riacho Cambé, em Londrina, pela distribuição de metais. *Química Nova*, 32(7):1744-1749. DOI: 10.1590/S0100-40422009000700012.

Jain, C.K. (2004) - Metal fractionation study on bed sediments of River Yamuna, India. *Water Research*, 38:569-578. DOI: 10.1016/j.watres.2003.10.042.

Kelderman, P.; Osman, A.A. (2007) - Effect of redox potential on heavy metal binding forms in polluted canal sediments in Delft (The Netherlands). *Water Research*, 41:4251-4261. DOI: 10.1016/j.watres.2007.05.058.

Marin, B.; Valladon, M.; Polve, M.; Monaco, A. (1997) - Reproducibility testing of a sequential extraction scheme for the determination of trace metal speciation in a marine reference sediment by inductively coupled plasma-mass spectrometry. *Analytica Chimica Acta*, 342:91-112. DOI: 10.1016/S0003-2670(96)00580-6.

Morillo, J.; Usero, J.; Gracia, I. (2004) - Heavy metal distribution in marine sediments from the southwest coast of Spain. *Chemosphere*, 55:431-442. DOI: 10.1016/j.chemosphere.2003.10.047.

Oliveira, M.L.J.; Vidal-Torrado, P.; Otero, X.L.; Ferreira, J.R. (2007) - Mercúrio total em solos de manguezais da baixada Santista e ilha do Cardoso, Estado de São Paulo. *Química Nova*, 30(3):519-524. DOI: 10.1590/S0100-40422007000300003.

Passos, E.A.; Alves, J.C.; Santos, I.S.; Alves, J.P.H; Garcia, C.A.B.; Costa, A.C.S. (2010) - Assessment of trace metals contamination in estuarine sediments using a sequential extraction technique and principal component analysis. *Microchemical Journal*, 96:50-57. DOI: 10.1016/j.microc.2010.01.018.

Pueyo, M., Rauret, G., Lück, D., Yli-Halla, M., Muntau, H., Quevauviller, Ph., López-Sánchez, J.F. (2001) - Certification of the extractable contents of Cd, Cr, Cu, Ni, Pb and Zn in a freshwater sediment following a collaboratively tested and optimised three-step sequential extraction procedure. Journal of Environmental Monitoring, 3(2):243-250. DOI: 10.1039/b010235k.

Rauret, G. (1998) - Extraction procedures for the determination of heavy metals in contaminated soil and sediment. *Talanta*, 46:449-455. DOI: 10.1016/S0039-9140(97)00406-2.

Rodrigues, A.R.; Eichler, P.P.B.; Eichler, B.B. (2003) - Utilização de foraminíferos no monitoramento do Canal de Bertioga (SP, Brasil). *Atlântica* (ISSN: 2236-7586), 25(1):35-51, Rio Grande, RS, Brazil.

Sakan, S.M., Dordevíc, D.S., Manojlovíc, D.D., Predrag, P.S. (2009) - Assessment of heavy metal pollutants accumulation in the Tisza river sediments. Journal of Environmental Management, 90:3382-3390. DOI: 10.1016/j.jenvman.2009.05.013.

Salaroli, A.B. (2013) - *Distribuição de elementos metálicos e As em sedimentos superficiais ao longo do Canal de Bertioga (SP)*. 105p., Dissertação de Mestrado, Instituto Oceanográfico da Universidade de São Paulo, São Paulo, SP, Brazil. Available on-line at http://www.teses.usp.br/teses/disponiveis/21/21137/tde-29012015-113936/pt-br.php

Silva, P.S.C; Damatto, S.R.; Maldonado, C.; Fávaro, D.I.T.; Mazzilli, B.P. (2011) - Metal distribution in sediment cores from São Paulo State Coast, Brazil. *Marine Pollution Bulletin*, 62:1130-1139. DOI: 10.1016/j.marpolbul.2011.02.046.

Singh, K.P.; Mohan, D.; Singh, V.K.; Malik, A. (2005) - Studies on distribution and fractionation of heavy metals in Gomti river sediments - A tributary of the Ganges, India. *Journal of Hydrology*, 312:14-27. DOI: 10.1016/j.jhydrol.2005.01.021.

Siqueira, G.W.; Braga, E.S.; Pereira, S.F.P.; Silva, E. (2005) – Distribuição do mercúrio em sedimentos de fundo do Estuário de Santos-SP/Brasil. Revista Escola de Minas, 58(4):309-316, DOI: 10.1590/S0370-44672005000400004.

Zakir, H.M.; Shikazono, N. (2011) - Environmental mobility and geochemical partitioning of Fe, Mn, Co, Ni and Mo in sediments of an urban river. *Journal of Environmental Chemistry and Ecotoxicology*, (ISSN-2141-226X), 3(5):116-126. Available on-line at http://www.academicjournals.org/article/article1380006213_Zakir and Shikazono.pdf

Zar, J.H. (2010) - *Biostatistical Analysis*. 5th ed., 944p, Pearson Prentice Hall. ISBN: 978-0321656865.

Zoumis, T., Schmidt, A., Grigorova, L., Calmano, W. (2001) - Contaminants in sediments: remobilisation and demobilisation. *Science of the Total Environment*, 266:195-202. DOI: 10.1016/S0048-9697(00)00740-3

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Endocrine disruptors: strategies for determination and occurrence in marine environments *

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ABSTRACT

Research examining the occurrence of endocrine disruptors (ED) in the marine environment has substantially increased. These contaminants have been observed in several environmental compartments and matrices, and they may cause severe adverse effects in humans and ecosystems. In this study more than 240 papers investigating the analytical developments regarding the analysis on ED in environmental matrices and the occurrence of these compounds were critically evaluated. Modern sample preparation procedures aiming the use of minimal sample manipulation, minimal amount of solvents and energy according to the Green Chemistry principles are widely used. The ED in marine environments occurs in trace concentrations and their quantification still represents a challenge. The effects of these contaminants in marine ecosystems are poorly understood. However, due to their large use, it is predicted that new analytical developments to deal with ED contamination will promote a large increase in the number of scientific publications in the near future. Regulations and mitigation measures for the presence of these contaminants in the environment are still scarce and need to be quickly implemented to reduce potential future adverse effects on ecosystem services of coastal environments.

Keywords: Emerging contaminants; Endocrine disrupters; Contamination; Sample preparation; Environmental analysis

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RESUMO

Pesquisas que examinam a ocorrência de interferentes endócrinos (IE) no ambiente marinho têm aumentado substancialmente. Estes contaminantes podem causar efeitos adversos em seres humanos e nos ecossistemas e têm sido observados em vários compartimentos e matrizes ambientais. Neste estudo, mais de 240 trabalhos que relataram o desenvolvimento analítico de IE em diversas matrizes e a ocorrência destes compostos no ambiente marinho foram criticamente avaliados. Procedimentos de preparo de amostra, visando a mínima manipulação, a mínima quantidade de solventes e energia de acordo com os princípios de Química Verde estão sendo amplamente utilizados. Os IE em ambientes marinhos ocorrem em concentrações traço e sua quantificação ainda representa um grande desafio. Como resultado, os efeitos desses contaminantes em ecossistemas marinhos ainda são mal compreendidos. No entanto, devido ao amplo uso destes compostos é previsto que novos desenvolvimentos analíticos para a determinação de IE irão promover um grande aumento no número de publicações científicas no futuro. Regulações e medidas mitigadoras para a ocorrência destes contaminantes ainda são bastante reduzida e precisam ser rapidamente implementadas para reduzir os futuros potenciais efeitos adversos nos serviços ecossistêmicos dos ecossistemas costeiros.

1. Introduction

The lifestyle adopted by humans in the modern society has favored the occurrence of continuous physical, chemical and biological changes in the environment. The contamination of water bodies due to the presence of domestic and industrial wastewater, water runoff and agricultural activities stand out among the major human impacts on the coastal zones. Thousands of substances (e.g., pharmaceuticals, personal care products, surfactants, nanomaterials, metals, phthalates, and hydrocarbons, among others), which have allegedly subsidized the improvement of the quality of human life and ensured the growth of activities such as aquaculture and agriculture, are produced and released in the environment.

The development of new analytical techniques of separation, identification and quantification of substances (e.g., high performance liquid chromatography (HPLC) coupled to mass spectroscopy, among others) has allowed the identification of a large number of compounds in samples of water, air, sediments and biological tissues so far unknown (Locatelli *et al*., 2016; Casatta *et al*., 2015; Emnet *et al*., 2015; Benjamin *et al*., 2015; Cai *et al*., 2012a, 2012b; Bartolomé *et al*. 2010; Richardson & Ternes, 2011; Rubio & Pérez-Bendito, 2009). The sensitivity of many analytical techniques has improved, reducing the limits of detection from parts per million to parts per trillion and, in some cases, to parts per quadrillion (Huerta *et al*., 2015; Bhandari *et al*., 2009). As a result, the potential for studying traces of contaminants in the environment, especially in complex matrices, such as seawater, has also increased. The substantial improvement in analytical sensitivity enabled the detection of a series of compounds known, generically, as emerging contaminants (EC). Emerging contaminants can be defined as a class of natural or synthetic chemicals, or any group of microorganisms that are not naturally found in the environment (Richardson & Ternes, 2011; EPA, 1997). In general, the ECs are present unknown toxicity, large industrial production and they are ubiquitous in the environment (Birch *et al*., 2015; De la Cruz *et al.*, 2012; Deblonde *et al*., 2011; Bhandari *et al*., 2009). ECs are not necessarily new compounds, they are input in environment for several years. However, the identification and quantification of these compounds was only possible after the development of new analytical techniques that allows detection of trace and ultratrace concentrations.

Among the emerging contaminants, a number of compounds have been receiving special attention from the scientific community, due to their potential capacity of interfering with the functioning of the endocrine system of organisms. The literature uses several names for these compounds: xenobiotics, pseudo-estrogens, pseudo-androgens, endocrine disruptors (ED), and interfering endocrines (Lisboa *et al*., 2013; Menzies *et al*., 2013; Grassi *et al*., 2013; Ghiselli & Jardim, 2007; Lathers, 2002; Kardinaal *et al*., 1997). Many of them are not degraded or broken down by any biochemical and/or natural photochemical pathways and may also undergo bioaccumulation and/or biomagnification (Colin *et al*., 2016). In this paper, this group of compounds will be referred to as endocrine disruptors.

Several contaminants, both organics and inorganics, have their ecotoxicological profiles and modes of action well determined. As a result decision makers can plan accordingly in order to regulate their use, minimize adverse effects for the provision of ecosystems services or even ban some compounds. The literature has already showed examples of the positive effect of such regulations in contamination levels in the environment. For instance, Sutton *et al*. (2014) observed declines in Polybrominated compounds in sediment and biota of San Francisco Bay. However, for most of the EDs dealt in this manuscript it still is necessary a better knowledge and understanding of the environmental cycles and toxicity in order to subsidize the development of regulations and management practices.

2. Importance and relevance of endocrine disruptors

The United States Environmental Protection Agency (U.S. EPA) defines endocrine disruptors as exogenous agents that interfere with the synthesis, secretion, transport, binding, action or elimination of hormones that are responsible for reproduction, development, behavior and maintenance of body homeostasis (EPA, 1997). Although there are multiple mechanisms of action of endocrine disruptors in biota, the vast majority of the observed disturbances are attributed to the functioning of the gonads, responsible for secondary sexual characteristics, and the development and functioning of sexual organs (Gu *et al*., 2016; Gavrilescu *et al*., 2015; Christiansen *et al*., 2012; Boisen *et al*., 2005; Lintelmann *et al*., 2003; Toppari *et al*., 2001; Paulozzi, 1999).

In humans, EDs may cause serious problems such as precocious puberty (Buttke *et al*., 2012), testicular (Huyghe *et al*., 2003), breast (Lee & Choi, 2013; Macon & Fentton, 2013), and prostate cancers (Bedia *et al*., 2015; Prins, 2008), gynecomastia (irregular breast growing in men) (Vandenberg *et al*., 2013), tract disorders in the male reproductive system such as cryptorchidism (irregular descent of the testicles from the abdominal cavity) (Main *et al*., 2010; Toppari *et al*., 2001), hypospadias (congenital malformation of the urinary meatus) (Thorup *et al*., 2014; Main *et al*., 2010; Boisen *et al*., 2005; Toppari *et al*., 2001; Paulozzi, 1999) low count and poor quality semen (Paoli *et al*., 2015; Jouannet *et al*., 2001). It is estimated that more than 87,000 commercialized chemicals need to be tested in order to determine their potential influence on the endocrine system of humans and biota (EPA, 1997).

It has been known that EDs can be either natural and/or synthetic compounds, originated through domestic and industrial uses (Gravilescu *et al*., 2015; Nurulnadia *et al*., 2014; Diamanti-Kandarakis *et al*., 2009; Pojana *et al*., 2004). Natural ED compounds of known effect include steroidal hormones such as estrogen, progesterone and testosterone, produced by both humans and animals. In addition, there are also the phytosterols, which are natural substances present in several plants that also possess hormonal activity. In turn, synthetic compounds include artificial hormones (contraceptives or additives used in animal food) as well as the xenosteroids, substances produced for use in the industry, agriculture and in the manufacture of several products (Li *et al*., 2014; Kinani *et al*., 2008; Ghiselli & Jardim, 2007; Birkett & Lester, 2003).

The most commonly known or classified as ED xenosteroids are the alkylphenols polyethoxylated (APEOs), organotin compounds, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), phthalates, polybrominated flame retardants (PBFRs), dioxins, furans, pesticides, and pharmaceutical and personal care products (PPCPs), among others (Richardson & Ternes, 2014; Tan *et al*., 2007b; Lintelmann *et al*., 2003). The EDs can be grouped according to their chemical characteristics and utilization (Table 1).

Phytosterols are substances with estrogenic and androgenic activities (Hwang *et al*., 2006) found in plants such as soybean, wheat, rice, carrots, beans, potatoes, cherries and apples (Richardson & Ternes, 2014; Richardson, 2002). The main representatives of this class of EDs are isoflavones (genistein, daidzein, biochanin A, formononetin, equol, and demetilangolensine, among others), lignans (enterodiol, enterolactone, secoisolariciresinol, and metairesinol, among others), and coumestans (coumestrol) (Clapauch *et al*., 2002). Although the capacity of the endocrine interference of phytosterols is low, between one and two orders of magnitude smaller than estradiol (Bovee *et al*., 2004), some studies have reported the presence of these compounds in water bodies at levels that may cause endocrine disruption (Ribeiro *et al*., 2009; Kuster *et al*., 2009).

Pesticides belong to a class of EDs with a several representatives. Although the use of various pesticides has been prohibited in different countries, residues of these compounds are still present in the environment, as in the case of DDT and its metabolites. This reflects the high persistence and lipophilic properties of these substances (Garcia-Jares *et al*., 2009). The main compounds used as pesticides that can behave as EDs are DDT, DDT metabolites (i.e., DDE and DDD), methoxychlor, chlorinated cyclodiene, vinclozolin, linuron and diuron, among others (Mnif *et al*., 2011; Čeh & Majdič, 2010; Lintelmann *et al*., 2003). Each of these compounds has distinct effects on the endocrine systems of organisms. For instance, the herbicide diuron is capable of inhibiting the androgens (Thibaut & Porte, 2004) while the DDT metabolites mimic the action of estrogens (Bulayeva & Watson, 2004). However the possibilities and pathways of pesticides may cause disturbance in endocrine systems as well as their endpoints in individuals still is not well understood (Ventura *et al*., 2016; Monteagudo *et al*., 2016; Marx-Stoelting *et al*., 2014).

PAHs are generated in the processes of incomplete combustion or pyrolysis of organic matter (e.g., coal, oil, gas and wood) and traditionally have been used as tracers of burning fuels (Santos *et al*., 2016; Sun *et al*., 2013; Da Rocha, *et al*., 2009) and oil refineries (Bayat *et al*., 2015; Zrafi-nouira *et al*., 2010). Antiestrogenic effects of PAHs have been reported in the literature for mollusks from contaminated areas (Gagné *et al*., 2002). Weiss *et al*. (2009) suggested that the PAHs contribute to the anti-androgenic activity of sediments in rivers.

Another group of EDs that has received attention is the PCBs, which are compounds resulted from the addition

Table 1. Main classes of endocrine disruptors and use.

Group	*Main Species*	*Application and/or source*
Estrogen hormones[a,b]	Estrone (E1) 17β-estradiol (E2) Estriol (E3) 17α-ethynylestradiol (EE2)	Natural estrogens (human or animal production) Synthetic estrogen (contraceptives)
Phthalates[b,c]	Dimethyl phtalate (DMP), Diethyl phthalate (DEP), Di-n-buthyl phthalate (DnBP), Diisobuthyl phthalate (DiBP), Di(2-ethylhexyl) phthalate (DEHP) Di-n-octhyl phthalate (DnOP)	Plasticizers in polymers. Additives in pesticides, paints, cosmetics, floor coverings, ceilings, or insulators in electrical devices, among others
Alkylphenols (APs)[b]	APEO 4-n-nonylphenol (4-n-NP) 4-tert-nonylphenol (4-t-NP) 4-n-octhylphenol (4-n-OP) 4-tert-octhylphenol (4-t-OP) Bisphenol A (BPA)	Detergents, paints, propellants in pesticides, personal care products, plasticizers, elastomers, polymerization of acrylic and vinyl acetate
Phytosterols (phytoestrogens and fitoandrogens)[b]	Isoflavones (Genistein) Lignans (Metairesinol)	Soybean Linseed and wheat
Pesticides[b]	dichloro-diphenyl-dichloroethane (DDD) dichloro-diphenyl-trichloroethane (DDT) dichloro-diphenyl-dichloroethene (DDE) Methoxychlorine Linuron Diuron	Insecticides. Use banned in most countries Insecticide DDT substitute Herbicides
PAHs[b]	Anthracene Benzo(a)pyrene Phenantrene Fluoranthene Naphthalene Pyrene	Incomplete combustion of organic matter (coal, oil, petroleum, wood) Burning of fossil fuels
PCBs[b,d]	Addition of chlorine atoms to phenylbenzene or biphenyl. Several species	Plasticizers, pesticides, disinfectants, capacitor and transformer fluid, among other
PBFRs[b,e]	Several species	For Avoiding the easy fire ignition in electrical and electronic equipment
Organotin compounds[f]	Monobutyltin Dibutyltin Tributyltin	Antifouling used on boats, buoys, refrigeration system, dock, etc.; wood preservatives; disinfectant.
Dioxins[b,g]	2,3,7,8- tetrachlorodibenzo-p-dioxin	Byproducts of reactions: Synthesis of chlorine, Production of hydrocarbons
Furans[b,g]	2,3,7,8-tetrachlorodibenzofuran	Pyrolysis and incomplete combustion of organic material in the presence of chlorine

[a]Beausse, 2004; [b]Birkett *et al*., 2003; [c]Gómez-Hens & Aguilar-Caballos, 2003; [d]Carpenter, 2006; [e]Eriksson *et al*., 2001; [f]Lintelmann *et al*., 2003; [g]Assunção & Pesquero, 1999.

of chlorine atoms to the byphenyl molecule. PCBs were used as dielectric fluids in large transformers and capacitors, plasticizers, heat fluids, hydraulic lubricants, paints, and adhesives, among other applications (Anezaki & Nakano, 2015; Liu *et al*., 2015; Pocar *et al*., 2003). Although many countries have banned the production of PCBs in the 1970s and 1980s, it is believed that about 10^8 kg of PCBs are still spread out in the environment, mainly due to their persistent characteristics (Anezaki & Nakano, 2015; Scheringer *et al*., 2009; Boyle *et al*., 1992). There are evidences that PCBs inhibit estrogen activity, effectively increasing the bioavailability of estrogen in the body (Kester *et al*., 2000) and, therefore, disturbing the functions controlled by this hormone. Together with PCBs, PBFRs are part of the halogenated organic compounds group, which are considered or accepted to be EDs. Although some studies have reported the endocrine disrupting potential of these compounds, there are no restrictions regarding their production and/or use (Richardson & Ternes, 2015; Kabir *et al*., 2015; Mankidy *et al*., 2013a; Gereckea *et al*., 2008; Trachsel, 2008; Darnerud, 2008; Vos *et al*., 2003; Legle & Brouwer, 2003). Besides those EDs already described, estrogenic hormones, alkylphenols (APs), bisphenol A (BPA) and phthalates are noteworthy for having high capacity of endocrine interference, yet they are of concern due to the large industrial production, and consumption on a global scale. Thus, these groups of substances will be discussed in more detail in this text.

2.1. Estrogenic Hormones

Estrogens are hormones that take part of a larger group of substances, the steroids. Figure 1 illustrates the structure of these substances which have an arrangement derived from the cyclepent[α]phenanthrene molecule (Moss, 1989). Estrogens are liposoluble, and this characteristic allows them to pass through the cell membranes, thus transmiting information by coupling themselves to intracellular receptors (Tata, 2005). Natural estrogens are responsible for female secondary characteristics, for the development of the male reproductive system, for processes associated with growth, metabolism, reproduction, development, besides acting in the maintenance of bones, cardiovascular and central nervous systems (Hampl *et al*., 2016; Tata, 2005; Shimada *et al*., 2001).

Estrogens have a tetracyclic structure arranged in a phenol, two cyclohexanes, and a cyclopentane condensed ring. Estrogens strutuctures are differentiated from each other by the functional groups attached to carbons C16 and C17 (Figure 1) (Moss, 1989). Estrone (E1) and estradiol present a carbonyl group and a hydroxyl group, respectively, bonded to the carbon C17 of the tetracyclic structure (Table 2).

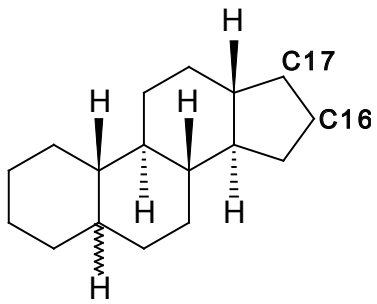


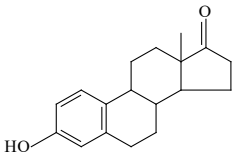
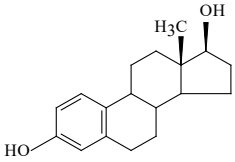
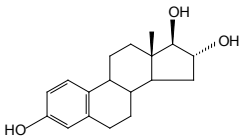
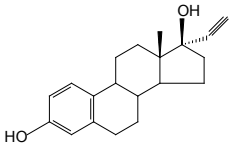
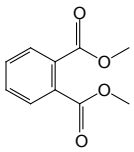
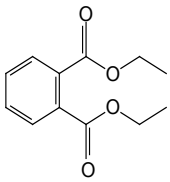
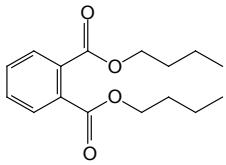
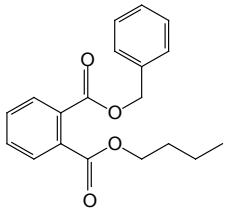
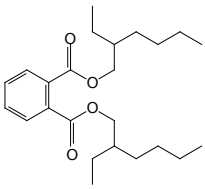
Figure 1. Cyclopent[α]phenathrene.

The three-dimensional arrangement of the hydroxyl group attached to the C17 in the estradiol originates the 17β-estradiol (E2) or the 17α-estradiol. In turn, estriol (E3) presents two hydroxyls, one is connected to the C16 and the other to the C17; while the 17α-ethynylestradiol (EE2), a synthetic estrogen used in many contraceptives and therapeutic agents, presents an ethynyl group bonded to the C17. All these estrogens have very low vapor pressures, ranging between 2.3 x 10^{-10} and 6.7 x 10^{-15} mmHg (Table 2), responsible for the low volatility of these compounds. The partition coefficients of estrogens between octanol and water (Log K_{ow}) are high, ranging between 2.81 and 4.15 (Lu, 2009).

The E1, E2 and E3 are produced mostly by ovaries and are the main natural estrogens. These estrogens, together with the synthetic hormone EE2, have been detected in domestic wastewater and efluents from wastewater treatment plants (WWTP) (Xu *et al*., 2012; Behera *et al*., 2011; Quednow & Püttmann, 2008; Tan *et* al., 2007a; Tan *et* al., 2007b) that are discharged in superficial water bodies (Lisboa *et al*., 2013; Noppe *et al*., 2007). Although most of the estrogen is excreted in their inactive form, the action of bacteria transforms them into biologically active compounds that are capable of producing adverse effects (Zheng *et al*., 2012; D'Ascenzo *et al*., 2003; Panter *et al*., 1999; Belfroid *et al*., 1999). Many studies have shown that these estrogens, in concentration as low as few ng L^{-1}, may have adverse effects on the reproductive systems of biota and humans (Luzio *et al*., 2016; Palanza *et al*., 2016; Salvador *et al*., 2007; Kuster *et al*., 2004; Grist *et al*., 2003). Human exposure to high concentrations of estrogens can cause various disorders such as gynecomastia, libido decrease, impotence, and sperm counting decrease. In addition to direct effects on the reproductive system, these estrogens and/or their metabolites may cause breast, prostate, and/or ovary cancers (Palanza *et al*., 2016; Frye *et al*., 2011; Xu *et al*., 2007; Xu *et al*., 2005).

The estrogenic hormones are compounds with the highest interference potential in the endocrine system (Ghiselli & Jardim, 2007; Aksglaede *et al*., 2006; Reis Filho *et al*., 2006. Laws *et al*., 2000). Although they have relatively short half-lives, when compared to other

Table 2. Physicochemical properties of steroids and phthalates.

Compound	Molar mass[a]	Solubility[b]	Vapor pressure[c]	Log K_{ow} [d]	Chemical structure
Estrone (E1)	270.4	13	2.3×10^{-10}	3.43	
17β-estradiol (E2)	272.4	13	2.3×10^{-10}	3.94	
Estriol (E3)	288.4	13	6.7×10^{-15}	2.81	
17α-ethynylestradiol (EE2)	296.4	4.8	4.5×10^{-11}	4.15	
Dimethyl phtalate (DMP)	194	7,273	0.258	1.41	
Diethyl phthalate (DEP)	222	808	6.95×10^{-2}	2.35	
Di-n-buthyl phthalate (DnBP)	278	9.9	5.16×10^{-3}	4.22	
Butylbenzyl phthalate (BBP)	312	0.93	1.27×10^{-3}	5.22	
Di(2-ethylhexyl) phthalate (DEHP)	391	2.09×10^{-3}	3.65×10^{-5}	7.7	

Adapted from Lu, 2009. [a]Molar mass (g mol^{-1}); [b]Solubility in water (mg L^{-1} at 20 ° C); [c] Vapor pressure (mmHg); [d] Octanol / water partition coefficient

organic compounds (e.g. pesticides, PCBs and PAHs), estrogens are introduced into the environment in a continuous and large scale way (Johnson & Williams, 2004) and thus becoming a pseudopersistent pollutant. Therefore, estrogens are potential sources of a large number of adverse effects in the environment. For instance, fish cultivated in waters contaminated by estrogenic hormones have shown altered hormone levels and anatomical changes in the reproduction organs (Luzio *et al*., 2016; Volkova *et al*., 2015; Dzieweczynski & Buckman, 2013; Larsson & Förlin, 2002). It was also observed a total reversion of male to female sex in medaka fish (*Oryzias latipes*), when exposed to natural estrogens in concentration of 140 ng L^{-1} (Hirai *et al*., 2006).

2.2. Alkylphenols and Bisphenol A

Alkylphenols (APs) and Bisphenol A (BPA) are the endocrine disrupting substances most intensively studied. The APs are substances formed by a phenol group attached to a carbon chain (Table 3). APs, including nonylphenols (NPs) and octylphenols (OPs) are used directly in the production of a large range of products or can be originated from the degradation of APEO (Funakoshi & Kasuya, 2009). APEOs and APs belong to a class of non-ionic surfactants used in the production of phenolic resins, detergents, adhesives, paper, plastic additives, acrylic, vinyl acetate, emulsifiers, wetting agents, spermicides, among other applications (Hotta *et al*., 2010; David *et al*., 2009; Isidori *et al*., 2006; Tsuda *et al*., 2000).

NPs and OPs are names given to a large number of isomer compounds with structural formulas $C_{15}H_{24}O$ and $C_{14}H_{22}O$, respectively. In the context of endocrine disruptors, the most studied NPs and OPs are the 4-n-nonylphenol (4-n-NP), 4-tert-nonylphenol (4-t-NP), 4-n-octylphenol (4-n-OP), and the 4-tert-octyl-phenol (4-t-OP) (Koniecko *et al*., 2014; Quednow & Püttmann, 2008; Loos *et al*., 2008; Tsuda *et al*., 2000).

The effects of APs in humans are still unknown. However, their endocrine disrupting potential has already been established in laboratory experiments by the high multiplication of breast cancer cells, which are sensitive to estrogens (Kabir *et al*., 2015; Soto *et al*., 1995; Soto *et al*., 1991). Indeed, manipulative experiments with mice have shown an increase in the endometrial mitotic index when single doses of 20 and 50 mg of NP were administred (Soto *et al*., 1991). Kurihara *et al*., (2007) showed that NPs present in sediments of Tokyo Bay induced the production of vitellogenin (VTG) in male and young fish.

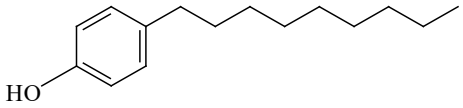
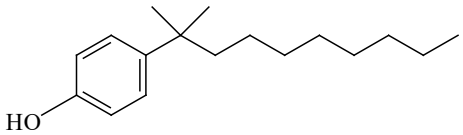
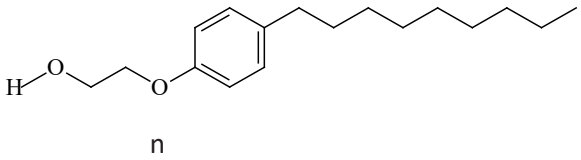
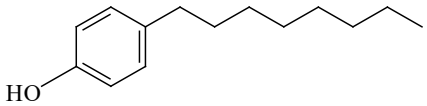
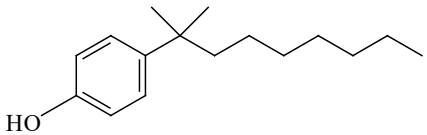
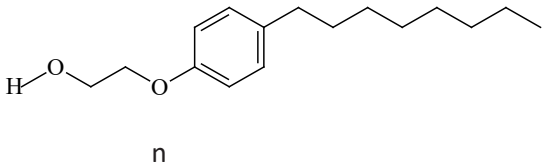
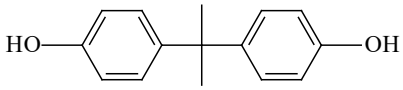
Oehlmann *et al*. (2000) described the enlargement of accessory sex glands, the stimulation of oocytes in females and a reduction in length of penis and prostate in males of the gastropod *Lapillus nucella* exposed to OP. The main sources of APs for the environment are the domestic, industrial and WWTP effluents (Bergé *et al*., 2014; Richardson & Ternes, 2014; Solé *et al*., 2000; EPA, 1997). APs can also be released into the marine environment due to fossil fuel activities, such as the release of water produced in oil rigs (Boitsov *et al*., 2007).

In WWTP and in the environment, APEOs may only be partially degraded microbiologically, which may generate shorter chain APs (e.g., NPs, OPs and mono-, di-, and tri- etoxylated APs) that are more persistent (David *et al*., 2009; Zhang *et al*., 2008; Ying *et al*., 2002a; Renner *et al*., 1997). In general, compounds originated from the degradation of APEOs present higher estrogenic activity, are more insoluble in water and have lower coefficients of octanol/water (K_{OW}) (Table 3). As a result, they are more lipophilic and susceptible to accumulation in fauna and humans (Gu *et al*., 2016; Casatta *et al*., 2015; Nurulnadia *et al*., 2014; Bouzas *et al*., 2011; Basheer *et al*., 2004; Ying *et al*., 2002a).

Bisphenol is a generic name given to a group of hydroxylated diphenylalkanes, being the bisphenol A (BPA) the main substance of this group (Perez *et al*., 1998). BPA is used in various applications, such as the production of polymers (e.g., polyvinyl chloride - PVC), epoxy resins, polyester resins, polycarbonates, fungicides, antioxidants, flame retardants, and resin for dental filling (Frye *et al*., 2011; Yi *et al*., 2010; Lintelmann *et al.,* 2003). Additionally, BPA is used in plastic films and packaging, routinely used into food packages. This is a fact of concern given the known ability of BPA to migrate from the packaging to the food (Gu *et al*., 2016; Casatta *et al*., 2015; Emnet *et al*., 2014; Nurulnadia *et al*., 2014; Fasano *et al*., 2012; Bouzas *et al*., 2011; Basheer *et al*., 2004). In some countries, such as Canada, USA, France, and more recently in Brazil, BPA has been banned from use in children utensils and toys (ANVISA, RDC 41/2011; Lintelmann *et al*., 2003).

The estrogenic potency of BPA is 10^{-3} to 10^{-5} times smaller than that of estradiol (Lintelmann *et al*., 2003; Milligan *et al*., 1998). However, its estrogenic capacity can be amplified due to its wide release and large persistence in the environment. The first evidence of estrogenic activity of BPA was reported in the late 1930s (Dodds & Lawson, 1938; Dodds & Lawson, 1936). Overtime, various toxicological studies confirmed the estrogenic behavior of bisphenol A (Xu *et al*., 2015; Mandich *et al*., 2007). Vandenberg *et al*. (2010) have examined 80 biomonitoring studies of BPA in tissues and fluids of humans, focusing on individuals exposed to BPA through the environment, or by non-occupational exposure. Levels of BPA between 2 to 150 ng L^{-1} were detected in children, teenagers and adults blood and urine samples. Those results suggest that this substance is possibly causing adverse effects in human health.

Table 3. Physicochemical properties of Alkylphenols, alkylphenols polyethoxylated e Bisphenol A.

Compound	Molar mass[a]	Solubility[b]	Log K_{OW}[c]	Chemical structure
4-n-Nonylphenol (4-n-NP)	220	5.43	4.48	
4-t-Nonylphenol (4-t-NP)	220	-	-	
Nonylphenol monoethoxylated	264	3.02	4.17	
Nonylphenol diethoxylated	308	3.38	4.21	
Nonylphenol polyethoxylated	-	-	-	
4-n-Octylphenol (4-n-OP)	206	12.6	4.12	
4-t-Octylphenol (4-t-OP)	206	-	-	
Octylphenol monoethoxylated	250	8.00	4.10	
Octylphenol diethoxylated	294	13.2	4.00	
Octylphenol polyethoxylated	-	-	-	
Bisphenol A	228	120	3.30	

Adapted from Ying *et al*., 2002a. [a]mole mass (g mol^{-1}); [b]Solubility in water (mg L^{-1} at 20 ° C); [c]Coefficient of octanol/water partition.

Experimental tests with biota showed that the action of BPA in mice may be associated to changes in the development of the mammary gland tissues (Lee et al., 2015; Vandenberg *et al*., 2007; Muñoz-de-Toro *et al*., 2005; Markey *et al*., 2001), behavioral disorders and premature sexual maturation (Talsness *et al*., 2009). Ortiz-Zarragoitia & Cajaraville (2005) reported the reabsorption of gametes in both genders of mussel *Mytilus edulis*, also as a result of exposure to BPA. Biological effects such as the increase synthesis of VTG, the inhibition of gonad growth, the increase of liver metabolism and the bioaccumulation of steroidal and phenolic EDs were assessed in high-back crucian carp (*Carassius auratus*) exposed to WWTP effluents (Liu *et al*., 2012).

The presence of BPA as well as APs in the environment are caused by leaching processes of materials with them in the constitution (Wang & Schnute, 2010). These compounds have been detected in several environmental compartments such as air, water, soil, sediment, and biota (Salgueiro-González *et al*., 2015; Nurulnadia *et al*., 2014; Jakimska *et al*., 2013; Maggioni *et al*., 2013; Bach *et al*., 2012). Due to the its higher water solubility when compared to AP and phthalates, and its relatively high log K_{ow} value (Table 3) it may be predicted that BPA has a wide distribution in the aquatic environment (Sun *et al*., 2012; Cunha *et al*., 2012). This hypothesis, however, needs to be further investigated.

2.3. Phthalates

Phthalates or phthalic acid esters are synthetic compounds that have been used in industrial activities since the 1930s. Their application includes plasticizers in polymers and additives for various products such as insecticides, paints, packaging, cosmetics, floor coverings, ceilings, clothing, and/or electrical insulating compounds additives (Net *et al*., 2015; Mankidy *et al*., 2013b; Li *et al*., 2008; Horn *et al*., 2004; Sumpter, 1998). The most commonly used phthalates are dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-buthyl phthalate (DnBP), diisobuthyl phthalate (DiBP), di(2-ethylhexyl) phthalate (DEHP) and butylbenzyl phthalate (BBP). A quarter of the whole world production of phthalate is represented by DEHPs, which is employed in the production of PVC (Net *et al*., 2015; Dargnat *et al*., 2009).

Although Brazil does not prohibit the use of phthalates in products such as cosmetics and food packaging, the World Health Organization (WHO) warns about the possible health problems caused by these compounds (WHO, 2012). Phthalates, especially DnBP, BBP and DEHP, have high values of log K_{ow} (Table 2), characteristic of lipophilic compounds, which allows the accumulation of these compounds in the organic matter present in soils and sediments (Benjamin *et al*., 2015; Net *et al*., 2015; Gavala *et al*., 2003).

The interfering nature of phthalates has been reported in a number of studies both *in vivo* and *in vitro* (Benjamin *et al*., 2015; Romani *et al*., 2014; Mankidy *et al*., 2013; Hashimoto *et al*., 2003; Picard *et al*., 2001; Körner *et al*., 1999). Phthalates became the subject of much concern once they are suspected to cause premature puberty (Tsai *et al*., 2016; Zhang *et al*., 2015; Fisher & Eugter, 2014; Colón *et al*., 2000).

In humans, phthalates can affect not only the endocrine and reproductive systems, but also may cause respiratory and dermatological problems (Pérez-Feás *et al*., 2011). In rodents, the exposure of males in the intrauterine period to DnBP, BBP and DEHP results in a series of reproductive abnormalities, such as damage to testicles (Foster, 2006; Gray *et al*., 2006; Foster *et al*., 2001). Other studies have shown carcinogenic effects and feminization in mice and fish even at low concentrations of phthalates (Benjamin *et al*., 2015; Valton *et al*., 2014; Martino-Andrade & Chahoud, 2010; Larsen *et al*., 2002).

In the environment, phthalates can suffer natural degradation (Benjamin *et al*., 2015; Liang *et al*., 2008). According to ecotoxicological models for mammals, fish and arthropods the degradation products of DEHP, such as 2-ethylhexanol and 2-ethylhexanal, present more toxicity than the original compound (Benjamin *et al*., 2015; Horn *et al*., 2004; Nalli *et al*., 2002). Therefore, environmental studies should take into account the presence and toxicity of both the original compounds and their metabolites.

The main routes of intake of phthalates in humans are inhalation associated with atmospheric particulate matter, direct contact with materials composed with phthalates and the ingestion of contaminated food (Net *et al*., 2015; Gärtner *et al*., 2009; Rudel *et al*., 2003). The addition of phthalates to food is not common. However, the foof contact to its package or even with plastic utensils used during food processing may generate food contamination. The phthalates, which are used as plasticizers, are not chemically bound to the polymer matrix, so they can be quickly released to the environment during their production, use and disposal (Net *et al*., 2015; Sax, 2010; Heudorf *et al*., 2007; Fromme *et al*., 2002). Considering the relatively high vapor pressures, when compared to other organic compounds (Table 2), phthalates can be volatilized into the atmosphere and be transferred to other environment compartments during their life cycle (Net *et al*., 2015; Xie *et al*., 2007).

3. Analytical techniques employed in the determination of EDs in the environment

Techniques for sample preparation

The development of new procedures for sample preparation should aim for simplification, automation, economy, minimal sample manipulation, minimal use of solvents and energy, according to the principles of the Green Chemistry (Huerta *et al*., 2015; Yan & Wang, 2013; Farré *et al*., 2010).

The determination of organic contaminants such as EDs in environmental samples is always challenging, not only due to the very low concentrations of analites but also due to the complexity and diversity of sample matrices. Matrix effects may have negative impacts to important analytical parameters (e.g., limit of detection (LOD), limit of quantification (LOQ), linearity, accuracy and precision), making the direct analysis of environmental samples very dificult (Farré *et al*., 2012; Wu *et al*., 2010). Therefore, the pretreatment of environmental samples,

especially for matrices such as coastal and ocean waters that have high salinities, is a real necessity. This step, nevertheless, usually takes up to 70-90 % of the analysis time (Zuloaga *et al*., 2012).

Sample preparation for the determination and quantification of organic compounds are based on three main steps: extraction, clean up and pre-concentration. The extraction step is a procedure performed to separate the analytes from the sample matrix. In the clean up step the possible interferences in the analysis, which difficult to identify and quantify the compounds of interest, are removed. EDs in environmental samples are usually present at concentration levels below the LOD of most analytical methods. Consequently, the pre-concentration it is a crucial step to improve detectability and to meet LOD and LOQ of analytical methods.

Sample preparation techniques are specific for each sample type. Solid phase extraction (SPE), for instance, has been the preferred technique in studies of EDs in liquid samples (Anumol e Snyder, 2015; Melo e Brito, 2014; Richardson & Ternes, 2014; Lisboa *et al*., 2013; Zhang *et al*., 2012; Richardson, 2012; Saravanabhavan *et al*., 2009; Fatoki & Noma, 2001). The SPE technique applied to aqueous samples has the advantage of aggregating three steps, i.e., extraction, clean up and preconcentration, in a single stage. In addition, SPE offers a wide variety of solid phases for extraction, resulting in different types of interactions with the analytes and, then, wide applicability. Another advantage of SPE is the possibility of automation, which facilitates its use in environmental studies when it is necessary to process a large number of samples. However, SPE has limitations, such as the blocking of the extraction phase pores by the matrix components, several operational steps, and analytical variations among extraction cartridges (Richardson & Ternes, 2014; Queiroz & Lanças, 2005; Lisboa *et al*., 2013). Even with these limitations, the SPE has been the extraction procedure most used in EDs studies. Shan *et al*. (2014) analyzed BPA, 4-n-OP and 4-n-NP in tap and bottled water using SPE C18 with minimum detectable concentrations of 0.75-1.0 ng L^{-1} and the recoveries ranged from 87.0 % to 106.9%. Zhang *et al*. (2012) used C18 as stationary phase in SPE and found limits of determination for OP, NP, E1, E2, E3, EE2 and BPA in wastewater below 0.8 ng L^{-1}, with recoveries higher than 80%. Ribeiro *et al*. (2009) investigated the presence of estradiol, estrogen, 17α-ethinylestradiol, bisphenol A, 4-octylphenol, 4-nonylphenol in estuarine waters, using Oasis HLB cartridges and found BPA concentrations up to 800 ng L^{-1}.

In the case of solid samples, such as suspended particulate matter, sediment and biota, the most used sample preparation procedures are microwave assisted extraction (MAE) (Vega-Morales *et al.*, 2013; Liu *et al.*, 2012; Dévier *et al.*, 2010), ultrasound assisted extraction (UAE) (Huerta *et al.*, 2015; Yu *et al.*, 2011; Sánchez-Avila *et al.*, 2011) and pressurized liquid extraction (PLE) (Salgueiro-Gonzales *et al.*,2014; Ma *et al.*, 2013; Jakimska *et al.*, 2013). They have been the main alternatives to replace the extractions traditionaly performed by Soxhlet (Bossio *et al*., 2008; Wang *et al*., 2007). Both soxhlet and liquid liquid extraction (LLE) extractions use large amounts of solvents, generate a large amount of organic residues, are time consuming and also difficult to automate. These factors decrease their analytical speed, and make them unattractive for the preparation of a large number of samples, as required in monitoring programs. Due to the large complexity of the solid matrices, such as sediment, soil or animal tissues, it is necessary to perform clean up steps. These procedures are intended to minimize or eliminate the impurities that may cause equipment damage or even interfere with the determination. Additionally, after their first step extraction, those solid sample extracts obtained by MAE, UAE and PLE are further cleaned up using mainly the SPE technique. The main strategy used to perform the clean up in solid samples is the SPE with C18 and/or florisil cartridges (Zhang *et al*., 2012; Arditsoglou & Voutsa, 2008a; Braga *et al*., 2005).

Yu *et al*. (2011) have used the UAE for the extraction of hormones, BPA and personal care products and have quantified them by ultra high performance liquid chromatography coupled with tandem mass spectrometry. The analytes were extracted for 15 minutes with a mixture of acetonitrile/water, centrifuged and cleaned up with C18 cartridges. The method was applied to sludge and sediment samples with recoveries ranging between 63 % and 119 % and LOQs between 0.1 and 3 ng g^{-1}, for the sludge samples, and from 0.02 to 0.5 ng g^{-1}, for sediments. Matějíček (2011) has developed a method for extraction of estrogens in sediments based on MAE. The samples were extracted with a mixture of methanol/water for 10 minutes, filtered and determined by HPLC. Recoveries ranged 99-110 % and limits of detection were 90 ng g^{-1} (E2), 180 ng g^{-1} (E1), and 250 ng g^{-1} (EE2). Ma *et al*. (2013) have optimized a method on GC-MS combined with PLE for the determination of six phthalates in soil samples. The LOQs of the proposed method ranged from 0.02 to 0.29 μg g^{-1} and recoveries varied between 90 and 110%.

The LOD and recoveries reported in the literature for MAE, PLE and UAE are very variable depending on the sample size, solvent volumes and equipments used. However, these techniques offer several benefits compared to traditional Soxhlet technique, for instance relatively fast extraction, reduced solvent consumption, and a smaller amount of sample handling.

Methods for ED analysis

The HPLC and gas chromatography (GC) are the most commonly analytical techniques used for the determination of persistent organic pollutants (POP), EDs, and ECs in environmental samples. GC and liquid chromatography (LC) are powerful separation techniques and should be combined with highly sensitivity detectors for enabling the analytes determination. EDs are analyzed mainly by liquid chromatography with ultraviolet, fluorescence, and/or mass spectrometry detectors or by GC with mass spectrometry detector (Huerta *et al*., 2016; Birch *et al*., 2015; Emnet *et al*., 2015; Zhang *et al*., 2014; Selvaraj *et al*., 2014; Melo & Brito, 2014; Lisboa *et al*., 2013; Villar-Navarro *et al*., 2013; Ribeiro *et al*., 2009; Bossio *et al*., 2008; Xie *et al*., 2007; Fatoki & Noma, 2001; Khim *et al*., 1999). The coupling of a chromatograph with mass spectrometer combines the advantages of the chromatography technique (which are high selectivity and separation efficiency) with the advantages of mass spectrometry (*e.g.* structural information and high selectivity) (Vekey, 2001).

GC is a relatively inexpensive, rapid and reproductible technique for a large number of compounds in environmental samples. The GC presents high resolution and the possibility to be coupled to selective and sensitive detectors such as mass spectrometry (MS) and electron capture detector (ECD), among other possibilities. However, GC is a technique that mainly requires analytes to be volatile or semi-volatile, thermally stable and non-polar in order to facilitate the maximum number of successive interactions between the analyte and the stationary phase, reducing the height and increasing the number of theoretical plates (*H* and *N*, respectively). Although polar-bonded phase columns are commercially available, in general, studies mostly use DB-1 (100% polysiloxane) or DB-5 (95% polysiloxane and 5% phenyl) columns since they present higher robustness and better reproductibility and repeatability. For the analyses of PAHs, several pesticides, phthalates and PCBs, among others, the GC can be used without the need of analyte modification. However, the determination of hormones, antibiotics and other drugs, APs and bisphenol A, among other EDs by GC requires the use of a derivatization step (Farajzadeh *et al*., 2014; Wu *et al*., 2010) in order to prevent those analyte adsorption and decomposition in the column or in the injector, resulting in non-reproducible peak areas or heights and shapes. Moreover, the purpose of derivatization is also the improvement of LOD and selectivity (Farajzadeh *et al*., 2014). Derivatization is a transformation the chemical compound into a specific product with caraceristicas with features that allow its determination.

On the other hand, a growing number of studies has been done using LC, coupled to diode array detectors (DAD), with fluorescence detectors (FLD) and/or of mass spectrometer detectors (Huerta *et al.,* 2015; Torres *et al.,* 2015; Valdés *et al.,* 2015; Anumol e Snyder, 2015; Salgueiro-Gonzales *et al.,* 2014; Melo e Brito, 2014; Ammann *et al*., 2014; Lisboa *et al*., 2013; Zhang *et al*., 2012; Jardim *et al*., 2012; Matějíček, 2011; Labadie & Hill, 2007; Ferguson *et al*., 2000; Khim *et al*., 1999). A good advantage of the liquid chromatography is that derivatization is mostly unnecessary. In this way, a relatively complicated and time-consuming derivatization procedure, which may lead to an underestimation of ED concentrations and possibly contamination of samples, is then eliminated. Another interesting LC advantage is its applicability for the determination of polar organic pollutants, thermolabile substances and/or those easily decomposed, and, hence cannot be analyzable by GC systems.

The best technique (GC or LC) and the best detector (DAD, FLD, flame ionization (FID), ECD or MS) for the determination of EDs in environmental samples will depend on the study goals, the type of matrix to be studied, and the physicochemical characteristics of the analytes. It also should be taken into account the following parameters: sensitivity, number of samples, availability of instrumentation, costs and the analyst skills. Liquid and gas chromatography are complementary techniques, and both have interesting innovations in order to achieve LOD in the range of few ng L^{-1}.

The recent advances in LC, GC, types of columns, detectors (especially for mass spectrometers), the interface chromatograph-detector and their speed of data acquisition have been providing significant improvements in the separation of complex samples in short analyses, with little use of solvent and good selectivity and sensitivity. With this, the current and future trend is to find EDs and ECs at even lower concentrations levels in an increasing number of matrices and places around the world. It is also expected that studies are likely to switch focus, *i.e*., from descriptive studies of EDs occurrence in several environmental compartments towards processes studies. These changes will subsidize a better understanding in the processes controlling transformations, transport, fate and interactions between environmental compartiments. Ecological, (eco)toxicological and human health risk assessments will contribute even further for the evaluation of behavior and possible adverse effects of ED inputs into the ecosystems.

4. Occurrence of EDs in marine environment

The origins of EDs in the aquatic environment are highly variable and are often attributed to human activity. In general, coastal environments, such as estuaries, bays and mangroves, serve as major receptors of domestic, industrial, hospital, agricultural, and aquiculture

effluents. Submarine outfalls, port and ship activities, surface runoffs are also important sources of EDs. The relative inefficiency of conventional WWTP in the complete removal of EDs makes them one of the most important sources of these compounds to water bodies (Deblonde *et al*. 2011; Pal *et al*., 2010; Santos *et al*., 2010; Kuster *et al*., 2009).

Once in the environment, EDs may undertake different pathways: *(i)* distribution between environmental compartments, such as water, air, soil, sediment, suspended particulate matter and biota, *(ii)* degradation and subsequent transport and distribution of their metabolites in the environment, *(iii)* bioaccumulation and/or biomagnification (Lintelmann, 2003).

The presence, behavior, ecotoxicity and the interfering effects of EDs have been reported for riverine environments (Gu *et al*., 2016; Esteban *et al*., 2016; Kabir *et al*., 2015; Li *et al*., 2014; Fu *et al*., 2007; Fatoki & Noma, 2001,) while the effects and fate of EDs in the marine environments is still unknown. Coastal regions, in special estuaries, are dilution zones, where river water mixes with marine waters. In general, coastal waters have lower levels of contaminants than freshwaters, either due to distance from sources or to the occurrence of attenuation processes (i.e., dilution, sorption, precipitation and photooxidation). Tables 4, 5 and 6 shows a review of the occurrence of EDs studies in coastal environments, which will be discussed below.

Among the EDs discussed here, APs and BPA are the most studied EDs in marine environments. As previously discussed, APEOs, their degradation products (e.g., NPs and OPs), and BPA are synthetic and their presence in the environment is a result of human activity. Industrial and domestic effluents, WWTPs (effluents and sludge) as well as the application of pesticides are the main sources of APs, APEOs and BPA to the marine environment (Kabir *et al*., 2015; Gravilescu *et al*., 2015; Quednow & Püttmann, 2008; Soares *et al*., 2008; Ying e*t al*., 2002a).

The high partition coefficients of NP, OP and BPA, according to log K_{OW} values of 4.48, 4.12, and 3.30, respectively, suggest that these compounds, when entering the aquatic environment they are sorbed in suspended particulate matter and sediments.

NP concentrations in saline waters (Table 4) range from 0.002 ng L^{-1}, in the sea of Japan (Kannan *et al*., 1998), to 4100 ng L^{-1}, in the coast of Spain (Petrovic *et al*., 2002). In turn, OP concentrations in water ranged from 0.013 ng L^{-1}, in the North Sea (Xie *et al*., 2006), to 800 ng L^{-1}, in Singapore (Basheer *et al*., 2004). The concentrations of NP are up to an order of magnitude above the concentrations of OP, probably due to the highest use of polyethoxylated nonylphenol (Isobe *et al*., 2001). In general, the most contaminated areas are estuaries and coastal regions under the influence of industrial and domestic effluents and WWTP. In the ocean, concentrations decrease abruptly with distance from the coast. In the North Sea waters, however, the concentrations of OP (0.013 to 3 ng L^{-1}) and NP (0.09 to 1.40 ng L^{-1}) increased with the distance from the coast (Xie *et al*., 2006). The authors have suggested that atmospheric deposition of OP and NP, from the burning of aircraft fuels, was the main source.

In general, there is a negative correlation between the concentrations of OP and NP with salinity. This relationship is primarily due to dilution (physical mixing processes) with distance from the source. Studies also showed the influence of salinity on the distribution of AP and APEO (Li *et al*., 2005; Ferguson *et al*., 2001). Nevertheless, according to these studies the increase of salinity favors the removal and degradation processes of AP and PEA in the water column. This is the result of the salting out. This process results from the decrease in the solubility of organic compounds in water due to the effect of ionic strength on their activity coefficients but also represents these substances are going to be preferentially absorbed in environmental matrices with less polar nature as well as higher content of organic matter, such as SPM, sediments and biota. Furthermore, as a result of the reduced solubility, and high affinity for organic matter, it is expected that these compounds participate in processes of aggregation, flocculation and and the fate is usualy the accumulation in sediments.

In sediments, concentrations of NPs (Table 5) ranged from 0.01 ng g^{-1}, in Morro Bay, California (Diehl *et al*., 2012) to 32000 ng g^{-1}, in Auckland, New Zealand (Stewart *et al*., 2014), while the concentrations of OPs ranged from 0.01 ng g^{-1}, in the estuary Urdaibai in Spain (Puy-Azurmendi *et al*., 2010), to 179 ng g^{-1}, in Masan Bay, South Korea (Khim *et al*., 1999). Similarly to the processes that occur in the water column, the concentration of APs in sediments decreases with increase distance from the coast, due to dilution processes.

The presence of organic matter is the main factor influencing on the accumulation of APs in sediments, mainly due to lipophilic characteristics of these compounds. Jonkers *et al*. (2003), found high correlations between organic carbon and concentrations of NP in sediments from Scheldt and Rhine estuaries. The accumulation and persistency of AP in estuarine sediments (Shang *et al*., 1999) suggests that benthic macrofauna may be subject to long term exposition to these contaminants, potentially causing chronic effects in biota. The presence of AP in marine organisms (e.g. fish, oysters, squid, mussels, prawns, etc.) has been reported in several regions around the world (e.g., USA, Italy, Taiwan, Greece, Singapore and Japan) (Colin *et al*., 2016; Casatta *et al*., 2015; Emnet *et al*., 2015; Lee *et al*., 2015; Arditsoglou & Voutsa, 2012; Bouzas *et al*., 2011; Bartolomé *et al*., 2010; Wang *et al*., 2010; Kumar *et al*., 2008; Ferrara *et al*., 2008; Isobe *et al*., 2007; Pojana

Table 4. Endocrine disruptors (BPA, AP and estrogens) in seawater (ng L^{-1}) around the world.

Site	BPA	E1	E2	E3	EE2	OP	NP
Todos os Santos Bay, Brazil[a]	<LOD-48.2	<LOD	<LOD-18.2	<LOD-37.9	<LOD	<LOD-134	<LOD
Morro Bay, United States[b]	-	-	-	-	-	-	100-900
La Coruña Beach, Spain[c]	35	-	-	-	-	175	70-199
Biscay Bay, Spain[d]	60-130	-	-	-	-	50-100	1110-1460
Southeast Coast of California, United States[e]	-	-	-	-	-	<LOD-42	<LOD-230
Thermaikos Gulf, Greece[f]	10.6-52.3	<LOD	<LOD	<LOD	<LOD	1.7-18.2	22-201
Northeast Coast, Spain[g]	7.1-35	-	-	-	-	3.8-39	29-712
Aveiro Coast, Portugal[h]	2.6-13	<LOD-0.5	<LOD-1.1	-	<LOD	-	15-98
Mondego Estuary, Portugal[i]	178-589	<LOD	<LOD	-	<LOD	<LOD	-
Halifax and St. John Port, Canada[j]	-	1.4-7.5	1.8	-	<LOD	-	-
Thessaloniki Coast, Greece[k]	25-59	-	-	-	-	8-29	181-915
Laguna Venice, Italy[l]	3.4-145	3.2-6.7	3.0-175	-	4.6-28	-	4.0-211
Scheldt Estuary, the Netherlands[m]	-	0.37-10	<LOD	<LOD	<LOD	-	-
Suruga Bay, Japan[n]	3.6-1070	<LOD-9.2	<LOD	-	<LOD	<LOD	28.2-276
Acushnet Estuary in Buzzards Bay, United States[o]	-	0.78-1.2	0.56-0.83	-	3.01-4.67	-	-
North Sea, German Creek[p]	-	-	-	-	-	0.013-3	0.09-1.4
North Sea[q]	-	-	-	-	-	0.013-0.3	0.09-1.4
Taiwan Coast[r]	-	-	-	-	-	61-66	290-370
Baltic Sea, German[s]	0.1-5.7	0.13-0.54	<LOD	<LOD	1.6-17.9	0.1-1.1	1.3-7.5
Singapore coast[t]	2-2470	-	-	-	-	10-800	290-370
Rhine Estuary, the Netherlands[u]	-	-	-	-	-	-	31-147
Scheldt Estuary, the Netherlands[u]	-	-	-	-	-	-	35-934
Coast of Spain, Mediterranean and Atlantic[v]	-	-	-	-	-	300	300-4100
North Sea, German Creek[w]	1.6-6	-	-	-	-	0.02-1.6	0.8-63
Jamaica Bay[x]	-	-	-	-	-	1.56-8.3	77.4-416
Jamaica Bay[y]	-	-	-	-	-	3.3	201
Japan Sea[z]	-	-	-	-	-	-	0.002-0.093
Pearl River Delta and coastal[aa]	10-227	<LOD-3,1	-	-	<LOD-1,56	-	11-234
Cape D'Aguilar Marine Reserve, Hong Kong[ab]	14,1-206,5	-	-	-	-	-	91.7- 473.9
Gulf of Gdansk, Southern Baltic[ac]	<LOD-713.9	-	-	-	-	<LOD - 834.8	<LOD-3659.6
Yangtze River Estuary, China[ad]	0.98–43.8	<LOD-1.43	<LOD	-	<LOD-0.11	-	-

[a]Lisboa *et al*., 2013; [b]Diehl *et al*., 2012; [c]Salgueiro-González *et al*., 2012; [d]de los Ríos *et al*., 2012; [e]Vidal-Dorsch *et al*., 2012; [f]Arditsoglou & Voutsa, 2012; [g]Sánchez-Avila *et al*., 2011; [h]Jonkers *et al*., 2010; [i]Ribeiro *et al*., 2009; [j]Saravanabhavan *et al*., 2009; [k]Arditsoglou & Voutsa, 2008b; [l]Pojana *et al*., 2007; [m]Noppe *et al*., 2007; [n]Hashimoto *et al*., 2007; [o]Zuo *et al*., 2006; [p]Xie *et al*., 2006; [q]Ebinghaus & Xie, 2006; [r]Cheng *et al*., 2006; [s]Beck *et al*., 2005; [t]Basheer *et al*., 2004; [u]Jonkers *et al*., 2003; [v]Petrovic *et al*., 2002; [w]Heemken *et al*., 2001; [x]Ferguson *et al.,* 2001; [y]Ferguson *et al*., 2000; [z]Kannan *et al*.,1998; [aa]Xu *et al*., 2014; [ab]Xu *et al*., 2015; [ac] Staniszewska *et al*., 2015; [ad]Shi *et al*., 2014.

Table 5. Endocrine disruptors (BPA, AP and estrogens) in marine sediments (ng g^{-1}).

Site	BPA	E1	E2	E3	EE2	OP	NP
Abra and Urdaibai Estuary, Spain[a]	<LOD-0.04	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD-0.2
Morro Bay, United States[b]	-	-	-	-	-	-	0.01-157
Biscay Bay, Santander Coast, Spain[c]	4-59	-	-	-	-	9-14	150-210
Thermaikos Golf, Greece[d]	7.2-39	<LOD	<LOD	<LOD	<LOD	6.0-25	223-2695
Northeast Coast, Spain[e]	-	-	-	-	-	38-39	79-521
South-central Coast, Chile[f]	-	0.06-4.61	0.06-16.81	0.01-53.21	4.18-48.14	-	-
Urdaibai Estuary, Spain[g]	0.01-43	<LOD	<LOD	<LOD	<LOD	0.01-0.03	154-264
Northeast Coast, China[h]	-	-	-	-	-	-	8.8-1000
Yangtze Estuary, China[i]	0.72-13.2	-	-	-	-	-	1.56-35.8
Xiamen Bay, China[j]	1.7-121.9	1.1-7.4	1.0-2.4	<LOD	0.9-2.2	1.4-24.0	12.9-1160.0
Thessaloniki, Greece[k]	17	<LOD	<LOD	<LOD	<LOD	8	266
Masan Bay, Japan[l]	-	-	-	-	-	-	92-557
Savannah Estuary, United States[m]	-	-	-	-	-	0.86-6.9	4.1-18
Laguna Venice, Italy[n]	3.4-145	<LOD	<LOD	-	12-41	-	47-192
Tóquio Bay, Japan[o]	-	0.05-3.6	<LOD-0.59	-	-	-	-
Taiwan Coast[p]	-	-	-	-	-	27-49	130-190
Yeongil Bay, Korea[q]	<LOD-191	-	-	-	-	<LOD-24.3	<LOD-1430
East Coast of Sidney, Australia[r]	-	0.16-1.17	0.22-2.48	-	0.05-0.5	-	-
Califórnia Coast, United States[s]	-	<LOD-0.6	0.16-0.45	-	-	1.9-8.2	122-3200
Rhine Estuary, the Netherlands[t]	-	-	-	-	-	-	1.5-92.2
Scheldt Estuary, the Netherlands[t]	-	-	-	-	-	-	0.4-1080
Spain Coast, Mediteranean and Atlantic Ocean[u]	-	-	-	-	-	17-145	18-1050
Tóquio Bay, Japan[v]	-	-	-	-	-	6-10	120-640
Jamaica Bay[w]	-	-	-	-	-	<LOD-45	6.99-13700
Jamaica Bay[x]	-	-	-	-	-	8.1	846
Masan Bay, South Korea[y]	2.7-50.3	-	-	-	-	4-179	113-3890
Auckland, New Zealand[z]	<LOD-145	<LOD-2.2	<LOD-1.0	-	<LOD	<LOD-135	<LOD-32000
Gulf of Gdansk (Baltic Sea)[aa]	-	-	-	-	-	<LOD-48.88	<LOD-249.08
Yellow Sea[ab]	-	-	-	-	-	0.8-9.3	349.5-1642.8
East China Sea[ab]	-	-	-	-	-	0.7–11.1	31.3-1423.7
Cape D'Aguilar Marine Reserve, Hong Kong[ac]	60,8-265,9	-	-	-	-	-	527,3-800,0
Yangtze River Estuary, China[ad]	<LOD-7.87	<LOD-1.92	<LOD-0.30	-	<LOD-0.72	-	-

LOD=linit of detection. [a]Puy-Azurmendi *et al*., 2013; [b]Diehl *et al*., 2012; [c]de los Ríos *et al*., 2012; [d]Arditsoglou & Voutsa, 2012; [e]Sánchez-Avila *et al*., 2011; [f]Bertin *et al*., 2011; [g]Puy-Azurmendi *et al*., 2010; [h]Wang *et al*., 2010; [i]Bian *et al*., 2010; [j]Zhang *et al*., 2009; [k]Arditsoglou & Voutsa, 2008b; [l]Li *et al*., 2008; [m]Kumar *et al*., 2008; [n]Pojana *et al*., 2007; [o]Isobe *et al*., 2006; [p]Cheng *et al*., 2006; [q]Koh *et al*., 2006; [r]Braga *et al*., 2005; [s]Schlenk *et al*., 2005; [t]Jonkers *et al*., 2003; [u]Petrovic *et al*., 2002; [v]Isobe *et al*., 2001; [w]Ferguson *et al*., 2001; [x]Ferguson *et al*., 2000; [y]Khim *et al.,*1999; [z] Stewart *et al*., 2014; [aa]Koniecko *et al*., 2014; [ab]Duan *et al*., 2014; [ac]Xu *et al*., 2015; [ad]Shi *et al*., 2014

Table 6. Phthalates in sediments (ng g^{-1}) and water (ng L^{-1})

Site	Sample	DMP	DEP	DBP	DEHP	BBP	DnOP
Abra and Urdaibai Estuary, Spain[a]	Sediment	<LOD	<LOD-6218	<LOD-1010	688-2530	-	-
Biscay Bay, Santander Coast, Spain[b]	Water	<LOD	3330-37360	4450-5960	7080-85360	-	-
	Sediment	<LOD	170-7670	630-1040	1120-15190	-	-
Southeastern California Coast, United States[c]	Water	-	-	-	-	-	<LOD-85
Northeastern Coast, Spain[d]	Water	9.4-21	43-4482	-	4.6-138	2.6-658	-
	Sediment	12-26	22-4317	-	1.9-107	12-3297	-
Urdaibai Estuary, Spain[e]	Sediment	<LOD	908-6377	466-1168	346-4376	-	-
Cantábria Coast, Spain[f]	Sediment	<LOD	<LOD	<LOD	190-2800	<LOD	
Kavala Coast, Greece[g]	Water	-	-	370-700	600-1300	300-6000	-
Arctic Sea, Norway[h]	Water	0.013-0.312	0.008-0.795	0.0002-0.048	0.024-3.330	-	-
North Sea[i]	Water	<LOD-0.68	0.03-4.0	0.45-6.6	<LOD-5.3	<LOD-0.26	-
Elizabeth Port and East London, South Africa[j]	Water	500-350800	4400-398300	700-1028100	2100-2306800	-	-
Auckland, New Zealand[k]	Sediment	<LOD	<LOD	<LOD	<LOD-11500	<LOD -1600	<LOD
Anzali wetlands, Iran[l]	Sediment	-	-	0.12-19.02	0.25-43.12	-	-

LOD – Detection limit. [a]Puy-Azurmendi *et al*., 2013; [b]de los Ríos *et al*., 2012; [c]Vidal-Dorsch *et al*., 2012; [d]Sánchez-Avila *et al*., 2011; [e]Puy-Azurmendi *et al*., 2010; [f]Antizar-Ladislao, 2009; [g]Grigoriadou *et al*., 2008; [h]Xie *et al*., 2007; [i]Ebinghaus & Xie, 2006; [j]Fatoki & Noma, 2001; [k]Stewart *et al*., 2014; [l]Hassanzadeh *et al*., 2014

et al., 2007; Cheng *et al*., 2006; Basheer *et al*., 2004). NPs concentrations ranged from 1.2 ng g^{-1} in oysters, at Savannah, USA (Kumar *et al*., 2008), to 7600 ng g^{-1} in mussels and oysters from the northeastern coast of China (Wang *et al*., 2010a). Concentrations of OPs ranged from 0.2 ng g^{-1}, in anchovies in the Tyrrhenian Sea (Ferrara *et al*., 2008), to 1460 ng g^{-1}, in oysters collected on the coast of Taiwan (Cheng *et al*., 2006). In many studies a significant relationship between the concentrations of NP and OP in biota and in the water column was not observed (Tsuda *et al*., 2000). The absence of this correlation is not only associated with the high water dynamics, but also to the fact that the concentration of biological tissues reflects the contamination exposure integrated over the animal lifetime.

OP concentrations were positively correlated with NP concentrations in oysters that inhabit the Taiwan Coast. This was similar to that found between OP and NP in the marine gastropod *Thais clavigera*,, which is a predator of oysters *Crassostrea gigas,* from the same region. Cheng *et al*. (2006), by analyzing these two trophic levels, suggested that there was biomagnification of NP and OP.. Studies of biomagnification of EDs, nevertheless, are still scarce and efforts should be made to understand the mechanisms associated to the transfer and accumulation of contaminants trofic levels.

In the studies reviewed, concentrations of NPs in sediments and biota were always higher than the concentrations of OP, similarly to the observed in water. Moreover, NP present higher lipophilicity (log K_{OW} NP > log K_{OW} OP), therefore it is accumulated in higher proportion in sediments and biota when compared to OP.

Concentrations of OP and NP in coastal sediments are much lower than concentrations found in rivers. Fu *et al*. (2007) have reported concentrations of NP up to 31704 ng g^{-1} in rivers that flow into the bay of Jiaozhou, China,. In turn, for marine environments the NP values were below 14000 ng g^{-1} (Gu *et al*., 2016; Isolbe *et al*., 2007; Pojana *et al*., 2007; Ferguson *et al*., 2001;). Attenuation due to dilution and degradation processes is possibly the main reason for the differences in the concentrations observed between riverine and marine environments.

The BPA concentrations (Table 4) in seawater ranged from 0.1 ng L^{-1} in the Eastern Baltic Sea, Germany (Beck *et al*., 2005), to 2470 ng L^{-1} in waters from Singapore coast

(Basheer *et al*., 2004). The BPA concentration is mainly attributed to industrial activity and the WWTP effluents. As a result, it was observed a decreasing gradient of BPA concentration with the distance increase from the sources. This variation in the BPA concentrations has been mainly attributed to dilution and degradation processes. It is estimated that BPA present half-life between 2.5 - 4 days in marine waters (Heemken *et al*., 2001). Thus BPA molecules that are not sorbed and tranferred to sediment may be rapidly degraded.

In sediments, BPA ranged from 0.01 ng g^{-1}, in sediments from Urdaibai estuary, Spain (Puy-Azurmendi *et al*., 2010), to 266 ng g^{-1} in sediments of Cape D'Aguilar Marine Reserve, Hong Kong (Xu *et al*., 2015). There are few studies describing the presence of BPA in marine organisms, among these, a study with mussels reported BPA concentrations ranging from 0.54 ng g^{-1} and 213 ng g^{-1} (Isobe *et al*., 2007). AP and BPA concentrations in mussels are generally higher than those obtained for fish since they feed on suspended material and accumulate large amounts of contaminants (Basheer *et al*., 2004), including trace metals and PHA.

Unlike the AP, the BPA concentrations in sediment and biota were, in many cases, lower than its concentrations in water. This pattern can be explained by the lower lipophilicity of BPA compared to AP, and its high solubility. It seems like that these compounds degrade before reaching the sediments (Gu *et al*., 2016; Casatta *et al*., 2015; Emnet *et al*., 2015; Miège *et al*., 2012; Bouzas *et al*., 2011 Isolbe *et al*., 2007; Pojana *et al*., 2007; Cheng *et al*., 2006; Heemken *et al*., 2001).

E1, E2, E3 and EE2 are the most studied hormones, primarily because of their large inputs in the environment and their high endocrine disruption potential. The concentrations of E1 in water, sediment and mussels range from 0.13 ng L^{-1} (Beck *et al*., 2005) to 52 ng L^{-1} (Noppe *et al*., 2007), 0.05 ng g^{-1} (Isobe *et al*., 2006) to 7.4 ng g^{-1}, (Zhang *et al*., 2009) and 0.2 ng g^{-1} to 0.4 ng g^{-1} (Saravanabhavan *et al*., 2009), respectively. The E2 in water and sediment was found at concentrations ranging from 0.56 ng L^{-1} (Zuo *et al*., 2006) to 175 ng L^{-1} (Pojana *et al*., 2007), and 0.06 ng g^{-1} to 16.8 ng g^{-1} (Bertin *et al*., 2011) respectively, while E2 has not been detected in organisms. Among the studied hormones, the synthetic EE2 is the only one that has exclusively anthropogenic sources. EE2 in water, sediment and biota was found in concentrations ranging from 1.6 ng L^{-1} (Beck *et al*., 2005) to 28 ng L^{-1} (Pojana *et al*., 2007), 0.05 ng g^{-1} (Braga *et al*., 2005) to 48 ng g^{-1} (Bertin *et al*., 2011), and 7.2 ng g^{-1} to 38 ng g^{-1} (Pojana *et al*., 2007), respectively. On the other hand, E3 was only identified in sediments of the south-central coast of Chile (Bertin *et al*., 2011) ranging from 0.01 ng g^{-1} to 53.2 ng g^{-1}.

Estrogenic hormones are released into the environment in their inactive conjugated forms (*i.e.* glucuronic or sulfate acid). However, they are rapidly transformed in their interfering forms through the activity of microorganisms present in environment (Ying *et al*., 2002b). Like other EDs, estrogens are presented in relatively low concentrations in the marine environment, due to dilution and/or attenuation processes.

High concentrations of estrogens were not found in the sediments, possibly due to their relatively fast degradation before the occurrence of other processes such us sorption, flocculation and/or deposition. Bowman *et al*., (2003) reported half-lives from 2.8 to 3 days for E1 and E2. However EE2, with slower degradation rate than natural hormones (Braga *et al*., 2005), has the potential to accumulate and to present high concentrations in sediments. Evaluations of estrogenic hormones in marine biota showed very low concentrations, reflecting the concentrations observed in environment (Gu *et al*., 2016; Emnet *et al*., 2015; Casatta *et al*., 2015; Miège *et al*., 2012; Bouzas *et al*., 2011; Saravanabhavan *et al*., 2009; Pojana *et al*., 2007; Isolbe *et al*., 2007; Cheng *et al*., 2006).

Table 6 presents the occurrence of phthalates in water and sediment from coastal regions. The highest concentrations of phthalates were found in areas near large harbors, quite possibly due to effluents and plastic waste originating from them (Fatoki & Noma, 2001). Urban and industrial effluents from neighboring regions may also have been important sources of phthalates in these regions. As for the other studied EDs, salinity and content of organic matter in the water influence the transfer of phthalates to sediments (Mackintosh *et al*., 2006) or biota (Cheng *et al*., 2013; Bartolomé *et al*., 2010; Dargnat *et al*., 2009). In general, with increasing salinity the balance between the concentrations of phthalates in the sediment and water may be affected. Phthalates can be mobilized and transferred between compartments, besides being degraded through biological processes. The biodegradation processes occur with higher intensity in aerobic conditions. In the anoxic environments biodegradation processes are minimized (Fromme *et al*., 2002). Similarly to other classes of contaminants, phthalates can be stored in anoxic sediments for a long period of time and in medium to large temporal scales sediments may be remobilized and they may act as a source of contaminants.

5. Conclusions

A large variety of emerging contaminants, and among them, those ones which are likely to cause endocrine disruption in some level, are emitted by ever-growing and diverse man-made sources, effectively spreading themselves out to every environmental compartiment throughout the globe. The limited knowledge about the chemistry, transport, toxicity and fate of endocrine disruptors, associated to its wide use in anthropogenic

activities have promoted a growing interest in the development of analytical methods and its applications to study the distribution and behavior of these contaminants in the environment. Yet, problably the quantity of new compounds considered "emerging" or "endocrine disruptors" which has been recently synthetized, developed, and released for use by industrial, farmaceutical, agricultural, and aquicultural sectors are continuously increasing, and faster than analysis systems and analytical methods are possibly progressing. This happens, in part, in order to benefit humanity for increasing its well being conditions, but it also happens for creating substitute molecules for those ones being banned of use because are considered nocive for the environment, biota and/or human beings. However, an important portion of the problem is associated with the accelerated development and registry of new substances without a proper study of their cycle of life (which includes environmental risk evaluation and the development of degradation and removal processes for them), which is time-consuming and cost-effective. So, it is quite possible these new substances are going to be accumulated in the environment soon after they started to be utilized. In spite the recent advances in Analytical Chemistry regarding sample preparation and detection systems for the study of EDs, it is believed that a large amount of micropolutants remain unindentified and undetected in the environment. If they persist unkwown, it is quite possible that identification of sources, transport and fate of these contaminants are underestimated or not existent at all. And, therefore, subsidizing the development of regulatory measures, source control and decision-making to promote the sustainable management of ecosystems and the preservation of the environment and human health is delayed or biased.

Studies around the world indicated that estuaries and coastal regions under the influence of domestic or industrial and WWTP effluents have increasing levels of EDs, and hence this topic needs to be addressed. However, the number of these studies is still very incipient to produce a good diagnosis of the real situation of these contaminants in marine environments. If on one hand this data reflects the relative novelty of this subject, on the other hand the major impediments to the development of this topic is the complexity of marine waters (*i.e.,* high ionic strength, dissolved organic matter and high content of dissolved salts, which are in general the main interfering species in chemical analysis) and the low concentration levels of EDs. These factors represent significant challenges for the coming years. Additionally, it is well accepted conventional water-treatment systems are inefficient to remove EDs from their inffluents, which eventually are realeased to superficial waters and then reaching estuarine and coastal regions. In this way, it becomes necessary the development of new and more efficient water treatment systems, possibly employing advanced oxidative methods or biodegradation by microrganisms (such as bacteria, fungi, enzimes, yeasts, and/or genetically modified organisms) able to break ED molecules down. If new and more adequate WWTP systems are developed, lower levels of residual EDs in the effluents would be reached. In this way, it is possible to a substancial lower amount of EDs could reach coastal areas resulting in the decrease of contamination levels, what could facilitate the management of those areas. In the same direction, the development and application of mitigation and/or remediation of affected areas would alliviate the environmental pressure in regard to EDs to the already impacted regions. New and more studies are needed in these research areas.

It is also urgent the acquisition of robust databases through long-term investigations about EDs behavior and distribution in different compartments and how they participate in food chain in order to access their possible bioaccumulation and/or biomagnification among different trophic levels. The real understanding of ED effects in the aquatic environment is far from understood. In addition, studies about the possible adverse human health effects of endocrine disruptors are scarce. Until robust analytical procedures, with high selectivity and sensitivity could be developed to the analysis of a large number of samples, as it is required in monitoring studies, the behavior of these contaminants in the environment as well as their fate and effects in biota may not be fully understood. Indeed, cause-effect manipulative studies and ecotoxicology tests are still in an embrionary stage of development, and represent a major challenge.

References

Agência Nacional de Vigilância Sanitária (ANVISA); Resolução RE nº 41, 2011.

Aksglaede, L.; Juul, A.; Leffers, H.; Skakkebaek, N. E.; Andersson, A. M. (2006) - The sensitivity of the child to sex steroids: possible impact of exogenous estrogens. *Human Reproduction Update*, 12(4):341-349. DOI:10.1093/humupd/dml018

Ammann, A. A.; Macikova, P.; Groh, K. J.; Schirmer, K.; Suter, M. J. F. (2014) - LC-MS/MS determination of potential endocrine disruptors of cortico signalling in rivers and wastewaters. *Analytical and Bioanalytical Chemistry*, 406(29):7653–7665. DOI: 10.1007/s00216-014-8206-9

Anezaki, K.; Nakano, T. (2015) - Unintentional PCB in chlorophenylsilanes as a source of contamination in environmental samples. *Journal of Hazardous Materials*, *287*:111–7. DOI:10.1016/j.jhazmat.2015.01.026

Antizar-Ladislao, B. (2009) - Polycyclic aromatic hydrocarbons, polychlorinated biphenyls, phthalates and organotins in northern Atlantic Spain's coastal marine sediments. *Journal of Environmental Monitoring*, 11(1):85-91. DOI: 10.1039/b808668k

Anumol, T.; Snyder, S. A. (2015) - Rapid analysis of trace organic compounds in water by automated online solid-phase extraction coupled to liquid chromatography–tandem mass spectrometry. *Talanta*, 132: 77–86. DOI:10.1016/j.talanta.2014.08.011

Arditsoglou, A.; Voutsa, D. (2008a) - Determination of Phenolic and Steroid Endocrine Disrupting Compounds in Environmental Matrices. *Environmental Science and Pollution Research*, 15(3):228-236. DOI: 10.1065/espr2007.12.459

Arditsoglou, A., Voutsa, D. (2008b) - Passive sampling of selected endocrine disrupting compounds using polar organic chemical integrative samplers. *Environmental Pollution*, 156:316–324. DOI:10.1016/j.envpol.2008.02.007

Arditsoglou, A.; Voutsa, D. (2012) - Occurrence and partitioning of endocrine-disrupting compounds in the marine environment of Thermaikos Gulf, Northern Aegean Sea, Greece. *Marine Pollution Bulletin*, 64(11):2443-2452. DOI: 10.1016/j.marpolbul.2012.07.048

Assunção, J. V. de; Pesquero, C. R. (1999) - Dioxinas e furanos: origens e riscos. *Revista de Saúde Pública*, 33(5):523-530. DOI: 10.1590/S0034-89101999000500014

Bach, C.; Dauchy, X.; Chagnon, M.-C.; Etienne, S. (2012) - Chemical compounds and toxicological assessments of drinking water stored in polyethylene terephthalate (PET) bottles: A source of controversy reviewed. *Water Research*, 46(3):571-583. DOI:10.1016/j.watres.2011.11.062

Bartolomé, L.; Etxebarria, N.; Martínez-Arkarazo, I.; Raposo, J. C.; Usobiaga, A.; Zuloaga, O.; Raingerard, D.; Ortiz-Zarragoitia, M.; Cajaraville, M. P. (2010) - Distribution of organic microcontaminants, butyltins, amd metals in mussels from the estuary of Bilbao. *Archives of Environmental Contamination and Toxicology,* 59:244-254. DOI: 10.1007/s00244-009-9458-9

Basheer, C.; Lee, H. K.; Tan, K. S. (2004) - Endocrine disrupting alkylphenols and bisphenol-A in coastal waters and supermarket seafood from Singapore. *Marine Pollution Bulletin*, 48 (11-12):1161-1167. DOI: 10.1016/j.marpolbul.2004.04.009

Bayat, J.; Hashemi, S. H.; Khoshbakht, K.; Deihimfard, R.; Shahbazi, A.; Momeni-Vesalian, R. (2015). Monitoring of polycyclic aromatic hydrocarbons on agricultural lands surrounding Tehran oil refinery. *Environmental Monitoring and Assessment*, *187*(7):451. DOI:10.1007/s10661-015-4646-8

Beausse, J. (2004) - Selected drugs in solid matrices: A review of environmental determination, occurrence and properties of principal substances. *Trends in Analytical Chemistry*, 23:753-761. DOI:10.1016/j.trac.2004.08.005

Beck, I.-C.; Bruhn, R.; Gandrass, J.; Ruck, W. (2005) - Liquid chromatography–tandem mass spectrometry analysis of estrogenic compounds in coastal surface water of the Baltic Sea. *Journal of Chromatography A*, 1090(1-2):98-106. DOI: 10.1016/j.chroma.2005.07.013

Bedia, C.; Dalmau, N.; Jaumot, J.; Tauler, R. (2015) - Phenotypic malignant changes and untargeted lipidomic analysis of long-term exposed prostate cancer cells to endocrine disruptors. *Environmental Research*, 140:18–31. DOI:10.1016/j.envres.2015.03.014

Behera, S. K.; Kim, H. W.; Oh, J.-E.; Park, H.-S. (2011) - Occurrence and removal of antibiotics, hormones and several other pharmaceuticals in wastewater treatment plants of the largest industrial city of Korea. *Science of the Total Environment*, 409(20):4351-4360. DOI:10.1016/j.scitotenv.2011.07.015

Belfroid, A. C.; Van der Horst, A.; Vethaak, A. D.; Schäfer, A. J.; Rijs, G. B.; Wegener, J.; Cofino, W. P. (1999) - Analysis and occurrence of estrogenic hormones and their glucuronides in surface water and waste water in The Netherlands. *Science of the Total Environment*, 225(1-2):101-108. DOI: 10.1016/S0048-9697(98)00336-2

Benjamin, S.; Pradeep, S.; Josh, M. S.; Kumar, S. (2015) - A monograph on the remediation of hazardous phthalates. *Journal of Hazardous Materials,* 298:58-72. DOI: 10.1016/j.jhazmat.2015.05.004

Bergé, A.; Gasperi, J.; Rocher, V.; Gras, L.; Coursimault, A.; Moilleron, R. (2014). Phthalates and alkylphenols in industrial and domestic effluents: case of Paris conurbation (France). *The Science of the Total Environment*, *488-489*(2014):26–35. DOI:10.1016/j.scitotenv.2014.04.081

Bertin, A.; Inostroza, P. A.; Quiñones, R. A. (2011) - Estrogen pollution in a highly productive ecosystem off central-south Chile. *Marine Pollution Bulletin*, 62 (7):1530-1537. DOI:10.1016/j.marpolbul.2011.04.002

Bhandari, A.; Surampalli, R. Y.; Adams, C. D.; Champagne, P.; Ong, S. K.; Tyagi, R. D.; Zhang, T. C. (2009) - Contaminants of Emerging Environmental Concern. 496p., American Society of Civil Engineers; Reston: Virginia, USA. ISBN: 0784472661, 9780784472668.

Bian, H.; Li, Z.; Liu, P.; Pan, J. (2010) - Spatial distribution and deposition history of nonylphenol and bisphenol A in sediments from the Changjiang River (Yangtze River) Estuary and its adjacent East China Sea. *Acta Oceanologica Sinica*, 29(5):44-51. DOI: 10.1007/s13131-010-0062-7

Birch, G. F.; Drage, D. S.; Thompson, K.; Eaglesham, G.; Mueller, J. F. (2015). Emerging contaminants (pharmaceuticals, personal care products, a food additive and pesticides) in waters of Sydney estuary, Australia. Marine Pollution Bulletin, 97(1-2):56–66. DOI: 10.1016/j.marpolbul.2015.06.038

Birkett, J. W.; Lester, J. N. (2003) - Endocrine Disrupters in Wastewater and Sludge Treatment Processes. 285p., CRC Press LLC: Londres, Inglaterra. ISBN: 9781566706018 - CAT# L1601

Boisen, K. A.; Chellakooty, M.; Schmidt, I. M.; Kai, C. M.; Damgaard, I. N.; Suomi, A.-M.; Toppari, J.; Skakkebaek, N. E.; Main, K. M. (2005) - Hypospadias in a Cohort of 1072 Danish Newborn Boys: Prevalence and Relationship to Placental Weight, Anthropometrical Measurements at Birth, and Reproductive Hormone Levels at Three Months of Age. *The Journal of Clinical Endocrinology & Metabolism*, 90(7):4041-4046. DOI: 10.1210/jc.2005-0302

Boitsov, S.; Mjøs, S. A.; Meier, S. (2007) - Identification of estrogen-like alkylphenols in produced water from offshore oil installations. *Marine Environmental Research*, 64(5):651-665. DOI:10.1016/j.marenvres.2007.07.001

Bossio, J. P.; Harry, J.; Kinney, C. (2008) - Application of ultrasonic assisted extraction of chemically diverse organic compounds from soils and sediments. *Chemosphere*, 70(5):858-864. DOI:10.1016/j.chemosphere.2007.06.088

Bouzas, A.; Aguado, D.; Martí, N.; Pastor, J. M.; Herráez, R.; Campins, P.; Seco, A. (2011) - Alkylphenols and polycyclic aromatic hydrocarbons in eastern Mediterranean Spanish coastal marine bivalves. *Environmental Monitoring and Assessment,* 176:169-181. DOI: 10.1007/s10661-010-1574-5

Bovee, T. F. H.; Helsdingen, R. J. R.; Rietjens, I. M. C. M.; Keijer, J.; Hoogenboom, R. L. A. P. (2004) - Rapid yeast estrogen bioassays stably expressing human estrogen receptors α and β, and green fluorescent protein: a comparison of different compounds with both receptor types. *Journal of Steroid Biochemistry & Molecular Biology*, 91(3):99-109. DOI: 10.1016/j.jsbmb.2004.03.118

Bowman, J. C.; Readman, J. W.; Zhou, J. L. (2003) - Sorptionof the natural endocrine disruptors, oestrone and 17β-oestradiol in the

aquatic environment. *Environmental Geochemistry and Health,* 2, 25(1):63-67. DOI: 10.1023/A:1021296831175

Boyle, A. W.; Silvin, C. J.; Hassett, J. P.; Nakas, J. P.; Tanenbaum, S. W. (1992) - Bacterial PCB biodegradation. *Biodegradation*, 3(2):285-298. DOI: 10.1007/BF00129089

Braga, O.; Smythe, G.; Schäfer, I.; Feitz, J. (2005) - Steroid estrogens in ocean sediments. *Chemosphere*, 61(6) 827-833. DOI: 10.1016/j.chemosphere.2005.04.053

Bulayeva, N. N.; Watson, C. S. (2004) - Xenoestrogen-Induced ERK-1 and ERK-2 Activation via Multiple Membrane-Initiated Signaling Pathways. *Environmental Health Perspectives*, 112(15):1481-1487. DOI: 10.1289/ehp.7175

Buttke, D. E.; Sircar, K.; Martin, C. (2012) - Exposures to Endocrine-Disrupting Chemicals and Age of Menarche in Adolescent Girls in NHANES (2003 – 2008). *Environmental Health Perspectives*, 120(11):1613. DOI: 10.1289/ehp.1104748

Cai, M.; Yang, H.; Xie, Z.; Zhao, Z.; Wang, F.; Lu, Z.; Sturm, R.; Ebinghaus, R. (2012a) - Per- and polyfluoroalkyl substances in snow, lake, surface runoff water and coastal seawater in Fildes Peninsula, King George Island, Antarctica. *Journal of Hazardous Materials,* 209-210:335–342. DOI:10.1016/j.jhazmat.2012.01.030

Cai, M.; Zhao, Z.; Yang, H.; Yin, Z.; Hong, Q.; Sturm, R.; Ebinghaus, R.; Ahrens, L.; Cai, M.; He, J.; Xie, Z. (2012b) - Spatial distribution of per- and polyfluoroalkyl compounds in coastal waters from the East to South China Sea. *Environmental Pollution,* 161:162–169. DOI:10.1016/j.envpol.2011.09.045

Carpenter, D. O. (2006) - Polychlorinated Biphenyls (PCBs): Routes of Exposure and Effects on Human Health. *Reviews on Environmental Health*, 21(1):1-23. DOI: 10.1515/REVEH.2006.21.1.1

Casatta, N.; Mascolo, G.; Roscioli, C.; Vigano, L. (2015) - Tracing endocrine disrupting chemicals in a coastal lagoon (Sacca di Goro, Italy): Sediment contamination and bioaccumulation in Manila clams. *Science of the Total Environment,* 511:214-222. DOI: 10.1016/j.scitotenv.2014.12.051

Čeh, K.; Majdič, G. (2010) - Pesticides as endocrine disruptors. Slovenian Veterinary Research, 47, 163. ISSN 1580-4003. Ljubljana, Slovenia. Available: http://www.slovetres.si/index.php/SVR/issue/viewIssue/24/20

Cheng, C.-Y.; Liu, L.-L.; Ding, W.-H. (2006) - Occurrence and seasonal variation of alkylphenols in marine organisms from the coast of Taiwan. *Chemosphere*, 65(11):2152-2159. DOI:10.1016/j.chemosphere.2006.06.017

Cheng, Z.; Nie, X.P.; Wang, H. P.; Wong, M. H. (2013) - Risk assessments of human exposure to bioaccessible phthalate esters through market fish consumption. *Environment International*, 57-58, 75-80. DOI: 10.1016/j.envint.2013.04.005.

Christiansen, S.; Kortenkamp, A.; Axelstad, M.; Boberg, J.; Scholze, M.; Jacobsen, P. R.; Faust, M.; Lichtensteiger, W.; Schlumpf, M.; Burdorf, A.; Hass, U. (2012) - Mixtures of endocrine disrupting contaminants modelled on human high end exposures: an exploratory study in rats. *International journal of andrology*, 35(3):303-316. DOI: 10.1111/j.1365-2605.2011.01242.x

Clapauch, R.; Meirelles, R. M. R.; Julião, M. A. S. G.; Loureiro, C. K. C.; Giarodoli, P. B.; Pinheiro, S. A.; Harrigan, A. R.; Spritzer, P. M.; Pardini, D. P.; Weiss, R. V.; Athayde, A.; Russo, L. A.; Póvoa, L. C. (2002) - Fitoestrogênios: Posicionamento do departamento de endocrinologia feminina da sociedade brasileira de endocrinologia e metabologia (SBEM). *Arquivos Brasileiros de Endocrinologia e Metabologia*, 46(6):679-695. DOI: 10.1590/S0004-27302002000600013

Colin, N.; Porte, C.; Fernandes, D.; Barata, C.; Padrós, F.; Carrassón. M.; Monroy, M.; Cano-Rocabayera, O.; Sostoa, A.; Piña, B.; Maceda-Veiga, A. (2016) - Ecological relevance of biomarkers in monitoring studies of macro-vertebrates and fish in Mediterranean rivers. *Science of the Total Environment*, 540:307-323. DOI: 10.1016/j.scitotenv.2015.06.099

Colón, I.; Doris, C.; Bourdony, C. J.; Rosario, O. (2000) - Identification of pthalate esters in girls with premature breast development. *Environmental Health Perspectives*, 108(9):895-900. DOI: 10.1289/ehp.00108895

Cunha, B. B.; Botero, W. G.; Oliveira, L. C.; Carlos, V. M.; Pompêo, M. L. M.; Fraceto, L. F.; Rosa, A. H. (2012) - Kinetics and Adsorption Isotherms of Bisphenol A, Estrone, 17β-Estradiol, and 17α-Ethinylestradiol in Tropical Sediment Samples. Water, Air, & Soil Pollution, 223(1):329-336. DOI: 10.1007/s11270-011-0861-2

D'Ascenzo, G.; Di Corcia, A.; Gentili, A.; Mancini, R.; Mastropasqua, R.; Nazzari, M.; Samperi, R. (2003) - Fate of natural estrogen conjugates in municipal sewage transport and treatment facilities. Science of the Total Environment, 302(1-3):199-209. DOI: 10.1016/S0048-9697(02)00342-X

Da Rocha, G. O.; Lopes, W. A.; Pereira, P. A. D. P.; Vasconcellos, P. de C.; Oliveira, F. S.; Carvalho, L. S.; Conceição, L. dos S.; Andrade, J. B. D. (2009) - Quantification and Source Identification of Atmospheric Particulate Polycyclic Aromatic Hydrocarbons and their Dry Deposition Fluxes at Three Sites in Salvador Basin, Brazil, Impacted by Mobile and Stationary Sources. *Journal of the Brazilian Chemical Society*, 20(4):680-692. DOI: 10.1590/S0103-50532009000400012

Dargnat, C.; Teil, M.-J.; Chevreuil, M.; Blanchard, M. (2009) - Phthalate removal throughout wastewater treatment plant Case study of Marne Aval station (France). *Science of the Total Environment*, 407(4):1235-1244. DOI: 10.1016/j.scitotenv.2008.10.027.

Darnerud, P. O. (2008) - Brominated flame retardants as possible endocrine disrupters. International journal of andrology, 31(2):152-160. DOI: 10.1111/j.1365-2605.2008.00869.x.

David, A.; Fenet, H.; Gomez, E. (2009) - Alkylphenols in marine environments: Distribution monitoring strategies and detection considerations. Marine Pollution Bulletin, 58(7):953-960. DOI:10.1016/j.marpolbul.2009.04.021

De la Cruz, N.; Giménez, J.; Esplugas, S.; Grandjean, D.; de Alencastro, L. F.; Pulgarín, C. (2012) - Degradation of 32 emergent contaminants by UV and neutral photo-fenton in domestic wastewater effluent previously treated by activated sludge. *Water research*, 46(6):1947-1957. DOI: 10.1016/j.watres.2012.01.014

De los Ríos, A.; Juanes, J.; Ortiz-Zarragoitia, M.; López de Alda, M.; Barceló, D.; Cajaraville, M. P. (2012) - Assessment of the effects of a marine urban outfall discharge on caged mussels using chemical and biomarker analysis. *Marine Pollution Bulletin*, 64(3):563-573. DOI:10.1016/j.marpolbul.2011.12.018

Deblonde, T.; Cossu-leguille, C.; Hartemann, P. (2011) - Emerging pollutants in wastewater : A review of the literature. *The International Journal of Hygiene and Environmental Health*, 214:442–448. DOI:10.1016/j.ijheh.2011.08.002

Dévier, M.-H., Labadie, P., Togola, A., Budzinski, H. (2010). Simple methodology coupling microwave-assisted extraction to SPE/GC/MS for the analysis of natural steroids in biological tissues:

application to the monitoring of endogenous steroids in marine mussels Mytilus sp. Analytica Chimica Acta, 657(1):28–35. DOI: 10.1016/j.aca.2009.10.023

Diamanti-Kandarakis, E.; Bourguignon, J.-P.; Giudice, L. C.; Hauser, R.; Prins, G. S.; Soto, A. M.; Zoeller, R. T.; Gore, A. C. (2009) - Endocrine-Disrupting Chemicals: An Endocrine Society Scientific Statement. *Endocrine Reviews*, 30(4): 293-342. DOI: 10.1210/er.2009-0002

Diehl, J.; Johnson, S. E.; Xia, K.; West, A.; Tomanek, L. (2012) - The distribution of 4-nonylphenol in marine organisms of North American Pacific Coast estuaries. *Chemosphere*, 87(5):490-497. DOI:10.1016/j.chemosphere.2011.12.040

Dodds, E. C.; Lawson, W. (1936) - Synthetic OEstrogenic Agents without the Phenanthrene Nucleus. *Nature*, 137(3476): 996. DOI: 10.1038/137996a0

Dodds, E. C.; Lawson, W. (1938) - Molecular Structure in Relation to Oestrogenic Activity. Compounds without a Phenanthrene Nucleus. *Proceedings of the Royal Society B*, 125(839):222-232. DOI: 10.1098/rspb.1938.0023

Duan, X.; Li, Y.; Li, X.; Zhang, D.; Gao, Y. (2014) - Alkylphenols in surface sediments of the Yellow Sea and East China Sea inner shelf: Occurrence, distribution and fate. *Chemosphere*, 107: 265–273. DOI: 10.1016/j.chemosphere.2013.12.054

Dzieweczynski, T. L.; Buckman, M. C. (2013) - Acute exposure to 17α-ethinylestradiol disrupts audience effects on male–male interactions in Siamese fighting fish, Betta splendens. *Hormones and Behavior*, 63(3):497-502. DOI: 10.1016/j.yhbeh.2013.01.002

Ebinghaus, R.; Xie, Z. (2006) - Occurrence and air sea-exchange of novel organic pollutants in the marine environment. *Journal de Physique IV*, 139:211-237 DOI: 10.1051/jp4:2006139016

Emnet, P., Gaw, S., Northcott, G., Storey, B., Graham, L. (2015). Personal care products and steroid hormones in the Antarctic coastal environment associated with two Antarctic research stations, McMurdo Station and Scott Base. Environmental Research, 136:331–342. http://doi.org/10.1016/j.envres.2014.10.019

EPA (1997) - Special Report on Environmental Endocrine Disruption: An Effects Assessment and Analysis. Environmental Protection Agency, US EPA/630/R-96/012, February 1997.

Eriksson, P.; Jakobsson, E.; Fredriksson, A. (2001) - Brominated Flame Retardants: A Novel Class of Developmental Neurotoxicants in Our Environment? *Environmental Health Perspectives*, 109(9):903-908. DOI: 10.1289/ehp.01109903

Esteban, S.; Moreno-Merino, L.; Matellanes, R.; Catalá, M.; Gorga, M.; Petrovic, M.; Lopez de Alda, M.; Barceló, D.; Silva, A.; Duran, J. J.;Lopez-Martinez, J.; Valcarcel, Y. (2016) - Presence of endocrine disruptors in freshwater in the northern Antarctic Peninsula region. *Environmental Research*, 147:179-192. DOI: 10.1016/j.envres.2016.01.034.

Farajzadeh, M. A.; Nouri, N.; Khorram, P. (2014) - Derivatization and microextraction methods for determination of organic compounds by gas chromatography. *Trends in Analytical Chemistry*, 55:14-23. DOI: 10.1016/j.trac.2013.11.006

Farré, M.; Kantiani, L.; Petrovic, M.; Pérez, S.; Barceló, D. (2012) - Achievements and future trends in the analysis of emerging organic contaminants in environmental samples by mass spectrometry and bioanalytical techniques. *Journal of Chromatography A*, 1259:86-99. DOI: 10.1016/j.chroma.2012.07.024

Farré, M.; Pérez, S.; Gonçalves, C.; Alpendurada, M. F.; Barceló, D. (2010) - Green analytical chemistry in the determination of organic pollutants in the aquatic environment. *Trends in Analytical Chemistry*, 29(11):1347-1362. DOI: 10.1016/j.trac.2010.07.016

Fasano, E.; Bono-Blay, F.; Cirillo, T.; Montuori, P.; Lacorte, S. (2012) - Migration of phthalates, alkylphenols, bisphenol A and di(2-ethylhexyl)adipate from food packaging. *Food Control*, 27(1): 132-138. DOI: 10.1016/j.foodcont.2012.03.005

Fatoki, O. S.; Noma, A. (2001) - Determination of Phthalate Esters in the Aquatic Environment. *South African Journal of Chemistry*, 54: 69-83. ISSN: 0379-4350, South African. Available: http://reference.sabinet.co.za/webx/access/electronic_journals/chem/chem_v54_a4.pdf

Ferguson, P. L.; Iden, C. R.; Brownawell, B. J. (2000) - Analysis of alkylphenol ethoxylate metabolites in the aquatic environment using liquid chromatography-electrospray mass spectrometry. *Analytical Chemistry*, 72(18):4322–4330. DOI: 10.1021/ac000342n

Ferguson, P. L.; Iden, C. R.; Brownawell, B. J. (2001) - Distribution and Fate of Neutral Alkylphenol Ethoxylate Metabolites in a Sewage-Impacted Urban Estuary. *Environmental Science & Technology*, 35(12):2428-2435. DOI: 10.1021/es001871b

Ferrara, F.; Ademollo, N.; Delise, M.; Fabietti, F.; Funari, E. (2008) - Alkylphenols and their ethoxylates in seafood from the Tyrrhenian Sea. *Chemosphere*, 72(9):1279–1285. DOI: 10.1016/j.chemosphere.2008.04.060

Fisher, M. M.; Eugster, E. A. (2014) - What is in our environment that effects puberty? *Reproductive Toxicology*, 44:7-14. DOI: 10.1016/j.reprotox.2013.03.012.

Foster, P. M. D. (2006) - Disruption of reproductive development in male rat offspring following in utero exposure to phthalate esters. *International Journal of Andrology*, 29(1):140–147. DOI:10.1111/j.1365-2605.2005.00563.x

Foster, P. M.; Mylchreest, E.; Gaido, K. W.; Sar, M. (2001) - Effects of phthalate esters on the developing reproductive tract of male rats. *Human Reproduction Update*, 7:231–235. DOI: 10.1093/humupd/7.3.231

Fromme, H.; Teitelbaum, S. L.; Pinney, S. M.; Windham, G.; Liao, L.; Biro, F.; Kushi, L. H.; Erdmann, C.; Hiatt, R. A.; Rybak, M. E.; Calafat, A. M. (2002) - Occurrence of phthalates and bisphenol A and F in the environment. *Water Research*, 36(6):1429–1438. DOI: 10.1016/S0043-1354(01)00367-0

Frye, C. A.; Bo, E.; Calamandrei, G.; Calzà, L.; Dessì-fulgheri, F.; Fernández, M.; Fusani, L.; Kah, O.; Kajta, M.; Le Page, Y.; Patisaul, H. B.; Venerosi, A.; Wojtowicz, A. K.; Panzica, G. C. (2011) -Endocrine disrupters: a review of some sources, effects, and mechanisms of actions on behaviour and neuroendocrine systems. *Journal of Neuroendocrinology*, 24(1):144–159. DOI: 10.1111/j.1365-2826.2011.02229.x

Fu, M.; Li, Z.; Gao, H. (2007) - Distribution characteristics of nonylphenol in Jiaozhou Bay of Qingdao and its adjacent rivers. *Chemosphere*, 69(7):1009–1016. DOI: 10.1016/j.chemosphere.2007.04.061

Funakoshi, G.; Kasuya, S. (2009) - Influence of an estuary dam on the dynamics of bisphenol A and alkylphenols. *Chemosphere*, 75(4):491–497. DOI: 10.1016/j.chemosphere.2008.12.050.

Gagné, F.; Blaise, C.; Pellerin, J.; Gauthier-Clerc, S. (2002) - Alteration of the biochemical properties of female gonads and vitellins in the clam Mya arenaria at contaminated sites in the Saguenay Fjord. *Marine Environmental Research*, 53(3):295–310. DOI: 10.1016/S0141-1136(01)00122-2

Garcia-Jares, C.; Regueiro, J.; Barro, R.; Dagnac, T.; Llompart,

M. (2009) - Analysis of industrial contaminants in indoor air. Part 2. Emergent contaminants and pesticides. *Journal of Chromatography A*,1216(3):567–597. DOI: 10.1016/j.chroma.2008.10.020

Gärtner, S.; Balski, M.; Koch, M.; Nehls, I. (2009) - Analysis and migration of phthalates in infant food packed in recycled paperboard. *Journal of Agricultural and Food Chemistry*, 57(22):10675–10681. DOI: 10.1021/jf902683m

Gavala, H. N.; Alatriste-Mondragon, F.; Iranpour, R.; Ahring, B. K. (2003) - Biodegradation of phthalate esters during the mesophilic anaerobic digestion of sludge. *Chemosphere*, 52(10):673–682. DOI: 10.1016/S0045-6535(03)00126-7

Gavrilescu, M.; Demnerová, K.; Aamand, J.; Agathos, S.; Fava, F. (2015) - Emerging pollutants in the environment: Present and future challenges in biomonitoring, ecological risks and bioremediation. *New Biotechnology*, 32:147–156. DOI:10.1016/j.nbt.2014.01.001

Gereckea, A. C.; Schmid, P.; Bogdal, C.; Kohler, M.; Zennegg, M.; Heeb, N. V. (2008) - Brominated Flame Retardants – Endocrine-Disrupting Chemicals in the Swiss Environment. *Chimia*, 62(6):352-357. DOI: 10.2533/chimia.2008.352

Ghiselli, G.; Jardim, W. F. (2007) - Interferentes endócrinos no ambiente. *Quimíca Nova*, 30(3):695-706. DOI: 10.1590/S0100-40422007000300032

Gómez-Hens, A.; Aguilar-Caballos, M. (2003) - Social and economic interest in the control of phthalic acid esters. *Trends in Analytical Chemistry*, 22(11):847–857. DOI: 10.1016/S0165-9936(03)01201-9

Grassi, M.; Rizzo, L.; Farina, A. (2013) - Endocrine disruptors compounds, pharmaceuticals and personal care products in urban wastewater: implications for agricultural reuse and their removal by adsorption process. *Environmental Science and Pollution Research*, 20(6):3616- 3628. DOI: 10.1007/s11356-013-1636-7.

Gray, L. E.; Wilson, V. S.; Stoker, T.; Lambright, C.; Furr, J.; Noriega, N.; Howdeshell, K.; Ankley, G. T.; Guillette, L. (2006) - Adverse effects of environmental antiandrogens and androgens on reproductive development in mammals. *International Journal of Andrology*, 29(1):96-104. DOI: 10.1111/j.1365-2605.2005.00636.x

Grigoriadou, A.; Schwarzbauer, J.; Georgakopoulos, A. (2008) - Molecular indicators for pollution source identification in marine and terrestrial water of the industrial area of Kavala city, North Greece. *Environmental Pollution*, 151(1):231–242. DOI: 10.1016/j.envpol.2007.01.053

Grist, E. P. M.; Wells, N. C.; Whitehouse, P.; Brighty, G.; Crane, M. (2003) - Estimating the effects of 17alpha-ethinylestradiol on populations of the fathead minnow Pimephales promelas: are conventional toxicological endpoints adequate? *Environmental Science & Technology*, 37(8):1609–1616. DOI: 10.1021/es020086r

Gu, Y.; Yu, J.; Hu, X.; Yin, D. (2016) - Characteristics of the alkylphenol and bisphenol A distributions in marine organisms and implications for human health: A case study of the East China Sea. *Science of the Total Environment*, 539:460-469. DOI: 10.1016/j.scitotenv.2015.09.011.

Hampl, R.; Kubátová, J.; Stárka, L. (2016) - Steroids and endocrine disruptors—History, recent state of art and open questions. *The Journal of Steroid Biochemistry and Molecular Biology*, 155(Part B): 217-223. DOI: 10.1016/j.jsbmb.2014.04.013.

Hashimoto, S.; Ueda, Y.; Kurihara, R.; Shiraishi, F. (2007) - Comparison of the estrogenic activities of seawater extracts from Suruga Bay, Japan, based on chemical analysis or bioassay. *Environmental Toxicology and Chemistry*, 26(2):279–286. DOI: 10.1897/05-689R1.1

Hashimoto, Y.; Kawaguchi, M.; Miyazaki, K.; Nakamura, M. (2003) - Estrogenic activity of tissue conditioners in vitro. *Dental Materials*, 19(4):341-346. DOI:10.1016/S0109-5641(02)00064-7

Hassanzadeh, N.; Esmaili Sari, A.; Khodabandeh, S.; Bahramifar, N. (2014) - Occurrence and distribution of two phthalate esters in the sediments of the Anzali wetlands on the coast of the Caspian Sea (Iran). *Marine Pollution Bulletin*, 89(1-2):128–135. DOI: 10.1016/j.marpolbul.2014.10.017

Heemken, O. P.; Reincke, H.; Stachel, B.; Theobald, N. (2001) - The occurrence of xenoestrogens in the Elbe river and the North Sea. *Chemosphere*, 45(3):245–259. DOI:10.1016/S0045-6535(00)00570-1

Herrera-Herrera, A. V.; Asensio-Ramos, M.; Hernández-Borges, J.; Rodríguez-Delgado, M. Á. (2010) - Dispersive liquid-liquid microextraction for determination of organic analytes. *Trends in Analytical Chemistry*, 29 (7):728-751. DOI: 10.1016/j.trac.2010.03.016

Heudorf, U.; Mersch-Sundermann, V.; Angerer, J. (2007) - Phthalates: toxicology and exposure. *International Journal of Hygiene and Environmental Health*, 210(5):623-634. DOI: 10.1016/j.ijheh.2007.07.011

Hirai, N.; Nanba, A.; Koshio, M.; Kondo, T.; Morita, M.; Tatarazako, N. (2006) - Feminization of Japanese medaka (Oryzias latipes) exposed to 17 beta-estradiol: Effect of exposure period on spawning performance in sex-transformed females. *Aquatic Toxicology*, 79(3):288–295. DOI: 10.1016/j.aquatox.2006.06.018

Horn, O.; Nalli, S.; Cooper, D.; Nicell, J. (2004) - Plasticizer metabolites in the environment. *Water Research*, 38(17):3693–3698. DOI: 10.1016/j.watres.2004.06.012

Hotta, Y.; Hosoda, A.; Sano, F.; Wakayama, M.; Niwa, K.; Yoshikawa, H.; Tamura, H. (2010) - Ecotoxicity by the biodegradation of alkylphenol polyethoxylates depends on the effect of trace elements. Journal of Agricultural and Food Chemistry, 58(2):1062–1067. DOI: 10.1021/jf902772m

Huerta, B., Jakimska, A., Llorca, M., Ruhí, A., Margoutidis, G., Acuña, V., Sabater, S. (2015). Development of an extraction and purification method for the determination of multi-class pharmaceuticals and endocrine disruptors in freshwater invertebrates, Talanta, 132:373–381. DOI: 10.1016/j.talanta.2014.09.017

Huerta, B., Rodriguez-Mozaz, S., Nannou, C., Nakis, L., Ruhí, A., Acuña, V., Sabater, S., Barcelo, D. (2016). Determination of a broad spectrum of pharmaceuticals and endocrine disruptors in biofilm from a waste water treatment plant-impacted river. Science of the Total Environment, 540, 241–249. DOI: 10.1016/j.scitotenv.2015.05.049

Huyghe, E., Matsuda, T.; Thonneau, P. (2003) - Increasing incidence of testicular cancer worldwide: a review. *Journal of Urology*, 170(1):5–11. DOI: 10.1097/01.ju.0000053866.68623.da

Hwang, C. S.; Kwak, H. S.; Lim, H. J.; Lee, S. H.; Kang, Y. S.; Choe, T. B.; Hur, H. G.; Han, K. O. (2006) - Isoflavone metabolites and their in vitro dual functions: they can act as an estrogenic agonist or antagonist depending on the estrogen concentration. *The Journal of Steroid Biochemistry and Molecular Biology*, 101(4-5):246–253. DOI: 10.1016/j.jsbmb.2006.06.020

Isidori, M.; Lavorgna, M.; Nardelli, A.; Parrella, A. (2006) -

Toxicity on crustaceans and endocrine disrupting activity on Saccharomyces cerevisiae of eight alkylphenols. *Chemosphere*, 64(1):135-143. DOI: 10.1016/j.chemosphere.2005.10.047

Isobe, T.; Nishiyama, H.; Nakashima, A.; Takada, H. (2001) - Distribution and behavior of nonylphenol, octylphenol, and nonylphenol monoethoxylate in Tokyo metropolitan area: their association with aquatic particles and sedimentary distributions. *Environmental Science & Technology*, 35(6):1041–1049. DOI: 10.1021/es001250i

Isobe, T.; Serizawa, S.; Horiguchi, T.; Shibata, Y.; Managaki, S.; Takada, H.; Morita, M.; Shiraishi, H. (2006) - Horizontal distribution of steroid estrogens in surface sediments in Tokyo Bay. *Environmental Pollution*, 144(2):632–638. DOI:10.1016/j.envpol.2006.01.030

Isobe, T.; Takada, H.; Kanai, M. (2007) - Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) and phenolic endocrine disrupting chemicals in South and Southeast Asian mussels. *Environmental Monitoring and Assessment*, 135:423–440. DOI 10.1007/s10661-007-9661-y

Isolbe, T.; Takada, H.; Kanai, M.; Tsutsumi, S.; Isolbe, K. O.; Boonyatumanond, R.; Zakaria M. P. (2007) - Distribution of polycyclic aromatic hydrocarbons (PAHs) and phenolic endocrine disrupting chemicals in South and Southeast Asian mussels. *Environmental Monitoring and Assessment*, 135:423-440. DOI: 10.1007/s10661-007-9661-y

Jakimska, A.; Huerta, B.; Barganska, Z.; Kot-Wasik, A.; Rodríguez-Mozaz, S.; Barceló, D. (2013) - Development of a liquid chromatography–tandem mass spectrometry procedure for determination of endocrine disrupting compounds in fish from Mediterranean rivers. *Journal of Chromatography A*, 1306:44–58. DOI:10.1016/j.chroma.2013.07.050

Jardim, W. F.; Montagner, C. C.; Pescara, I. C.; Umbuzeiro, G. a.; Di Dea Bergamasco, A. M.; Eldridge, M. L.; Sodré, F. F. (2012) - An integrated approach to evaluate emerging contaminants in drinking water. *Separation and Purification Technology*, 84:3-8. DOI: 10.1016/j.seppur.2011.06.020

Johnson, A. C.; Williams, R. J. (2004) - A model to estimate influent and effluent concentrations of estradiol, estrone, and ethinylestradiol at sewage treatment works. *Environmental Science & Technology*, 38(13):3649–3658. DOI: 10.1021/es035342u

Jonkers, N.; Laane, R. W. P. M.; De Voogt, P. (2003) - Fate of nonylphenol ethoxylates and their metabolites in two Dutch estuaries: evidence of biodegradation in the field. *Environmental Science & Technology*, 37(2):321–327. DOI: 10.1021/es020121u

Jonkers, N.; Sousa, A.; Galante-Oliveira, S.; Barroso, C. M.; Kohler, H.-P. E.; Giger, W. (2010) - Occurrence and sources of selected phenolic endocrine disruptors in Ria de Aveiro, Portugal. *Environmental Science and Pollution Research*, 17(4):834–843. DOI: 10.1007/s11356-009-0275-5

Jouannet, P.; Wang, C.; Eustache, F.; Kold-Jensen, T.; Auger, J. (2001) - Semen quality and male reproductive health : the controversy about human sperm concentration decline. *Acta Pathologica Microbiologica et Immunologica Scandinavica*, 109(5):333–344. DOI: 10.1111/j.1600-0463.2001.tb05801.x

Kabir, E. R.; Rhamna, M. S.; Rhanman, I. (2015) - A review on endocrine disruptors and their possible impacts on human health. *Environmental Toxicology and Pharmacolog*, 40:241-258. DOI: 10.1016/j.etap.2015.06.009

Kannan, N.; Yamashita, N.; Petrick, G.; Duinker, J. C. (1998) - Polychlorinated Biphenyls and Nonylphenols in the Sea of Japan. *Environmental Science & Technology*, 32(12):1747–1753. DOI: 10.1021/es970713q

Kardinaal, A. F. M.; Walkens-Berendsen, D. H.; Arts, C. J. M. (1997) - Pseudo-oestrogens in the diet : Health benefits and safety concerns. *Trends in Food Science & Technology*, 8(10):327–333. DOI: 10.1016/S0924-2244(97)01070-4

Kester, M. H. A.; Bulduk, S.; Tirboel, D.; Meinl, W.; Glatt, H.; Falany, C. N.; Coughtrie, M. W. H.; Bergman, A.; Safe, S. H.; Kuiper, G. G. J. M.; Schuur, A.G.; Brouwer, A.; Visser, T. J. (2000) - Potent Inhibition of Estrogen Sulfotransferase by Hydroxylated PCB Metabolites: A Novel Pathway Explaining the Estrogenic Activity of PCBs. *Endocrinology*, 141(5):1897–1900. DOI: 10.1210/endo.141.5.7530

Khim, J. S.; Kannan, K.; Villeneuve, D. L.; Koh, C. H.; Giesy, J. P. (1999) - Characterization and Distribution of Trace Organic Contaminants in Sediment from Masan Bay , Korea: 1. Instrumental Analysis. *Environmental Science & Technology*, 33(23):4199–4205. DOI: 10.1021/es9904484

Kinani, S.; Bouchonnet, S.; Bourcier, S.; Creusot, N. (2008) - Extraction and purification procedures for simultaneous quantification of phenolic xenoestrogens and steroid estrogens in river sediment by gas chromatography/ion trap mass spectrometry. *Rapid Communications in Mass Spectrometry*, 22(22):3651–3661. DOI: 10.1002/rcm.3771

Koh, C.-H.; Khim, J. S.; Villeneuve, D. L.; Kannan, K.; Giesy, J. P. (2006) - Characterization of trace organic contaminants in marine sediment from Yeongil Bay, Korea: 1. *Instrumental Analyses. Environmental Pollution*, 142(1):39–47. DOI: 10.1016/j.envpol.2005.09.005

Koniecko, I.; Staniszewska, M.; Falkowska, L.; Burska, D.; Kielczewska, J.; Jasinska, A. (2014) - Alkylphenols in Surface Sediments of the Gulf of Gdansk (Baltic Sea). *Water Air Soil Pollution*, 225:2040. DOI 10.1007/s11270-014-2040-8

Körner, W.; Hanf, V.; Schuller, W.; Kempter, C.; Metzger, J.; Hagenmaier, H. (1999) - Development of a sensitive E-screen assay for quantitative analysis of estrogenic activity in municipal sewage plant effluents. *Science of the Total Environment*, 225(1-2):33–48. DOI: 10.1016/S0048-9697(99)80015-1

Kumar, K. S.; Sajwan, K. S.; Richardson, J. P.; Kannan, K. (2008) - Contamination profiles of heavy metals, organochlorine pesticides, polycyclic aromatic hydrocarbons and alkylphenols in sediment and oyster collected from marsh/estuarine Savannah GA, USA. *Marine Pollution Bulletin*, 56(1):136–149. DOI: 10.1016/j.marpolbul.2007.08.011

Kurihara, R.; Watanabe, E.; Ueda, Y.; Kakuno, A.; Fujii, K.; Shiraishi, F.; Hashimoto, S. (2007) -Estrogenic activity in sediments contaminated by nonylphenol in Tokyo Bay (Japan) evaluated by vitellogenin induction in male mummichogs (Fundulus heteroclitus). *Marine Pollution Bulletin*, 54(9):1315–1320. DOI:10.1016/j.marpolbul.2007.06.007

Kuster, M.; Azevedo, D. A.; López De Alda, M. J.; Aquino Neto, F. R.; Barceló, D. (2009) - Analysis of phytoestrogens, progestogens and estrogens in environmental waters from Rio de Janeiro (Brazil). *Environment International*, 35(7):997–1003. DOI: 10.1016/j.envint.2009.04.006.

Kuster, M.; José López de Alda, M.; Barceló, D. (2004) - Analysis and distribution of estrogens and progestogens in sewage sludge, soils and sediments. *Trends in Analytical Chemistry*, 23(10–11):790-798. DOI:10.1016/j.trac.2004.08.007.

Labadie, P.; Hill, E. M. (2007) - Analysis of estrogens in river sediments by liquid chromatography–electrospray ionisation

mass spectrometry Comparison of tandem mass spectrometry and time-of-flight mass spectrometry. *Journal of Chromatography A*, 1141(2):174-181. DOI: 10.1016/j.chroma.2006.12.045

Larsen, S. T.; Lund, R. M.; Nielsen, G. D.; Thygesen, P.; Poulsen, O. M. (2002) - Adjuvant effect of di-n-butyl-, di-n-octyl-, di-iso-nonyl- and di-iso-decyl phthalate in a subcutaneous injection model using BALB/c mice. *Pharmacology & Toxicology*, 91(5):264–272. DOI: 10.1034/j.1600-0773.2002.910508.x

Larsson, D. G. J.; Förlin, L. (2002) - Male-biased sex ratios of fish embryos near a pulp mill: temporary recovery after a short-term shutdown. Environmental Health Perspectives, 110(8):739-42. DOI: 10.1289/ehp.02110739

Lathers, C. M.; (2002) - Educational Issues in Clinical Pharmacology: Who Are Our Audiences and What Are TheirSpecialized Needs? One Specialized Need: "Understanding the Role of Veterinary Medicine in Public Health". *The Journal of Clinical Pharmacology*, 42:718-730. DOI: 10.1177/009127002401102669

Laws, S. C.; Carey, S. A.; Ferrell, J. M.; Bodman, G. J.; Cooper, R. L. (2000) - Estrogenic activity of octylphenol, nonylphenol, bisphenol A and methoxychlor in rats. *Toxicological Sciences*, 54(1):154–167. DOI: 10.1093/toxsci/54.1.154

Lee, C.-C.; Jiang, L.-Y.; Kuo, Y.-L.; Chen, C.-Y.; Hsieh, C.-Y.; Hung, C.-F.; Tien, C.-J. (2015) - Characteristics of nonylphenol and bisphenol A accumulation by fish and implications for ecological and human health. *Science of the Total Environment*, 502:417-425. DOI: 10.1016/j.scitotenv.2014.09.042.

Lee, H.-R.; Choi, K.-C. (2013) - 4-tert-Octylphenol stimulates the expression of cathepsins in human breast cancer cells and xenografted breast tumors of a mouse model via an estrogen receptor-mediated signaling pathway. *Toxicology*, 304:13–20. DOI: 10.1016/j.tox.2012.10.012

Legler, J.; Brouwer, A. (2003) - Are brominated flame retardants endocrine disruptors? *Environment International*, 29(6):879–885. DOI:10.1016/S0160-4120(03)00104-1

Li, D.; Dong, M.; Shim, W. J.; Hong, S. H.; Oh, J.-R.; Yim, U. H.; Jeung, J. H.; Kanan, N.; Kim, E. S.; Cho, S. R. (2005) - Seasonal and spatial distribution of nonylphenol and IBP in Saemangeum Bay, Korea. *Marine Pollution Bulletin*, 51(8-12):966–974. DOI: 10.1016/j.marpolbul.2004.11.006

Li, D.; Dong, M.; Shim, W. J.; Yim, U. H.; Hong, S. H.; Kannan, N. (2008) - Distribution characteristics of nonylphenolic chemicals in Masan Bay environments, Korea. *Chemosphere*, 71(6):1162–1172. DOI: 10.1016/j.chemosphere.2007.10.023

Li, W.C. (2014) - Occurrence, sources, and fate of pharmaceuticals in aquatic environment and soil. *Environmental Pollution*, 187C:193–201. DOI:10.1016/j.envpol.2014.01.015

Liang, D.-W.; Zhang, T.; Fang, H. H. P.; He, J. (2008) - Phthalates biodegradation in the environment. *Applied Microbiology and Biotechnology*, 80(2):183–198. DOI: 10.1007/s00253-008-1548-5

Lintelmann, J.; Katayama, A.; Kurihara, N.; Shore, L.; Wenzel, A. (2003) - Endocrine disruptors in the environment (IUPAC Technical Report). *Pure and Applied Chemistry*, 75(5):631–681. DOI: 10.1351/pac200375050631

Lisboa, N. S.; Fahning, C. S.; Cotrim, G.; Anjos, J. P.; Andrade, J. B.; Hatje, V.; Da Rocha, G. O. (2013) - A simple and sensitive UFLC-fluorescence method for endocrine disrupters determination in marine waters. Talanta, 117:168–175. DOI: 10.1016/j.talanta.2013.08.006

Liu, C.; Kolarik, B.; Gunnarsen, L.; Zhang, Y. (2015). C-Depth Method to Determine Diffusion Coefficient and Partition Coefficient of PCB in Building Materials. *Environmental Science & Technology*, *49*(20):12112–9. DOI:10.1021/acs.est.5b03352

Liu, J.; Wang, R. ; Huang, B.; Lin, C.; Zhou, J.; Pan, X. (2012) - Biological effects and bioaccumulation of steroidal and phenolic endocrine disrupting chemicals in high-back crucian carp exposed to wastewater treatment plant effluents. *Environmental Pollution*, 162:325-331. DOI:10.1016/j.envpol.2011.11.036

Locatelli, M., Sciascia, F., Cifelli, R., Malatesta, L., Bruni, P., Croce, F. (2016). Analytical methods for the endocrine disruptor compounds determination in environmental water samples. Journal of Chromatography A, 1434:1–18. DOI: 10.1016/j.chroma.2016.01.034

Loos, R.; Wollgast, J.; Castro-Jiménez, J.; Mariani, G.; Huber, T.; Locoro, G.; Hanke, G.; Umlauf, G.; Bidoglio, G.; Hohenblum, P.; Moche, W.; Weiss, S.; Schmid, H.; Leiendecker, F.; Ternes, T.; Ortega, a. N.; Hildebrandt, A.; Barceló, D.; Lepom, P.; Dimitrova, I.; Nitcheva, O.; Polesello, S.; Valsecchi, S.; Boutrup, S.; Sortkjaer, O.; de Boer, R.; Staeb, J. (2008) - Laboratory intercomparison stud for the analysis of nonylphenol and octylphenol in river water. *Trends in Analytical Chemistry*, 27(1):89-95. DOI: 10.1016/j.trac.2007.10.011

Lu, C. (2009) - Prediction of environmental properties in water-soil-air systems for phthalates. Bulletin of Environmental Contamination and Toxicology, 83(2):168–173. DOI: 10.1007/s00128-009-9728-2

Luzio, A.; Monteiro, S. M.; Rocha, E.; Fontainhas-Fernandes, A. A.; Coimbra, A. M. (2016) - Development and recovery of histopathological alterations in the gonads of zebrafish (*Danio rerio*) after single and combined exposure to endocrine disruptors (17α-ethinilestradiol and fadrozole). *Aquatic Toxicology*, 175:90-105. DOI: 10.1016/j.aquatox.2016.03.014.

Ma, T., Teng, Y., Christie, P., Luo, Y., Chen, Y., Ye, M., Huang, Y. (2013). A new procedure combining GC-MS with accelerated solvent extraction for the analysis of phthalic acid esters in contaminated soils. *Frontiers of Environmental Science & Engineering*, 7(1):31–42. DOI: 10.1007/s11783-012-0463-2

Mackintosh, C. E.; Maldonado, J. A.; Ikonomou, M. G.; Gobas, F. A. P. C. (2006) - Sorption of phthalate esters and PCBs in a marine ecosystem. *Environmental Science & Technology*, 40(11):3481–3488. DOI: 10.1021/es0519637

Macon, M. B.; Fenton, S. E. (2013) - Endocrine Disruptors and the Breast: Early Life Effects and Later Life Disease. *Journal Mammary Gland Biology and Neoplasia*, 18(1):43. DOI: 10.1007/s10911-013-9275-7

Maggioni, S.; Balaguer, P.; Chiozzotto, C.; Benfenati, E. (2013) - Screening of endocrine-disrupting phenols, herbicides, steroid estrogens, and estrogenicity in drinking water from the waterworks of 35 Italian cities and from PET-bottled mineral water. *Environmental Science and Pollution Research International*, 20(3):1649–1660. DOI: 10.1007/s11356-012-1075-x

Main, K. M.; Skakkebaek; N. E., Virtanen, H. E.; Toppari, J. (2010) - Genital anomalies in boys and the environment. Best Practice & Research. *Clinical Endocrinology & Metabolism*, 24(2):279–89. DOI:10.1016/j.beem.2009.10.003

Mandich, A.; Bottero, S.; Benfenati, E.; Cevasco, A.; Erratico, C.; Maggioni, S.; Massari, A.; Pedemonte, F.; Viganò, L (2007) - In vivo exposure of carp to graded concentrations of bisphenol A. *General and Comparative Endocrinology*, *153*(1-3):15–24. DOI:10.1016/j.ygcen.2007.01.004

Mankidy, R.; Ranjan, B.; Honaramooz, A.; Giesy, J. P. (2013a) - Effects of novel brominated flame retardants on steroidogenesis in

primary porcine testicular cells. *Toxicology Letters*, 224(13):141–146. DOI: 10.1016/j.toxlet.2013.10.018

Mankidy, R.; Wiseman, S.; Ma, H.; Giesy, J. P. (2013b) - Biological impact of phthalates. *Toxicology Letters*, 217(1):50–58. DOI: 10.1016/j.toxlet.2012.11.025

Markey, C. M.; Luque, E. H.; Munoz De Toro, M.; Sonnenschein, C.; Soto, A. M. (2001) - In utero exposure to bisphenol A alters the development and tissue organization of the mouse mammary gland. *Biology of Reproduction*, 65:1215-1223. DOI: 10.1043/0006-363(2001)065<1215:IUETBA>2.0.CO;2

Martino-Andrade, A. J.; Chahoud, I. (2010) - Reproductive toxicity of phthalate esters. *Molecular Nutrition & Food Research*, 54(1):148–157. DOI: 10.1002/mnfr.200800312

Marx-Stoelting, P'.; Niemann, L.; Ritz, V.; Ulbrich, B.; Gall, A.; Hirsch-Ernst, K. I.; Pfeil, R.; Solecki, R. (2014) - Assessment of three approaches for regulatory decision making on pesticides with endocrine disrupting properties. *Regulatory Toxicology and Pharmacology*, 70(3):590-604. DOI: 10.1016/j.yrtph.2014.09.001.

Matějíček, D. (2011) - On-line two-dimensional liquid chromatography-tandem mass spectrometric determination of estrogens in sediments. *Journal of Chromatography A*, 1218(16):2292–2300. DOI: 10.1016/j.chroma.2011.02.041

Melo, S. M.; Brito, N. M. (2014) - Analysis and Occurrence of Endocrine Disruptors in Brazilian Water by HPLC-Fluorescence Detection. *Water Air Soil Pollution*, 225:1783. DOI: 10.1007/s11270-013-1783-y

Menzies, R.; Quinete, N. S.; Gardinali, P.; Seba, D. (2013) - Baseline occurrence of organochlorine pesticides and other xenobiotics in the marine environment: Caribbean and Pacific collections. *Marine Pollution Bulletin*, 70(1-2):289–295. DOI: 10.1016/j.marpolbul.2013.03.003

Miège, C.; Peretti, A.; Labadie, P.; Budzinski, H.; Le Bizec, B.; Vorkamp, K.; Tronczynski, J.; Persat, H.; Coquery, M.; Babut, M. (2012) - Occurrence of priority and emerging organic compounds in fishes from the Rhone River (France). *Analytical and Bioanalytical Chemistry*, 404:2721-2735. DOI: 10.1007/s00216-012-6187-0.

Milligan, S. R.; Balasubramanian, A. V.; Kalita, J. C. (1998) - Relative potency of xenobiotic estrogens in an acute in vivo mammalian assay. *Environmental Health Perspective*, 106(1): 23–26. DOI: 10.1289/ehp.9810623

Mnif, W.; Hassine, A. I. H.; Bouaziz, A.; Bartegi, A.; Thomas, O.; Roig, B. (2011) - Effect of endocrine disruptor pesticides: A review. *International Journal of Environmental Research and Public Health,* 8(6):2265–2303. DOI: 10.3390/ijerph8062265

Monteagudo, C.; Mariscal-Arcas, M'; Heras-Gonzalez, L.; Ibanez-Peinado, D.; Rivas, A.; Olea-Serrano, F. (2016) - Effects of maternal diet and environmental exposure to organochlorine pesticides on newborn weight in Southern Spain. *Chemosphere*, 156:135-142. DOI: 10.1016/j.chemosphere.2016.04.103.

Moss, G. P. (1989) - Nomenclature of steroids. *Pure and Applied Chemistry*, 61(10):1783–1822. DOI: 10.1351/pac198961101783

Muñoz-de-Toro, M.; Markey, C. M.; Wadia, P. R.; Luque, E. H.; Rubin, B. S.; Sonnenschein, C.; Soto, A. M. (2005) - Perinatal exposure to bisphenol-A alters peripubertal mammary gland development in mice. *Endocrinology*, 146(9):4138-4147. DOI: 10.1210/en.2005-0340

Nalli, S., Cooper, D. G.; Nicell, J. A. (2002) - Biodegradation of plasticizers by Rhodococcus rhodochrous. *Biodegradation*, 13(5):343–352. DOI: 10.1023/A:1022313810852

Net, S.; Sempéré, R.; Delmont, A.; Paluselli, A.; Ouddane, B. (2015) - Occurrence, fate, behavior and ecotoxicological state of phthalates in different environmental matrices. *Environmental Science & Technology*, 49:4019-4035. DOI: 10.1021/es505233b

Noppe, H.; Verslycke, T.; De Wulf, E.; Verheyden, K.; Monteyne, E.; Van Caeter, P.; Janssen, C. R.; De brabanderHubert F. (2007a) - Occurrence of estrogens in the Scheldt estuary: A 2-year survey. *Ecotoxicology and Environmental Safety*, 66(1):1-8. DOI: 10.1016/j.ecoenv.2006.04.005

Nurulnadia, M. Y.; Koyama, J.; Uno, S.; Kito, A.; Kokushi, E.; Bacolod, E. T.; Ito, K.; Chuman, Y. (2014) - Accumulation of endocrine disrupting chemicals (EDCs) in the polychaete Paraprionospio sp. from the Yodo River mouth, Osaka Bay, Japan. *Environmental Monitoring and Assessment*, 186(3):1453-1463. DOI: 10.1007/s10661-013-3466-y

Oehlmann, J.; Schulte-Oehlmann, U.; Tillmann, M.; Markert, B. (2000) - Effects of endocrine disruptors on prosobranch snails (Mollusca: Gastropoda) in the laboratory. Part I: Bisphenol A and octylphenol as xeno-estrogens. *Ecotoxicology*, 9(6):383–397. DOI: 10.1023/A:1008972518019

Ortiz-Zarragoitia, M.; Cajaraville, M. P. (2005) - Effects of selected xenoestrogens on liver peroxisomes, vitellogenin levels and spermatogenic cell proliferation in male zebrafish. *Comparative Biochemistry and Physiology*, 141(2):133–144. DOI: 10.1016/j.cca.2005.05.010

Ortiz-Zarragoitia, M.; Cajaraville, M.P. (2006) - Biomarkers of exposure and reproduction-related effects in mussels exposed to endocrine disrupters. *Archives of Environmental Contamination and Toxicology*, 50:361–369. DOI:10.1007/s00244-005-1082-8

Pal, A.; Gin, K. Y.-H.; Lin, A. Y.-C.; Reinhard, M. (2010) - Impacts of emerging organic contaminants on freshwater resources: review of recent occurrences, sources, fate and effects. *Science of the Total Environment*, 408(24):6062–6069. DOI: 10.1016/j.scitotenv.2010.09.026

Palanza, P.; Nagel, S. C.; Parmigiani, S.; vom Saal, F. S. (2016) - Perinatal exposure to endocrine disruptors: sex, timing and behavioral endpoints. *Current Opinion in Behavioral Sciences*, 7:69-75. DOI: 10.1016/j.cobeha.2015.11.017.

Panter, G. H.; Thompson, R. S.; Beresford, N.; Sumpter, J. P. (1999) - Transformation of a non-oestrogenic steroid metabolite to an oestrogenically active substance by minimal bacterial activity. *Chemosphere*, 38(15):3579-3596. DOI: 10.1016/S0045-6535(98)00572-4

Paoli, D.; Giannandrea, F.; Gallo, M.; Turci, R., Cattaruzza, M. S.; Lombardo, F.; Gandini, L. (2015) - Exposure to polychlorinated biphenyls and hexachlorobenzene, semen quality and testicular cancer risk. *Journal of Endocrinological Investigation*, 38(7):745–752. DOI:10.1007/s40618-015-0251-5

Paulozzi, L. J. (1999) - International trends in rates of hypospadias and cryptorchidism. *Environmental Health Perspectives*, 107(4):297–302. DOI: 10.1289/ehp.99107297

Perez, P.; Pulgar, R.; Olea-Serrano, F.; VillaloboS, M.; Rivas, A.; Metzler, M.; Pedraza, V.; Olea, N. (1998) - The estrogenicity of bisphenol A-related diphenylalkanes with various substituents at the central carbon and the hydroxy groups. *Environmental Health Perspectives*, 106(3):167–174. DOI: 10.1289/ehp.98106167

Pérez-Feás, C.; Barciela-Alonso, M. C.; Bermejo-Barrera, P. (2011)

- Presence of phthalates in contact lens and cleaning solutions. *Microchemical Journal*, 99(1):108-113. DOI: 10.1016/j.microc.2011.04.006

Petrovic, M.; Fernández-Alba, A. R.; Borrull, F.; Marce, R. M.; González, M. E.; Barceló, D. (2002) - Occurrence and distribution of nonionic surfactants, their degradation products, and linear alkylbenzene sulfonates in coastal waters and sediments in Spain. *Environmental Toxicology and Chemistry*, 21(1):37–46. DOI: 10.1002/etc.5620210106

Picard, K.; Lhuguenot, J. C.; Lavier-Canivenc, M. C.; Chagnon, M. C. (2001) - Estrogenic activity and metabolism of n-butyl benzyl phthalate in vitro: identification of the active molecule(s). *Toxicology and Applied Pharmacology*, 172(2):108-118. DOI: 10.1006/taap.2001.9141

Pocar, P.; Brevini, T. A. L.; Fischer, B.; Gandolfi, F. (2003) - The impact of endocrine disruptors on oocyte competence. Reproduction, 125(3):313–325. DOI: 10.1530/rep.0.1250313

Pojana, G.; Bonfà, A.; Busetti, F.; Collarin, A.; Marcomini, A. (2004) - Determination of natural and synthetic estrogenic compounds in coastal lagoon waters by HPLC-electrospray-mass spectrometry. *International Journal of Environmental Analytical Chemistry*, 84(10):717–727. DOI: 10.1080/03067310410001729060

Pojana, G.; Gomiero, A.; Jonkers, N.; Marcomini, A. (2007) - Natural and synthetic endocrine disrupting compounds (EDCs) in water, sediment and biota of a coastal lagoon. *Environment International*, 33(7):929–936. DOI: 10.1016/j.envint.2007.05.003

Porte, C.; Janer, G.; Lorusso, L. C.; Ortiz-Zarragoitia, M.; Cajaraville, M. P.; Fossi, M. C.; Canesi, L. (2006) - Endocrine disruptors in marine organisms: approaches and perspectives. *Comparative Biochemistry and Physiology*, 143(3):303–315. DOI: 10.1016/j.cbpc.2006.03.004

Prins, G. S. (2008) - Endocrine disruptors and prostate cancer risk. *Endocrine Related Cancer*, 15(3):649–656. DOI: 10.1677/ERC-08-0043

Puy-Azurmendi, E.; Ortiz-Zarragoitia, M.; Kuster, M.; Martínez, E.; Guillamón, M.; Domínguez, C.; Serrano, T.; Barbero, Mari C.; De Alda, M. L.; Bayona, J. M.; Barceló, D.; Cajaraville, M. P. (2010) - An integrated study of endocrine disruptors in sediments and reproduction-related parameters in bivalve molluscs from the Biosphere's Reserve of Urdaibai (Bay of Biscay). *Marine Environmental Research*, *69*:S63–S66. DOI:10.1016/j.marenvres.2009.10.003

Puy-Azurmendi, E.; Ortiz-Zarragoitia, M.; Villagrasa, M.; Kuster, M.; Aragón, P.; Atienza, J.; Puchades, R.; Maquieira, A.; Domínguez, C.; López De Alda, M.; Fernandes, D.; Porte, C.; Bayona, J. M.; Barceló, D.; Cajaraville, M. P. (2013) - Endocrine disruption in thicklip grey mullet (Chelon labrosus) from the Urdaibai Biosphere Reserve (Bay of Biscay, Southwestern Europe). *Science of the Total Environment*, 443:233–244. DOI: 10.1016/j.scitotenv.2012.10.078

Quednow, K.; Püttmann, W. (2008) - Endocrine disruptors in freshwater streams of Hesse, Germany: changes in concentration levels in the time span from 2003 to 2005. *Environmental Pollution*, 152(2):476–483. DOI: 10.1016/j.envpol.2007.05.032

Queiroz, M. E. C.; Lanças, F. M. (2005) - Análise de fármacos em material biológico: acoplamento microextração em fase sólida "no tubo" e cromatografia líquida de alta eficiência. *Quimica Nova*, 28(5):880-886. DOI: 10.1590/S0100-40422005000500027

Reis Filho, R. W.; Araújo, J. C. de; Vieira, E. M. (2006) - Hormônios sexuais estrógenos: contaminantes bioativos. Quimica Nova, 29(4):817-822. DOI: 10.1590/S0100-40422006000400032.

Renner, R. (1997) - European Bans on Surfactant Trigger Transatlantic Debate. *Environmental Science & Technology*, 31(7):316–320. DOI: 10.1021/es972366q

Ribeiro, C.; Pardal, M. A.; Martinho, F.; Margalho, R.; Tiritan, M. E.; Rocha, E.; Rocha, M. J. (2009) - Distribution of endocrine disruptors in the Mondego River estuary, Portugal. *Environmental Monitoring and Assessment*, 149(1-4):183–193. DOI: 10.1007/s10661-008-0192-y

Richardson, S. D. (2002) - Environmental mass spectrometry: emerging contaminants and current issues. *Analytical Chemistry*, 74(12):2719–2742. DOI: 10.1021/ac020211h

Richardson, S. D. (2012) - Environmental mass spectrometry: emerging contaminants and current issues. *Analytical Chemistry*, 84(2):747-778. DOI: 10.1021/ac202903d

Richardson, S. D.; Ternes, T. A. (2014) - Water analysis: emerging contaminants and current issues. *Analytical Chemistry*, 86(6):2813–2848. DOI:10.1021/ac500508t

Richardson, S.; Ternes, T. A. (2011) - Water Analysis: Emerging Contaminants and Current Issues. *Analytical Chemistry*, 83(12):4614-4648. DOI: 10.1021/ac200915r

Richardson, S.D.; Ternes, T.A. (2015) - Water Analysis: Emerging Contaminants and Current Issues. Analytical Chemistry, 75:3809–3836. DOI:10.1021/ac500508t

Romani, F.; Tropea, A.; Scarinci, E.; Federico, A.; Russo, C. D.; Lisi, L.; Catino, S.; Lanzone, A.; Apa, R. (2014) - Endocrine disruptors and human reproductive failure: the in vitro effect of phthalates on human luteal cells. *Fertility and Sterility*, 102(3):831-837. DOI: 10.1016/j.fertnstert.2014.05.041

Rubio, S.; Pérez-Bendito, D. (2009) - Recent advances in environmental analysis. *Analytical Chemistry*, 81(12):4601–4622. DOI: 10.1021/ac900738s

Rudel, R. A.; Camann, D. E.; Spengler, J. D.; Korn, L. R.; Brody, J. G. (2003) - Phthalates, Alkylphenols, Pesticides, Polybrominated Diphenyl Ethers, and Other Endocrine-Disrupting Compounds in Indoor Air and Dust. *Environmental Science & Technology*, 37(20):4543–4553. DOI: 10.1021/es0264596

Salgueiro-González, N., Turnes-Carou, I., Muniategui-Lorenzo, S., López-Mahía, P., Prada-Rodríguez, D. (2014). Analysis of endocrine disruptor compounds in marine sediments by in cell clean up-pressurized liquid extraction-liquid chromatography tandem mass spectrometry determination. *Analytica Chimica Acta*, 852:112–120. DOI: 10.1016/j.aca.2014.09.041

Salgueiro-González, N.; Concha-Graña, E.; Turnes-Carou, I.; Muniategui-Lorenzo, S.; López-Mahía, P.; Prada-Rodríguez, D. (2012) - Determination of alkylphenols and bisphenol A in seawater samples by dispersive liquid-liquid microextraction and liquid chromatography tandem mass spectrometry for compliance with environmental quality standards (Directive 2008/105/EC). *Journal of Chromatography A*, 1223:1–8. DOI: 10.1016/j.chroma.2011.12.011

Salgueiro-González, N.; Turnes-Carou, I.; Besada, V.; Muniategui-Lorenzo, S.; López-Mahía, P.; Prada-Rodríguez, D. (2015) - Occurrence, distribution and bioaccumulation of endocrine disrupting compounds in water, sediment and biota samples from a European river basin. *Science of the Total Environment*, 529:121–130. DOI:10.1016/j.scitotenv.2015.05.048

Salvador, A.; Moretton, C.; Piram, A.; Faure, R.; (2007) - On-line solid-phase extraction with on-support derivatization for high-

sensitivity liquid chromatography tandem mass spectrometry of estrogens in influent/effluent of wastewater treatment plants. *Journal of Chromatography A*, 1145(1-2):102-109. DOI: 10.1016/j.chroma.2007.01.055

Sánchez-Avila, J.; Fernandez-Sanjuan, M.; Vicente, J.; Lacorte, S. (2011) - Development of a multi-residue method for the determination of organic micropollutants in water, sediment and mussels using gas chromatography-tandem mass spectrometry. *Journal of Chromatography A*, 1218 (38):6799–6811. DOI: 10.1016/j.chroma.2011.07.056

Santos, A. G.; Regis, A. C. D.; da Rocha, G. O.; Bezerra, M. A.; Jesus, R. M.; de Andrade, J. B. (2016) - A simple, comprehensive, and miniaturized solvent extraction method for determination of particulate-phase polycyclic aromatic compounds in air. *Journal of Chromatography A*, 1435:6-17. DOI: 10.1016/j.chroma.2016.01.018.

Santos, L. H. M. L. M.; Araújo, A. N.; Fachini, A.; Pena, A.; Delerue-Matos, C.; Montenegro, M. C. B. S. M. (2010) - Ecotoxicological aspects related to the presence of pharmaceuticals in the aquatic environment. *Journal of Hazardous Materials*, 175(1-3):45–95. DOI: 10.1016/j.jhazmat.2009.10.100

Saravanabhavan, G., Helleur, R.; Hellou, J. (2009) - GC-MS/MS measurement of natural and synthetic estrogens in receiving waters and mussels close to a raw sewage ocean outfall. *Chemosphere*, 76(8):1156–1162. DOI: 10.1016/j.chemosphere.2009.04.006

Sax, L. (2010) - Polyethylene terephthalate may yield endocrine disruptors. *Environmental Health Perspectives*, 118(4):445–448. DOI: 10.1289/ehp.0901253

Scheringer, M.; Jones, K. C.; Matthies, M.; Simonich, S.; Van De Meent, D. (2009) - Multimedia partitioning, overall persistence, and long-range transport potential in the context of POPs and PBT chemical assessments. *Integrated Environmental Assessment and Management*, 5(4):557–576. DOI: 10.1897/IEAM_2009-007.1

Schlenk, D.; Sapozhnikova, Y.; Irwin, M. A.; Xie, L.; Hwang, W.; Reddy, S.; Brownawell, B. J.; Armstrong, J.; Kelly, M.; Montagne, D. E.; Kolodziej, E. P.; Sedlak, D.; Snyder, S. (2005) - In vivo bioassay-guided fractionation of marine sediment extracts from the southern california bight, USA, for estrogenic activity. *Environmental Toxicology and Chemistry*, 24(11):2820–2826. DOI: 10.1897/05-116R.1

Selvaraj, K. K.; Shanmugam, G.; Sampath, S.; Larsson, D. G. J.; Ramaswamy, B. R. (2014) - GC-MS determination of bisphenol A and alkylphenol ethoxylates in river water from India and their ecotoxicological risk assessment. *Ecotoxicology and Environmental Safety*, 99:13–20. DOI: 10.1016/j.ecoenv.2013.09.006

Shan, X. M.; Shen, D. H.; Wang, B. S.; Lu, B. B.; Huang, F. Y. (2014) - Simultaneous determination of bisphenols and alkylphenols in water by solid phase extraction and ultra performance liquid chromatography-tandem mass spectrometry. *Biomedical and Environmental Sciences*, *27*(6):471–4. DOI:10.3967/bes2014.076

Shang, D. Y.; Macdonald, R. W.; Ikonomou, M. G. (1999) - Persistence of Nonylphenol Ethoxylate Surfactants and Their Primary Degradation Products in Sediments from near a Municipal Outfall in the Strait of Georgia, British Columbia, Canada. *Environmental Science & Technology*, 33(9):1366–1372. DOI: 10.1021/es980966z

Shi, J.; Liu, X.; Chen, Q.; Zhang, H. (2014) - Spatial and seasonal distributions of estrogens and bisphenol A in the Yangtze River Estuary and the adjacent East China Sea. *Chemosphere* 111:336–343. DOI: 10.1016/j.chemosphere.2014.04.046

Shimada, K.; Mitamura, K.; Higashi, T. (2001) - Gas chromatography and high-performance liquid chromatography of natural steroids. *Journal of Chromatography A*, 935(1-2):141–172. DOI: 10.1016/S0021-9673(01)00943-8

Soares, A.; Guieysse, B.; Jefferson, B.; Cartmell, E.; Lester, J. N. (2008) - Nonylphenol in the environment: a critical review on occurrence, fate, toxicity and treatment in wastewaters. *Environment International*, 34(7):1033–1049. DOI: 10.1016/j.envint.2008.01.004

Solé, M.; Alda, M. J. L.; Castillo, M.; Porte, C.; Ladegaard-Pedersen, K.; Barceló, D. (2000) - Estrogenicity Determination in Sewage Treatment Plants and Surface Waters from the Catalonian Area (NE Spain). *Environmental Science & Technology*, 34(24):5076–5083. DOI: 10.1021/es991335n

Soto, A M.; Justicia, H.; Wray, J. W.; Sonnenschein, C. (1991) - p-Nonyl-phenol: an estrogenic xenobiotic released from "modified" polystyrene. *Environ Health Perspect*, 92:167–173. DOI: 10.2307/3431154

Soto, A. M.; Sonnenschein, C.; Chung, K. L.; Fernandez, M. F.; Olea, N.; Serrano, F. O. (1995) - The E-SCREEN assay as a tool to identify estrogens: an update on estrogenic environmental pollutants. *Environmental Health Perspectives*, 103(7):113–122. DOI: 10.2307/3432519

Staniszewska, M.; Koniecko, I.; Falkowska, L.; Krzymyk, E. (2015) - Occurrence and distribution of bisphenol A and alkylphenols in the water of the gulf of Gdansk (Southern Baltic). *Marine Pollution Bulletin*, 91(1):372–379. DOI: 10.1016/j.marpolbul.2014.11.027

Stewart, M.; Olsen, G.; Hickey, C. W.; Ferreira, B.; Jelić, A.; Petrović, M.; Barcelo, D. (2014) - A survey of emerging contaminants in the estuarine receiving environment around Auckland, New Zealand. *Science of the Total Environment*. 468–469:202–210. DOI: 10.1016/j.scitotenv.2013.08.039

Sumpter, J. P. (1998) - Xenoendorine disrupters environmental impacts. *Toxicology Letters*, 102-103:337–342. DOI: 10.1016/S0378-4274(98)00328-2

Sun, K.; Jin, J.; Gao, B.; Zhang, Z.; Wang, Z.; Pan, Z.; Xu, D.; Zhao, Y. (2012) - Sorption of 17α-ethinyl estradiol, bisphenol A and phenanthrene to different size fractions of soil and sediment. *Chemosphere*, 88(5):577–583. DOI: 10.1016/j.chemosphere.2012.03.034

Sun, L.; Zang, S. Y.; Sun, H. J. (2014). Sources and history of PAHs in lake sediments from oil-producing and industrial areas, northeast China. *International Journal of Environmental Science and Technology*, *11*(7):2051–2060. DOI:10.1007/s13762-013-0396-8

Sutton, R.; Sedlak, M. D.; Yee, D.; Davis, A. J.; Crane, D.; Grace, R. (2014) - Declines in Polybrominated Diphenyl Ether Contamination of San Francisco Bay following Production Phase-Outs and Bans. *Environmental Science & Techinology*, 49(2):777-84. DOI:10.1021/es503727b.

Talsness, C. E.; Andrade, A. J. M.; Kuriyama, S. N.; Taylor, J. A.; Vom Saal, F. S. (2009) - Components of plastic: experimental studies in animals and relevance for human health. *Philosophical Transactions of the Royal Society B*, 364(1526):2079–2096. DOI: 10.1098/rstb.2008.0281

Tan, B. L. L.; Hawker, D. W.; Müller, J. F.; Leusch, F. D. L.; Tremblay, L. A.; Chapman, H. F. (2007a) - Modelling of the fate of selected endocrine disruptors in a municipal wastewater treatment plant in South East Queensland, Australia. *Chemosphere*, 69(4):644–654. DOI: 10.1016/j.chemosphere.2007.02.057

Tan, B. L. L.; Hawker, D.W.; Müller, J. F.; Leusch, F. D. L.; Tremblay, L. A.; Chapman, H. F. (2007b) - Comprehensive study of endocrine disrupting compounds using grab and passive sampling at selected wastewater treatment plants in South East Queensland, Australia. *Environment International*, 33(5):654–669. DOI: 10.1016/j.envint.2007.01.008

Tata, J. R. (2005) - One hundred years of hormones. *European Molecular Biology Organization*, 6(6):490–496, 2005. DOI: 10.1038/sj.embor.7400444

Thibaut, R.; Porte, C. (2004) - Effects of endocrine disrupters on sex steroid synthesis and metabolism pathways in fish. *The Journal of Steroid Biochemistry and Molecular Biology*, 92(5):485–494. DOI: 10.1016/j.jsbmb.2004.10.008

Thorup, J.; Nordenskjöld, A.; Hutson, J. M. (2014) - Genetic and environmental origins of hypospadias. Current Opinion in Endocrinology, *Diabetes, and Obesity*, 21(3):227–32. DOI:10.1097/MED.0000000000000063

Toppari, J., Kaleva, M.; Virtanen, H. E. (2001) - Trends in the incidence of cryptorchidism and hypospadias, and methodological limitations of registry-based data. *Human Reproduction Update*, 7(3):282-286. DOI: 10.1093/humupd/7.3.282

Torres, N. H., Aguiar, M. M., Ferreira, L. F. R., Américo, J. H. P., Machado, Â. M., Cavalcanti, E. B., Tornisielo, V. L. (2015). Detection of hormones in surface and drinking water in Brazil by LC-ESI-MS/MS and ecotoxicological assessment with Daphnia magna. *Environmental Monitoring and Assessment*, 187:379. DOI: 10.1007/s10661-015-4626-z

Trachsel, M. (2008) - Results of the Consensus Platforms: Positions and Recommendations Derived from Scientific Findings in a Joint Effort of Academics, Industry, and Authorities. *Chimia*, 62(5):432-438. DOI: 10.2533/chimia.2008.432

Tsai, Y.-A.; Lin, C;-L.; Hou, J.-W.; Huang, P.-C.; Lee, M.-C.; Chen, B.-H.; Wu, M.-T.; Chen, C.-C.; Wang, S.-L.; Lee, C.-C.; Hsiung, C. A.; Chen, M.-L. (2016) - Effects of high di(2-ethylhexyl)phthalate (DEHP) exposure due to tainted food intake on pre-pubertal growth characteristics in a Taiwanese population. *Environmental Research*, 149:197-205. DOI: 10.1016/j.envres.2016.05.005.

Tsuda, T.; Takino, A.; Kojima, M.; Harada, H.; Muraki, K.; Tsuji, M. (2000) - 4-Nonylphenols and 4-tert-octylphenol in water and fish from rivers flowing into Lake Biwa. *Chemosphere*, 41(5):757–762. DOI: 10.1016/S0045-6535(99)00465-8

Valdés, M. E., Marino, D. J., Wunderlin, D. A. Somoza, G. M. Ronco, A. E. Carriquiriborde, P. (2015). Screening concentration of E1, E2 and EE2 in sewage effluents and surface waters of the "Pampas" region and the "Rio de la Plata" estuary (Argentina). Bulletin of Environmental Contamination and Toxicology, 94(1):29–33. DOI: 10.1007/s00128-014-1417-0

Valton, A. S.; Serre-Dargnat, C.; Blanchard, M.; Alliot, F.; Chevreuil, M.; Teil, M. J. (2014) - Determination of Phthalates and Their by-Products in Tissues of Roach (Rutilus Rutilus) from the Orge River (France). *Environmental Science and Pollution Research*, 21:12723–12730. DOI: 10.1007/s11356-014-3213-0

Vandenberg, L. N.; Chahoud, I.; Heindel, J. J.; Padmanabhan, V.; Paumgartten, F. J. R.; Schoenfelder, G. (2010) - Urinary, circulating, and tissue biomonitoring studies indicate widespread exposure to bisphenol A. *Environmental Health Perspectives,* 118(8):1055–1070. DOI: 10.1289/ehp.0901716

Vandenberg, L. N.; Maffini, M. V.; Wadia, P. R.; Sonnenschein, C.; Rubin, B. S.; Soto, A. M. (2007) - Exposure to environmentally relevant doses of the xenoestrogen bisphenol-A alters development of the fetal mouse mammary gland. *Endocrinology*, 148(1):116–127. DOI: 10.1210/en.2006-0561

Vandenberg, L. N.; Schaeberle, C. M.; Rubin, B. S.; Sonnenschein, C.; Soto, A. M. (2013) - The male mammary gland: a target for the xenoestrogen bisphenol A. *Reproductive Toxicology*, 37:15–23. DOI: 10.1016/j.reprotox.2013.01.002

Vega-Morales, T.; Sosa-Ferrera, Z.; Santana-Rodríguez, J. J. (2013). Evaluation of the presence of endocrine-disrupting compounds in dissolved and solid wastewater treatment plant samples of Gran Canaria Island (Spain). *BioMed Research International*, 2013:1-15. DOI: 10.1155/2013/790570

Vekey, K. (2001) - Mass spectrometry and mass-selective detection in chromatography. *Journal of Chromatography A*, 921(2):227-236. DOI: 10.1016/S0021-9673(01)00825-1

Ventura, C.; Nieto, M. R. R.; Bourguignon, N.; Lux-Santos, V.; Rodriguez, H.; Cao, G.; Randi, A.; Nuñez, M. (2016) - Pesticides chlorpyrifos acts as an endocrine disruptor in adult rats causing changes in mammary glands and hormonal balance. *The Journal of Steroid Biochemistry and Molecular Biology*, 156:1-9. DOI: 10.1016/j.jsbmb.2015.10.010.

Vidal-Dorsch, D. E.; Bay, S. M.; Maruya, K.; Snyder, S. A.; Trenholm, R. A.; Vanderford, B. J. (2012) - Contaminants of emerging concern in municipal wastewater effluents and marine receiving water. *Environmental Toxicology and Chemistry*, 31(12):2674–2682. DOI: 10.1002/etc.2004

Villar-Navarro, M.; Ramos-Payán, M.; Fernández-Torres, R.; Callejón-Mochón, M.; Bello-López, M. Á. (2013) - A novel application of three phase hollow fiber based liquid phase microextraction (HF-LPME) for the HPLC determination of two endocrine disrupting compounds (EDCs), n-octylphenol and n-nonylphenol, in environmental waters. *Science of The Total Environment,* 443:1-6. DOI: 10.1016/j.scitotenv.2012.10.071

Volkova, K., Caspillo, N. R., Porseryd, T., Hallgren, S., DinnÉtz, P., Porsch-Hällström, I. (2015). Developmental exposure of zebrafish (Danio rerio) to 17α-ethinylestradiol affects non-reproductive behavior and fertility as adults, and increases anxiety in unexposed progeny. Hormones and Behavior, 73:30–38. DOI: 10.1016/j.yhbeh.2015.05.014

Vos, J. G.; Becher, G.; van den Berg, M.; de Boer, J.; Leonards, P. E. G. (2003) - Brominated flame retardants and endocrine disruption. *Pure and Applied Chemistry*, 75(11-12):2039-2046. DOI: 10.1351/pac200375112039

Wang, J.; Shim, W.; Yim, U.; Kannan, N.; Li, D. (2010) - Nonylphenol in bivalves and sediments in the northeast coast of China. *Journal of Environmental Sciences*, 22(11):1735–1740. DOI: 10.1016/S1001-0742(09)60313-2

Wang, W.; Meng, B.; Lu, X.; Liu, Y.; Tao, S. (2007) - Extraction of polycyclic aromatic hydrocarbons and organochlorine pesticides from soils: a comparison between Soxhlet extraction, microwave-assisted extraction and accelerated solvent extraction techniques. *Analytica Chimica Acta*, 602(2):211-222. DOI: 10.1016/j.aca.2007.09.023

Weiss, J. M.; Hamers, T.; Thomas, K. V.; Van Der Linden, S.; Leonards, P. E. G.; Lamoree, M. H. (2009) - Masking effect of anti-androgens on androgenic activity in European river sediment unveiled by effect-directed analysis. *Analytical and Bioanalytical Chemistry*, 394(5):1385–1397.DOI: 10.1007/s00216-009-2807-8

WHO. State of the Science of Endocrine Disrupting Chemicals. (United Nations Environment Programme), 2012, 30p.

Wu, J.; Zhang, L.; Yang, Z. (2010) - A Review on the Analysis of Emerging Contaminants in Aquatic Environment. *Critical Reviews in Analytical Chemistry*, 40(4):234-245. DOI: 10.1080/10408347.2010.515467

Xie, Z.; Ebinghaus, R.; Temme, C.; Lohmann, R.; Caba, A.; Ruck, W. (2007) - Occurrence and air-sea exchange of phthalates in the Arctic. *Environmental Science & Technology*, 41(13):4555–4560. DOI: 10.1021/es0630240

Xie, Z.; Lakaschus, S.; Ebinghaus, R.; Caba, A.; Ruck, W. (2006) - Atmospheric concentrations and airesea exchanges of nonylphenol , tertiary octylphenol and nonylphenol monoethoxylate in the North Sea. *Environmental Pollution*, 142(1):170–180. DOI: 10.1016/j.envpol.2005.08.073

Xu, E. G. B.; Morton, B.; Lee, J. H.W.; Leung, K. M.Y. (2015) - Environmental fate and ecological risks of nonylphenols and bisphenol A in the Cape D'Aguilar Marine Reserve, Hong Kong. *Marine Pollution Bulletin*, 91(1):128–138. DOI: 10.1016/j.marpolbul.2014.12.017

Xu, N.; Xu, Y.-F.; Xu, S.; Li, J.; Tao, H.-C. (2012) - Removal of estrogens in municipal wastewater treatment plants: a Chinese perspective. *Environmental Pollution*, 165:215–224. DOI: 10.1016/j.envpol.2011.12.025

Xu, W.; Yan, W.; Huang,W.; Miao, L.; Zhong, L. (2014) - Endocrine-disrupting chemicals in the Pearl River Delta and coastal environment: sources, transfer, and implications. *Environmental Geochemistry and Health*, 36(6):1095–1104. DOI: 10.1007/s10653-014-9618-3

Xu, X.; Roman, J. M.; Issaq, H. J.; Keefer, L. K.; Veenstra, T. D.; Ziegler, R. G. (2007) - Quantitative Measurement of Endogenous Estrogens and Estrogen Metabolites in Human Serum by Liquid Chromatography-Tandem Mass Spectrometry. *Analytical Chemistry*, 79(20):7813-7821. DOI: 10.1021/ac070494j

Xu, X.; Veenstra, T. D.; Fox, S. D.; Roman, J. M.; Issaq, H. J.; Falk, R.; Saavedra, J. E.; Keefer, L. K.; Ziegler, R. G. (2005) - Measuring Fifteen Endogenous Estrogens Simultaneously in Human Urine by High-Performance Liquid Chromatography-Mass Spectrometry. *Analytical Chemistry*, 77 (20):6646-6654. DOI: 10.1021/ac050697c

Yan, H.; Wang, H. (2013) - Recent development and applications of dispersive liquid–liquid microextraction. *Journal of Chromatography A*, 1295:1-15. DOI: 10.1016/j.chroma.2013.04.053

Yi, B.; Kim, C.; Yang, M. (2010) - Biological monitoring of bisphenol A with HLPC/FLD and LC/MS/MS assays. *Journal of Chromatography B*, 878(27):2606–2610. DOI: 10.1016/j.jchromb.2010.02.008

Ying, G.-G., Williams, B.; Kookana, R. (2002a) - Environmental fate of alkylphenols and alkylphenol ethoxylates--a review. *Environment International*, 28(3):215–226. DOI:10.1016/S0160-4120(02)00017-X

Ying, G.-G.; Kookana, R. S.; Ru, Y.-J. (2002b) - Occurrence and fate of hormone steroids in the environment. *Environment International*, 28(6):545–551. DOI: 10.1016/S0160-4120(02)00075-2

Yu, Y.; Huang, Q.; Cui, J.; Zhang, K.; Tang, C.; Peng, X. (2011) - Determination of pharmaceuticals, steroid hormones, and endocrine-disrupting personal care products in sewage sludge by ultra-high-performance liquid chromatography – tandem mass spectrometry. *Analytical and Bioanalytical Chemistry*, 399(2):891–902. DOI: 10.1007/s00216-010-4295-2

Zhang, J.; Yang, M.; Zhang, Y.; Chen, M. (2008) - Biotransformation of nonylphenol ethoxylates during sewage treatment under anaerobic and aerobic conditions. *Journal of Environmental Sciences*, 20(2):135–141. DOI: 10.1016/S1001-0742(08)60021-2

Zhang, S.; You, J.; Sun, Z.; Song, C.; Ning, S.; Zhao, C.; Suo, Y. (2012) - A sensitive method for extraction and determination of endocrine-disrupting compounds from wastewater using 10-ethyl-acridone-2-sulfonyl chloride as pre-column labeling reagent by high-performance liquid chromatography with fluorescence detection. *Microchemical Journal*, 103:90–96, 2012. DOI: 10.1016/j.microc.2012.01.009

Zhang, X.; Li, Q.; Li, G.; Wang, Z.; Yan, C. (2009) - Levels of estrogenic compounds in Xiamen Bay sediment, China. *Marine Pollution Bulletin*, 58(8):1210–1216. DOI: 10.1016/j.marpolbul.2009.03.011.

Zhang, Y.; Cao, Y.; Jiang, X.; Zhao, Y.; Fang, X., Xie, C. (2015) - Could exposure to phthalates speed up or delay pubertal onset and development? A 1.5-year follow-up of a school-base population. *Environment International*, 83:41-49. DOI: 10.1016/j.envint.2015.06.005.

Zhang, Z.; Ren, N.; Kannan, K.; Nan, J.; Liu, L.; Ma, W.; Qi, H.; Li, Y. (2014) - Occurrence of Endocrine-Disrupting Phenols and Estrogens in Water and Sediment of the Songhua River, Northeastern China. *Archives of Environmental Contamination and Toxicology*, 66(3):361-369. DOI: 10.1007/s00244-014-9998-5

Zheng, W.; Li, X.; Yates, S. R.; Bradford, S. A. (2012) - Anaerobic transformation kinetics and mechanism of steroid estrogenic hormones in dairy lagoon water. *Environmental Science & Technology*, 46:5471–5478. DOI: 10.1021/es301551h

Zrafi-Nouira, I.; Safi, N. M. D.; Bahri, R.; Mzoughi, N.; Aissi, A.; Abdennebi, H. B. E. N.; Saidane-Mosbahi, D. (2010) - Distribution and Sources of Polycyclic Aromatic Hydrocarbons Around a Petroleum Refinery Rejection Area in Jarzouna-Bizerte (Coastal Tunisia). *Soil and Sediment Contamination*, 19(3):292–306. DOI: 10.1080/15320381003695223

Zuloaga, O.; Nvarro, P.; Bizkarguenaga, E.; Iparraguirre, A.; Vallejo, A.; Olivares, M.; Prieto, A. (2012) - Overview of extraction, clean-up and detection techniques for the determination of organic pollutants in sewage sludge: A review. *Analytica Chimica Acta*, 736:7-29. DOI: 10.1080/15320381003695223

Zuo, Y.; Zhang, K.; Deng, Y. (2006) - Occurrence and photochemical degradation of 17alpha-ethinylestradiol in Acushnet River Estuary. *Chemosphere*, 63(9):1583–1590. DOI: 10.1016/j.chemosphere.2005.08.063

Zuo, Y.; Zhang, K.; Lin, Y. (2007) - Microwave-accelerated derivatization for the simultaneous gas chromatographic-mass spectrometric analysis of natural and synthetic estrogenic steroids. *Journal of Chromatography A*, 1148(2):211–218. DOI: 10.1016/j.chroma.2007.03.037

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A alimentação artificial como medida de redução do risco em praias suportadas por arribas rochosas na costa do Barlavento (Algarve, Portugal)

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RESUMO

O turismo baseado no produto "sol e praia" é a principal atividade económica da região do Algarve. Parte considerável das praias da costa do Barlavento corresponde a areais encaixados, acumulados no recorte irregular de arribas (falésias) rochosas cortadas em calcarenitos do Miocénico. A utilização balnear de praias suportadas por arribas determina a existência de perigo para os seus utentes (usuários) dado que uma fração do areal se acumula em faixas potencialmente atingidas pelos detritos de eventual desmoronamento das arribas. A alimentação artificial de praias é uma das possíveis intervenções de mitigação do perigo para os utentes das praias suportadas por arribas rochosas na medida em que diminui a frequência da incidência direta das ondas na base das arribas e, aumentando a área de areal, fomenta o afastamento dos utentes do sopé das arribas. Com o propósito de reduzir o risco associado à geodinâmica das arribas foi executada alimentação artificial em seis praias encaixadas no Barlavento, em 2014 (Carvoeiro, Benagil, Nova, Cova Redonda, Castelo e Coelha). No presente artigo apresentam-se os resultados da variação da ocupação anual dos areais de duas praias (Nova e Cova Redonda) repartida pelas áreas dentro e fora das faixas de perigo das arribas ao longo da década 2006-2016. Os dados da ocupação foram obtidos através de contagens executadas ao longo de todo o ano, sem qualquer distinção etária, no período antes e após a intervenção de alimentação artificial. Os resultados atestam inequivocamente a reação natural dos utentes ao enchimento da praia, traduzido na migração natural da ocupação no sentido do plano de água, resultando no afastamento das áreas do areal contidas nas faixas de perigo das arribas. Na sequência da intervenção, a ocupação das faixas de perigo elevado e moderado reduziu muito significativamente, de 92% para 17% na praia Nova e de 44% para 12% na praia da Cova Redonda. Os resultados mostram que a intervenção de alimentação artificial executada nas praias Nova e Cova Redonda, em 2014, produziu redução muito significativa da ocupação das faixas de perigo em ambas as praias e o incremento para o quadruplo da ocupação no caso da praia Nova. Os resultados evidenciam a eficácia da opção de alimentação artificial como medida de redução do risco e a adequação deste tipo de opção numa região como o Algarve, muito dependente do turismo centrado na utilização do recurso praia.

Palavras-chave: alimentação artificial de praias, risco, arribas, Algarve, Portugal

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ABSTRACT

Beach nourishment as a hazard mitigation tool on beaches backed by rocky cliffs on the Barlavento Coast (Algarve, Portugal)

Tourism based on "sun and beach" is the main economic activity in the Algarve region. A considerable part of the beaches at the Barlavento coast corresponds to embedded sand accumulated in the irregular lacework coast line of rocky cliffs cut into Miocene calcarenites. The pattern of touristic occupation at the Algarve and the geodynamics of the rocky sea cliffs, reflected in the discontinuous and intermittent occurrence of slope mass movements produce the existence of risk to beach users at areas backed by rocky cliffs. The size distribution of slope mass movements runout ratio (the ratio between the radius of the base of cone of debris and the height of the movement) enables the definition of three cartographic hazard areas on beaches: the high hazard area (red zone) where if a slope mass movement occurs, the probability of being hit by debris is greater than 50%; the moderate hazard area (yellow area) where in the event of a slope mass movement occurs, the probability of being hit by debris is less than 50%; and the low hazard area (blue) where the probability of being hit by debris is less than 5%. Beach nourishment of pocket beaches provides extra area available for sunbathers out of the cliffs hazard zones. For purposes of mitigate the risk associated with the cliff geodynamics, artificial beach nourishment was executed in six pocket beaches on the Barlavento Coast, in 2014 (Carvoeiro, Benagil, Nova, Cova Redonda, Castelo and Coelha). In this paper we present and discus the results of the beach nourishment and the occupation patterns on Nova and Cova Redonda beaches within the decade 2006-2016, before and after beach nourishment. Occupation data was obtained throughout different epochs in the year by counting the number of beach users without any distinction of age using periodic and systematic photographs taken at strategic points that provide full coverage of the beach areas. Before beach nourishment the area of dry sand at half-tide under average summer wave conditions outside high and moderate hazard zones was 0% at the Nova beach and 24% on the Cova Redonda beach. Beach nourishment executed in the subaerial beach allowed the extension of sand in 50m on Nova beach and Cova Redonda beach. After the first winter, following the natural adjustment of the beach profile, the width of the beaches was reduced by 19% and 40% respectively. After beach nourishment the area of dry sand at half-tide under average summer wave conditions outside high and moderate hazard areas was 48% at the Nova beach and 55% on the Cova Redonda beach. The results show that the reaction of users to the beach fill was their natural migration towards the water, moving out from the cliff hazard areas. After the intervention, the occupation of high and moderate hazard areas reduced very significantly, from 92% to 17% in Nova beach and from 44% to 12% in the Cova Redonda beach. This reduction contrasts with the low 2% reduction of the occupation of hazard areas on the beach of Senhora da Rocha, (no intervened), which was associated with enhanced hazard signaling performed in the same year. This study shows that beach nourishment is an effective measure to reduce the risk to users of beaches backed by rocky cliffs, and in the case of Algarve, is an appropriate hazard management tool.

Keywords: *beach nourishment, hazard, rocky cliffs, Algarve, Portugal*

1. Introdução

As praias encaixadas em litoral de arriba rochosa são muito procuradas pelos turistas que visitam o Algarve, a região de Portugal cuja economia gravita e depende do turismo centrado no produto "sol e praia". Com vasta diversidade geomorfológica de enquadramento das praias, o sucesso original do turismo de praia do Algarve está associado à beleza natural das pequenas praias encaixadas, acumuladas nas reentrâncias do recorte irregular das arribas rochosas amarelas cortadas em calcarenitos do Miocénico da costa do Barlavento algarvio.

Pelo seu enquadramento geomorfológico, estas praias são normalmente de pequenas dimensões, com capacidade de carga muito reduzida. A intensa procura no verão e a reduzida dimensão dos areais promovem a ocupação intensiva destas praias até ao sopé das arribas, em áreas de perigo que potencialmente podem ser atingidas pelos detritos de qualquer movimento de massa. Em 21 de agosto de 2009 ocorreu tombamento de um leixão na praia Maria Luísa (fig.1a) de que resultou a morte de cinco pessoas e ferimentos noutras três (Marques e Andrade, 2009; Teixeira, 2009a). Desde então, a entidade gestora do litoral (atualmente a Agência Portuguesa do Ambiente) tem vindo a reforçar a sinalização de risco, visando alertar os utentes dos perigos decorrentes da geodinâmica das arribas. Foi desenvolvida rede de sinalética implantada em todos os acessos às praias suportadas por arribas rochosas, que pretende informar os utentes sobre as zonas de perigo, passíveis de serem atingidas pelos detritos de movimentos de massa e, portanto, potencialmente suscetíveis de causar danos graves a quem permaneça nessas zonas (Teixeira, 2014).

Prosseguindo o objetivo de mitigação do risco para os utentes das praias associado à geodinâmica natural das arribas, entre Agosto e Outubro de 2014 foi executada intervenção de alimentação artificial em seis praias encaixadas da costa do Barlavento: Carvoeiro, Benagil, Nova, Cova Redonda, Castelo e Coelha (fig.1a), resultando no alargamento do areal entre 30 m e 50 m. Esta obra, promovida pela Agência Portuguesa do Ambiente, implicou investimento global de 2,0 M€, envolveu a exploração de mancha de empréstimo de areias situada ao largo (fig.1a) e subsequente deposição de 338.000 m^3 de areia grosseira naquelas seis praias.

Com esta intervenção pretendeu-se reduzir o risco para os utilizadores das praias, quer por via da redução muito significativa da incidência das ondas na base da arriba (componente geodinâmica), quer por via da promoção da utilização da praia em zona mais afastada da base das arribas (componente antrópica), diminuindo a exposição dos utentes ao perigo.

O presente artigo pretende descrever os resultados da obra de 2014 e avaliar em que medida foram atingidos os objectivos de prevenção do risco associado à geodinâmica natural das arribas nas praias Nova e Cova Redonda, utilizando como padrão de comparação a praia da Senhora da Rocha, localizada entre as duas e não submetida a qualquer intervenção (fig. 1b).

2. Caracterização da área de estudo

2.1. Enquadramento geológico

O traço dominante da morfologia do Barlavento é dado por arribas rochosas amarelas, com alturas variáveis entre 6 m e 40 m, talhadas em calcarenitos miocénicos, intensamente fraturados e carsificados, sobre os quais assenta uma cobertura plio-plistocénica de areias argilosas vermelhas. Os contrastes de resistência dos materiais constituintes das arribas e a diversidade espacial das cavidades cársicas determinam um padrão de evolução do litoral muito irregular em planta, com modelado rendilhado, com profusão de leixões, arcos, furnas e algares, explorado como imagem de marca da paisagem do litoral do Algarve. O modelado recortado deste troço do litoral facilita a acumulação de dezenas de praias, com dimensões variáveis, algumas sem acesso por terra. A área de estudo corresponde a pequeno troço do litoral do Barlavento, com uma extensão de cerca de 1.5 km, que engloba as praias Nova, a poente, Senhora da Rocha e Cova Redonda, a nascente (fig.1b). Estas praias, individualizadas por esporões rochosos naturais, contêm areais de pequenas dimensões, acumulados sobre a plataforma de abrasão das arribas. Em condições de tempestade coincidentes com marés de águas vivas, o espraio das ondas varre a totalidade do areal, incidindo na base das arribas (fig. 2).

A praia Nova, contida entre dois promontórios, é suportada por arriba subvertical, elevando-se 22 m acima do areal. Com frente de mar de 300 m, antes da intervenção o areal desta praia era muito reduzido, com largura média de cerca de 20-25 m, sendo constituído pela acumulação de areias grosseiras D_{50}=0.65 phi (0.73 mm), com teor de carbonatos de 30-50% (Teixeira, 2009). Com desenvolvimento longilitoral, esta praia é sensível a alterações do rumo da ondulação incidente, acusando migração do areal para nascente, sob agitação marítima de SW e para poente, quando submetida à ondulação de SE (Teixeira, 2009). O pontal que delimita a praia a nascente tem comprimento de cerca de 100 m e atinge a profundidade de 5 m, abaixo do nível médio do mar (≈2 m acima do plano convencional do Zero Hidrográfico, referência hidrográfica utilizada em Portugal). A praia da Senhora da Rocha, com frente de mar de 150 m, contida entre pontais salientes, tem um areal com uma configuração planar semi-circular, com largura média de 60 m, a meia maré. Face ao encaixe desta praia, a rotação do areal em função do rumo da agitação marítima é menos pronunciada da que se verifica na praia Nova. Na zona central da praia o perfil apresenta berma bem desenvolvida, articulada com face da praia com declive médio de 7,3º. O perfil de praia acusa oscilações do areal que não excedem 16 m de largura, sobre o plano do nível médio do mar. Com desenvolvimento longilitoral numa frente de 230 m, a praia da Cova Redonda tem morfologia idêntica à morfologia da praia Nova, com largura da praia de cerca de 30-40 m. A evolução sazonal do areal traduz-se na oscilação da largura da praia em cerca de 10 m, mantendo a praia tipicamente uma face com inclinação média de 7,3º. O pontal natural que retém a praia a nascente tem comprimento de cerca de 75 m e mergulha até profundidade de 3.5 m abaixo do nível médio do mar.

2.2. Enquadramento climático e oceanográfico

A região do Algarve situa-se no extremo sudoeste da Europa, com clima mediterrâneo típico, com verões secos e invernos amenos (fig.3). A precipitação anual atinge 500-600 mm, 80% da qual concentrada no semestre húmido (outubro-março). O número médio anual de dias de chuva não ultrapassa 75 dias e no semestre seco (abril a setembro), em termos médios, não se registam mais de 18 dias de chuva (fig.3). Entre 15 de maio e 15 de outubro a temperatura média ultrapassa 20º C, atingindo 25º C nos meses de julho e agosto (fig.3). O regime de agitação marítima é moderado, com altura significativa média anual da ondulação de 1m (Costa *et al.*, 2001). A ondulação de tempestade (Hs≥2.5 m) ocorre quase exclusivamente durante o semestre húmido.

O rumo da ondulação na costa sul do Algarve é marcadamente bimodal, com prevalência das ondas com rumos do quadrante W (52.3%) e SW (18.3%). Os rumos de E e SE representam cerca de um quarto das ocorrências e estão associados ao vento de E, gerado na zona do estreito de Gibraltar (Pires, 1989). Desta dissimetria do rumo da agitação marítima resulta em saldo potencial de transporte sedimentar por via da deriva litoral, de W para E. O regime de maré é semi-diurno com amplitude média de maré de 2 m, atingindo 3 m em marés de águas-vivas e 3.5 m em marés de águas-vivas equinociais. De acordo com os dados registados na bóia de Faro, desde 2001, pelo Instituto Hidrográfico (disponíveis em http://www.hidrografico.pt/boias-ondografo.php), durante a época balnear (junho a setembro) a temperatura da água do mar mantém-se acima de 18º C, atingindo valores até 24º C em agosto e setembro.

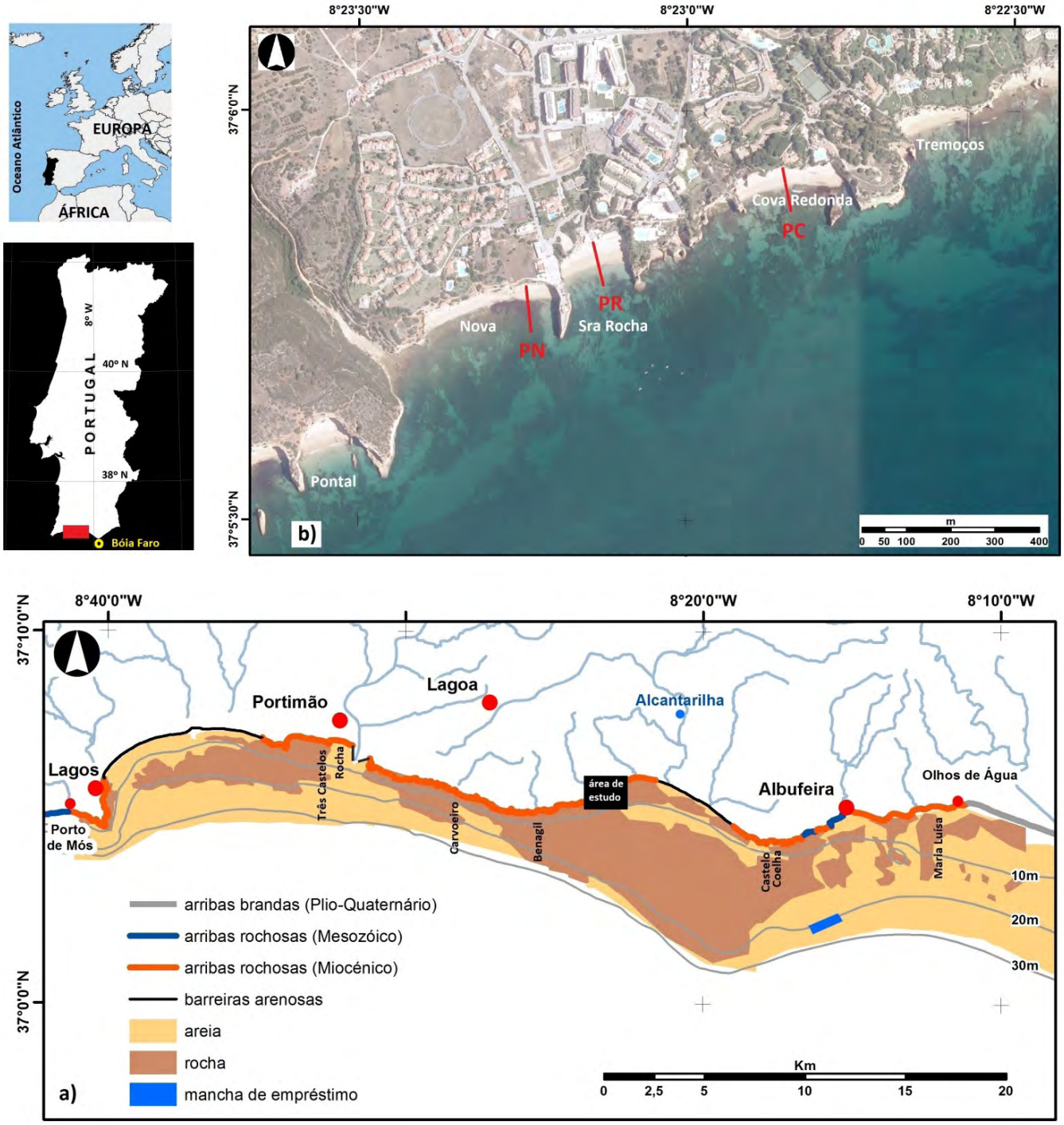

Figura 1 – Enquadramento da área de estudo. a) Geomorfologia da zona costeira do Barlavento do Algarve. Principais localidades assinaladas com círculos vermelhos, estação meteorológica de Alcantarilha assinalada com círculo azul. Localização das praias mencionadas no texto. Área da mancha de empréstimo utilizada na alimentação artificial assinalada a azul. b) Localização dos perfis de controlo das praias: PN – praia Nova, PS- praia Senhora da Rocha; PC, praia da Cova Redonda. (ortofotografia de 2012).

Figure 1 – Geographical setting of the study area. a) Geomorphology of the coastal area of Barlavento Coast. Main cities (red circles); Alcantarilha meteorological station (blue circle); Area of dreging site used for beach nourishment (blue).b) Control profile location:. PN – Nova beach; PS – Senhora da Rocha beach; PC – Cova Redonda beach (aerial ortophotograph 2012).

Figura 2 – Praia Nova, Senhora da Rocha e Cova Redonda em baixa-mar (BM) média, sob condições de agitação marítima média (painel esquerdo); em preia-mar de águas-vivas (PMAV), sob agitação marítima de tempestade (painel central); em preia-mar de águas- mortas (PMAM); sob condições de agitação marítima típicas do verão (painel direito).

Figure 2 – Nova, Senhora da Rocha and Cova Redonda beaches at average low-tide (BM), under average wave conditions (left panel); at high spring tide (PMAV), under storm conditions (central panel); at high tide on neap tide (PMAM), under average summer wave conditions (right panel).

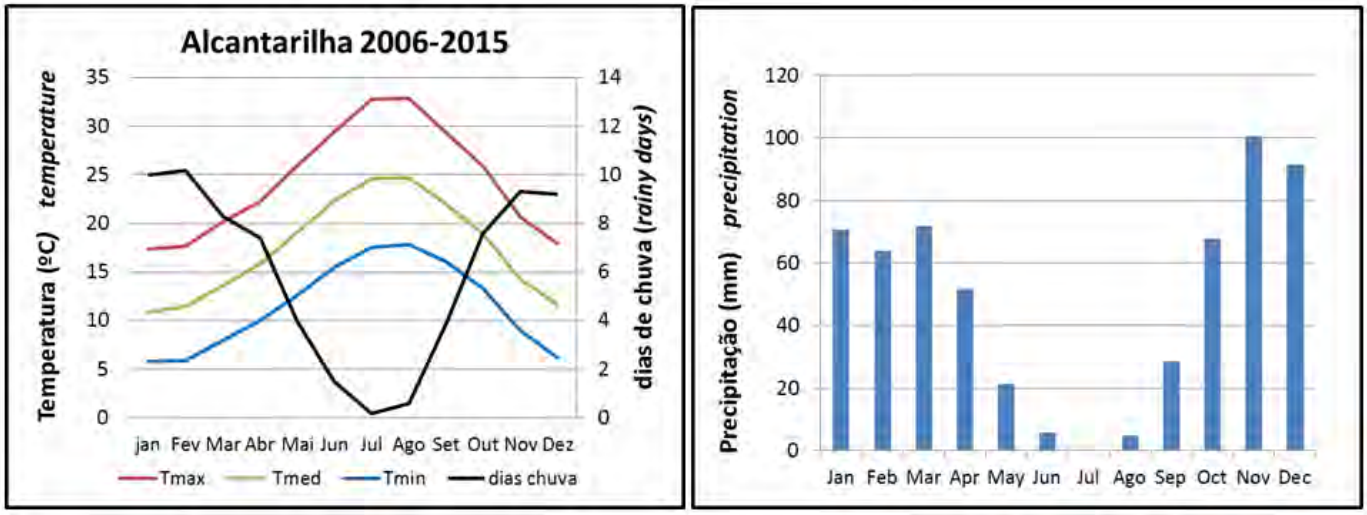

Figura 3 – Distribuição anual da precipitação e temperatura na década 2006-2015, registada na estação de Alcantarilha (localização na fig. 1a). Dados disponíveis em http://www.drapalg.min-agricultura.pt.

Figure 3 -. Annual distribution of precipitation and temperature in the 2006-2015 decade. Data from the Alcantarilha station (location on fig.1a), available on http://www.drapalg.min-agricultura.pt.

2.3. Ocupação turística

As características climáticas naturais do Algarve permitiram, a partir da década de 1960, o desenvolvimento de economia regional assente no turismo, baseada no produto "sol e praia", com uma forte componente sazonal, sendo agosto o mês de maior procura. A área de estudo está integrada na unidade morfológica do Barlavento do Algarve que corresponde à unidade central do Algarve, onde se concentra o núcleo da atividade turística da região. Ocupando apenas cerca de 30% do comprimento total da franja costeira do Algarve, o litoral do Barlavento acolhe 50% dos turistas que visitam ou utilizam as praias da região.

As dormidas nos estabelecimentos hoteleiros constituem um indicador da procura turística da região, cujas estatísticas estão disponíveis em http://www.turismodeportugal.pt. Utilizando esse proxy verifica-se que a evolução da ocupação dos estabelecimentos hoteleiros no Algarve na última década revela o efeito da crise económica global de 2009 traduzido na diminuição das dormidas. Entre 2006 e 2014 a amplitude da variação do indicador de dormidas no Algarve foi de 25%, com valores mínimos em 2009 e máximos em 2015 (fig.4). Em 2015, o valor de dormidas atingiu 116% do valor médio do período 2006-2014.

3. Perigo associado à geodinâmica das arribas

A evolução das arribas cortadas nos calcarenitos miocénicos do Barlavento processa-se segundo uma sequência descontínua e intermitente de movimentos de massa que se revestem de múltiplas formas, desde os grandes movimentos associados ao colapso de cavidades cársicas, que podem deslocar dezenas de milhares de metros cúbicos, com recuos instantâneos locais de mais de uma dezena de metros, ao simples desprendimento de pequenos blocos decimétricos. Em média, anualmente 0.2% da frente costeira de 46 km de arribas cortadas em miocénico é afetada por movimentos de massa (Marques, 1994, 1997; Teixeira, 2006, 2014). Os produtos dos movimentos de massa acumulados na base das arribas são, regra geral, rapidamente remobilizados pela ação direta da ondulação, constituindo fonte sedimentar importante das praias, podendo permanecer no sopé das vertentes alguns blocos mais resistentes ou de maior dimensão, por períodos de décadas. Na última década, na área de estudo, foram registados 10 movimentos de massa com largura superior a 1 m (fig. A na SI-I), mobilizando volume de 4600 m^3 e afetando frente de mar de 95 m. O movimento de maiores dimensões ocorreu em 29 de Novembro de 2014, promovendo recuo instantâneo máximo da crista da arriba de 7 m (fig. B na SI-I).

A geodinâmica natural das arribas e o modelo de ocupação turística do Barlavento determinam a existência de perigo para os utentes das praias. O regulamento do Plano de Ordenamento da Orla Costeira Burgau-Vilamoura (Resolução Conselho de Ministros nº 33/99, de 27 de abril) define especificamente a largura das faixas de risco para o mar, associadas à geodinâmica das arribas equivalente a 1.5x a altura da arriba rochosa. Com base na análise de mais de uma centena de movimentos de massa registados entre 1995 e 2014, Teixeira (2014) definiu tabela de perigosidade (de probabilidade de ocorrência) em função do afastamento à base da arriba. Os resultados então obtidos mostram que, na eventualidade de ocorrência de um movimento de massa, um utente repousando na

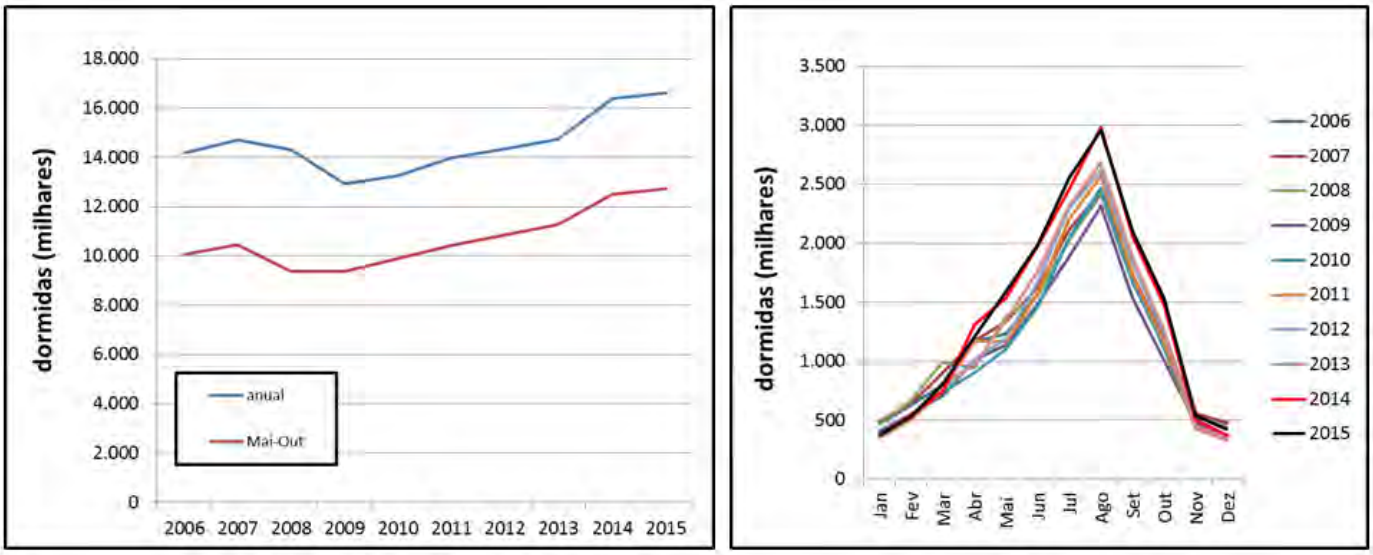

Figura 4- Evolução anual e mensal do nº de dormidas nos estabelecimentos hoteleiros, aldeamentos e apartamentos turísticos do Algarve na década 2006-2015. Dados de Turismo de Portugal, disponíveis em http://www.turismodeportugal.pt

Figure 4 – Annual and monthly evolution of the number of overnight stay (hotels, apartment hotels and tourist apartments) Data from Turismo de Portugal available on http://www.turismodeportugal.pt

areia de uma praia a uma distância superior a 0.86x a altura da arriba tem mais de 50% de probabilidade de não ser atingido pelos detritos gerados pelo movimento. Essa probabilidade sobe para 95% se a distância à base da arriba atingir 1.5x a altura da arriba. A partir destes resultados, a Agência Portuguesa do Ambiente elaborou cartografia de perigosidade em todas as praias suportadas por arribas rochosas do Algarve, sendo a informação colocada em painéis em todos os pontos de acesso às praias (disponível em http://www.apambiente.pt).

A figura 5 reproduz a cartografia resultante dessa informação nas praias Cova Redonda, Senhora da Rocha e Nova. Nessa cartografia individualizam-se duas faixas de perigo: a faixa vermelha (perigo elevado) corresponde à zona onde, na eventualidade de ocorrer desmoronamento, a probabilidade de ser atingida pelos detritos de rocha é superior a 50%. A faixa amarela (perigo moderado) cobre a área onde a probabilidade de ser atingida pelos detritos é inferior a 50%. Na área remanescente do areal não abrangida pelas duas faixas a probabilidade de ser atingida por detritos de eventual movimento de massa é inferior a 5%.

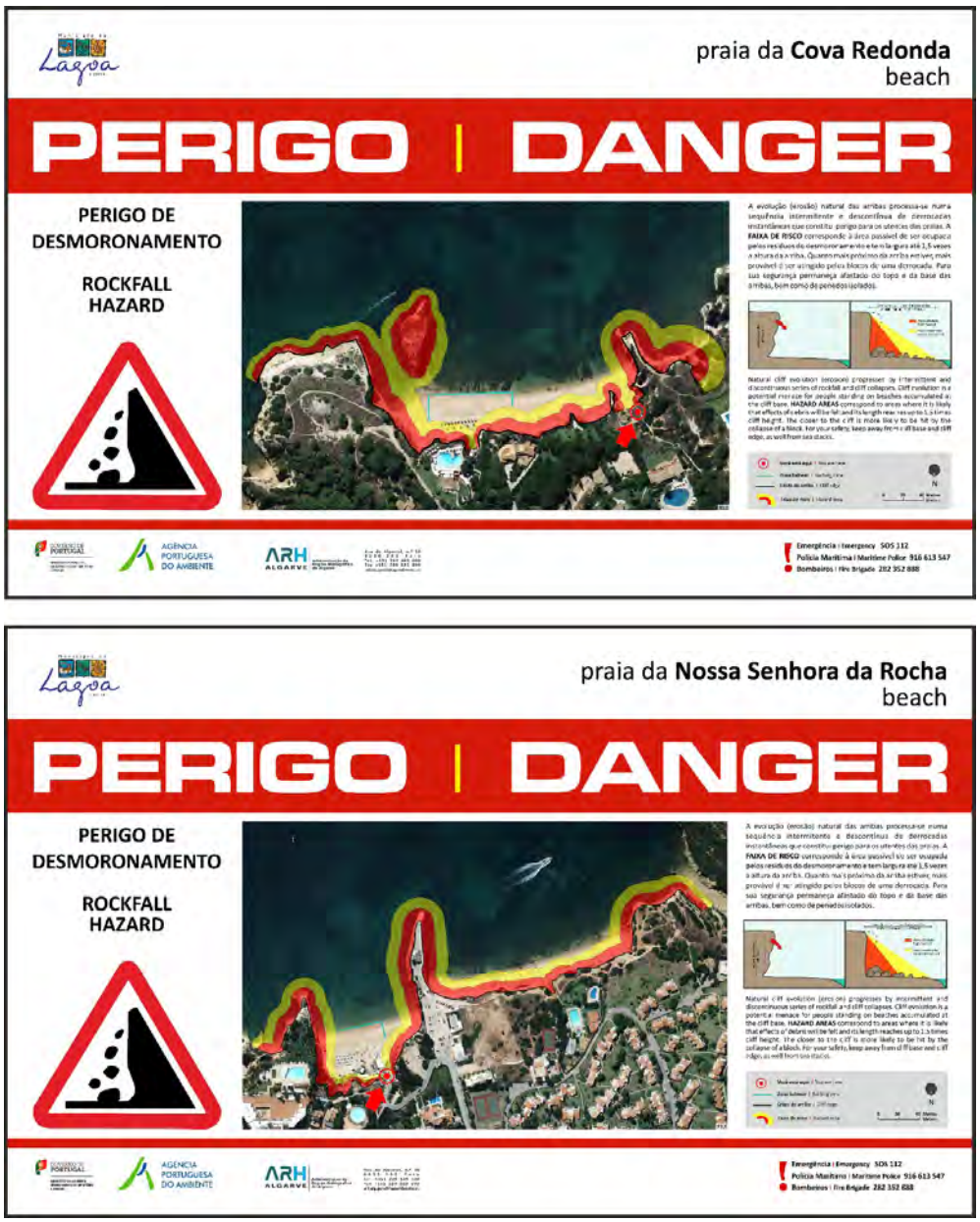

Figura 5 - Placas informativas das faixas de perigo, nas praias Cova Redonda, Senhora da Rocha e Nova. Disponível em http://www.apambiente.pt/index.php?ref=16&subref=7&sub2ref=10&sub3ref=923

Figure 5 – Sea cliff hazard signs of Cova Redonda, Senhora da Rocha and Nova beaches. Available on http://www.apambiente.pt/index.php?ref=16&subref=7&sub2ref=10&sub3ref=923

4. A alimentação artificial das praias

A alimentação artificial de praias é prática corrente em engenharia costeira, utilizada com objetivos diversos, seja o combate à erosão costeira (Van Rijn, 2011; Pinto *et al.* 2015), seja como medida preventiva do galgamento ou inundação (Hanson *et al.*, 2002, Gallien *et al.* 2015), ou visando o aumento da área disponível para os utilizadores da praia (Vera-Cruz, 1972), ou a melhoria do conforto dos utentes através da alteração da granulometria da areia (Anthony *et al.*, 2011).

A alimentação artificial das praias Nova e Cova Redonda decorreu entre agosto e setembro de 2014, quando foram depositados 157.200 m^3 de areia, repartidos pelas praias Nova (90.000 m^3) e Cova Redonda (67.200 m^3), correspondente a uma densidade de enchimento de cerca de 300 m^3/metro linear do comprimento da praia. A opção de alimentação artificial de praias assentou na deposição de areia diretamente na zona subaérea, na medida em que permite a utilização imediata da praia após a intervenção, apesar de implicar inevitáveis perdas decorrentes do subsequente reajuste do perfil de praia (Van de Graaff *et al.*, 1991). A experiência obtida em anteriores intervenções de alimentação artificial no Algarve mostra que no primeiro inverno após a deposição na zona subaérea o perfil de praia perde em média 25% da largura inicial após a conclusão da obra (Teixeira, 2011), pelo que os projectos de intervenção usualmente consideram sobrealimentação na zona subaérea da praia.

Na alimentação artificial foi utilizada mancha de empréstimo localizada ao largo (fig.1a), a profundidade de 20 m a 25 m, constituída por areias grosseiras com diâmetro médio de 1.0 mm (D_{50}=0.0 phi), com teor médio de carbonatos de 25%, com calibre superior à das areias nativas das praias. No Barlavento do Algarve a alimentação artificial foi executada pela primeira vez na praia da Rocha em 1970 (Gomes e Weinholtz, 1971) e posteriormente, em 1998, nas praias dos Três Castelos e Tremoços (Teixeira, 2011). Nestes três casos, a alimentação artificial foi complementada com a construção de estrutura de retenção de areia (molhes ou esporões), como forma de assegurar a longevidade da alimentação artificial e minimizar as perdas longilitorais. No caso em estudo, nas praias alimentadas não foi feita qualquer estrutura de contenção, antecipando que o recorte indentado da costa e o encaixe das praias, contidas entre pontais salientes, servisse o efeito natural de retenção das areias depositadas de forma artificial.

5. Métodos

5.1. Ocupação das praias

No sentido de proceder à avaliação da ocupação das praias da área de estudo foi utilizada vasta série de fotografias obtidas em locais que permitem a cobertura integral do areal e com definição suficiente que possibilite a contabilização da totalidade das pessoas presentes quer no areal, quer no plano de água associado, incluindo os utentes a banhos, no momento da obtenção da fotografia. Além das fotografias obtidas em pontos estratégicos em terra, foram também utilizadas as fotografias obtidas no âmbito das campanhas de monitorização da costa, quer as fotos aéreas oblíquas obtidas a bordo de aeronave, quer as fotos obtidas a bordo de embarcação. Uma vez que a intervenção de alimentação artificial foi executada em 2014, já no período de recuperação da atividade turística (fig. 4), e no sentido de absorver as alterações dos padrões de ocupação das praias do Algarve associados às oscilações da actividade económica, optou-se por utilizar os dados anteriormente à alimentação artificial por um intervalo mais largo, cobrindo o período pré, durante e pós crise económica global (2006-2014).

As fotografias obtidas durante o intervalo temporal de uma década, entre maio de 2006 e maio de 2016, repartidas por todo o ano, cobrem o intervalo horário entre as 8h00m e as 20h00m. No período anterior à intervenção de alimentação artificial (2006-2014), as fotografias foram obtidas de forma aleatória, determinadas pelas campanhas regulares de monitorização da evolução da costa. Após a intervenção houve um esforço maior de recolha de informação, concentrado na época balnear, por forma a caracterizar quer o efeito da alimentação artificial, quer o padrão sazonal de ocupação das praias.

As três praias em análise têm orientação longitudinal, sendo limitadas por pontais rochosos com direção próxima de N-S, enquadramento que implica a existência de sombra nos areais nas primeiras horas do dia e no final da tarde. Desta circunstância física, aliada ao usual padrão da prática balnear, resulta que no semestre entre maio e outubro a utilização das praias seja sobretudo concentrada entre as 10h30m e as 18h30m. Assim, para uniformizar a informação no período anterior e posterior à intervenção de alimentação artificial das praias, foram utilizadas as fotografias obtidas nos dias de semana entre as 10h30m e as 18h30m entre maio e outubro, e nos restantes meses, as fotografias obtidas no intervalo entre duas horas após o nascer do sol e duas horas antes do pôr do sol. Este conjunto de informação utilizada traduz-se num total de 603 observações (quadro I na SI-II).

Perante o recorte quase linear em planta e face à pequena variação altimétrica do topo das arribas, as faixas de perigo correspondem aproximadamente a bandas paralelas à base das arribas. A delimitação das faixas de perigo sobre as fotografias foi feita assumindo esse padrão linear, tomando como referências auxiliares pontos específicos para delimitar os limites das faixas, utilizados sistematicamente em todas as observações. Em cada fotografia analisada foi contabilizado o número total de utentes, repartidos por três grupos, consoante a sua localização relativamente às faixas de perigo das

arribas: o grupo que ocupa a faixa de perigo máximo (faixa vermelha), o grupo que ocupa a faixa de perigo moderado (faixa amarela) e o grupo que ocupa a área fora das faixas anteriores (risco baixo). O número de pessoas contabilizadas inclui todas as faixas etárias, incluindo crianças.

5.2. Perfis e levantamentos topohidrográficos

O levantamento periódico e sistemático de perfis de praia de controle num vasto conjunto de praias do Algarve é rotina da Agência Portuguesa do Ambiente (e dos organismos responsáveis pela gestão costeira que a antecederam) desde 1997. O levantamento periódico de perfis teve início em 2001, nas praias Nova e Senhora da Rocha e, em 2012, na praia da Cova Redonda. Os perfis de praia são realizados em locais constantes, no areal seco da praia subaérea com extensão condicionada pela altura da maré mas atingindo sempre cota +2m (ZH). Os levantamentos topohidrográficos utilizados no presente estudo correspondem aos levantamentos realizados no âmbito da obra de alimentação artificial das praias (escala 1:2000), antes (julho 2014), após (setembro 2014) e um ano após a intervenção (julho 2015).

6. Resultados e discussão

6.1. Alimentação artificial das praias

As oscilações do perfil de praia monitorizado na praia Nova, localizado no terço nascente da enseada (fig.1b), mostram que antes da alimentação artificial a amplitude da variação da largura da praia (medida sobre a curva +2m-ZH) atingia 40 m, cerca do dobro da largura média da praia (23 m) (fig.6). Apesar da magnitude das oscilações do areal, o perfil da praia mantinha-se essencialmente constante, exibindo apenas o elemento face da praia, com inclinação de 0,13 (7.4º).O enchimento da praia Nova produziu uma praia com um acréscimo imediato de 50m de largura, superior à largura total das faixas de risco elevado e moderado, associadas à geodinâmica das arribas. Após o primeiro Inverno, a largura média da praia atingiu 63 m, a que corresponde uma diminuição da largura da praia de 19%. Após o segundo inverno a largura média da praia era ainda de 64m, o que atesta a estabilidade das dimensões do areal. A evolução do perfil desta praia acusa a oscilação, anteriormente identificada, com uma face da praia com declive médio de 7º e com oscilação anual da largura de cerca de 15 m. Na praia da Senhora da Rocha, não submetida a qualquer alimentação, o perfil de praia manteve-se com a oscilação sazonal identificada na década anterior, mas os perfis de praia obtidos no segundo ano após a alimentação das praias contíguas mostram aparente reforço. Esta observação, que deverá ser acompanhada de perto no futuro próximo sugere que esta praia poderá ter já capturado uma fração da areia depositada na praia Nova. No perfil da praia da Cova Redonda, com largura média de 34 m antes da alimentação, o enchimento do areal possibilitou aumento imediato da largura para 82 m. Após o primeiro inverno, na sequência do reajustamento da areia às dimensões do encaixe da praia, a largura média atingia 63 m, traduzindo-se na redução de 40%, relativamente ao enchimento inicial. Após o segundo inverno, a largura média da praia é de 58 m, o que equivale a perda de 50% da alimentação artificial realizada em 2014. Apesar do sucessivo encurtamento do areal, o perfil da praia mantém-se essencialmente invariante, com face de declive de 7º. A diferença de perdas de areia nas praias Nova e Cova Redonda no período após a alimentação artificial mostra que a mobilização da areia tem componente longilitoral considerável e que os pontais que limitam as praias a nascente têm capacidade diferente de retenção dos sedimentos em trânsito por efeito da deriva litoral. O pontal nascente da praia da Cova Redonda, que mergulha a 3.5 m abaixo do nível médio do mar é menos eficaz na retenção de areia do que o pontal da praia Nova, que mergulha aos 5 m abaixo do nível médio do mar.

Com base nos levantamentos topográficos executados em julho de 2014 e em julho de 2015, previamente e após a alimentação artificial, foram calculadas as áreas de areal existentes nas três praias de estudo e avaliado o espaço disponível para os utentes, sob condições de agitação marítima média de verão (Hs=0.5 m), em condições de baixa-mar média, meia maré e preia-mar média. Utilizando as equações desenvolvidas por Teixeira (2009b) para o cálculo do espraio da onda na costa sul do Algarve, verifica-se que nas três praias, com declives muito similares, a altura do espraio das ondas atinge aproximadamente 1 m acima do plano de água da maré. Assim, foram calculadas as áreas do areal seco limitadas pelas curvas de 2 m (ZH), para a baixa-mar média, 3 m (ZH) para a meia maré e 4 m (ZH) para a preia-mar média. Esta informação foi cruzada com a cartografia das faixas de perigo, considerando-se, além das duas faixas de perigo elevado (vermelha) e perigo moderado (amarela), uma terceira faixa que contém o areal remanescente. Esta terceira faixa de perigo (baixo - azul) corresponde à área do areal onde, na eventualidade de ocorrer movimento de massa das arribas, a probabilidade de ser atingida pelos detritos é inferior a 5% (Teixeira, 2014).

Os resultados mostram que antes da alimentação artificial, na praia Nova, face à pequena largura da praia, a maior parte do areal seco estava incluído nas faixas de perigo máximo (fig.7) e moderado, pelo que os seus utentes só estavam salvaguardados desse perigo quando a tomar banho (fig.5). A meia maré, todo o areal seco estava contido nas faixas de perigo (fig.7). Nas mesmas condições de maré, na Cova Redonda a área do areal seco disponível fora das faixas de perigo máximo e moderado era de apenas 24%, percentagem que se

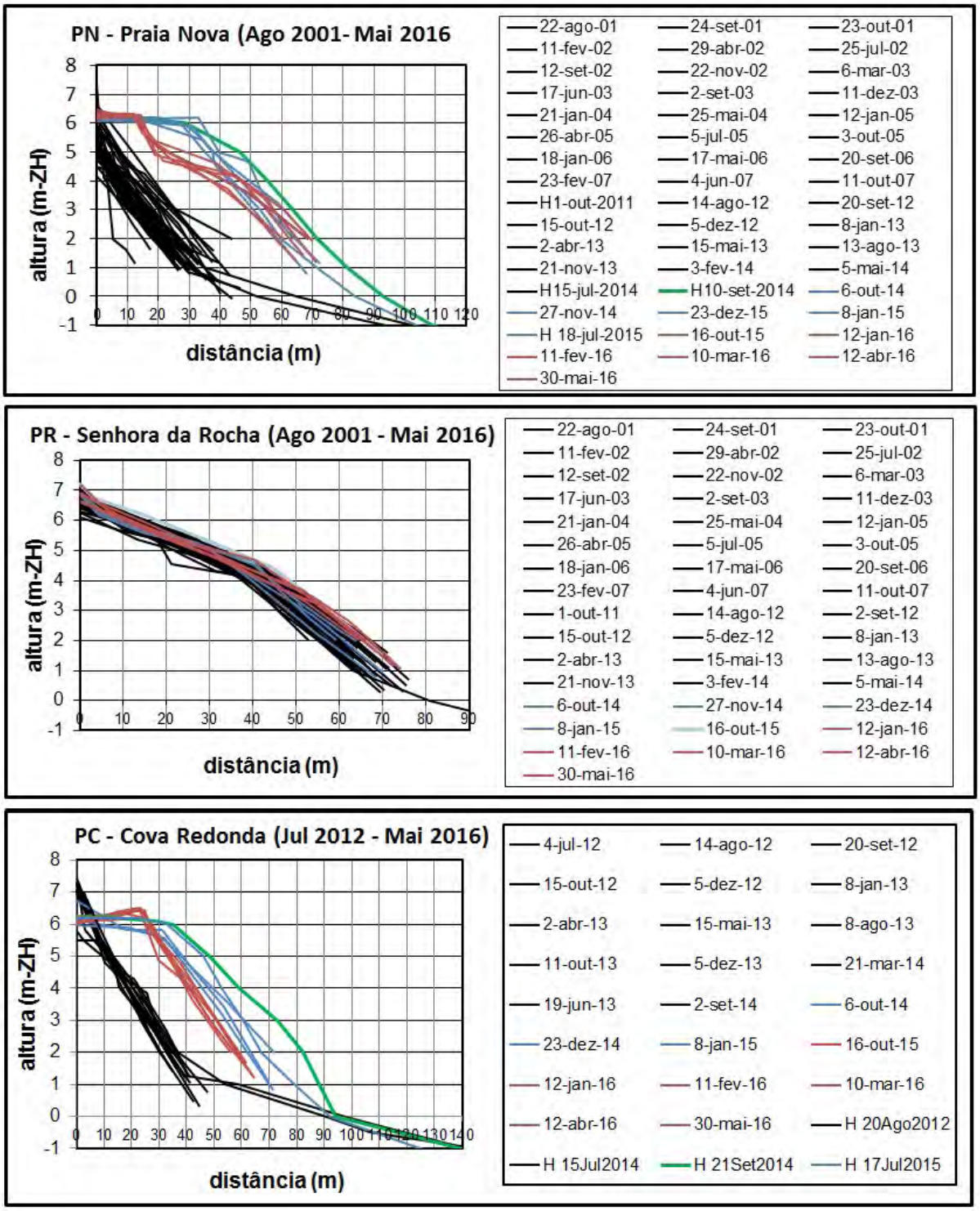

Figura 6 - Variação dos perfis da Praia Nova, Senhora da Rocha e Cova Redonda (localização na figura 2). Ordenadas em metros referentes ao Zero Hidrográfico (ZH), plano convencional localizado cerca de 2 m abaixo do nível médio do mar. Perfis antes da alimentação artificial (a negro), após a alimentação artificial (verde), no primeiro ano após o enchimento (azul) e no segundo ano após o enchimento (vermelho).

Figure 6 – Variation of cross-shore profiles on Nova, Senhora da Rocha and Cova Redonda beaches (location on fig. 1d). Y-axis (m) relative to Hidrographic Zero datum (ZH), Portuguese conventional plan lying ≈2 m below mean sea-level. Before beach nourishment (black), after beach nourishment (green); first year after beach nourishment (blue); second year after beach nourishment (red).

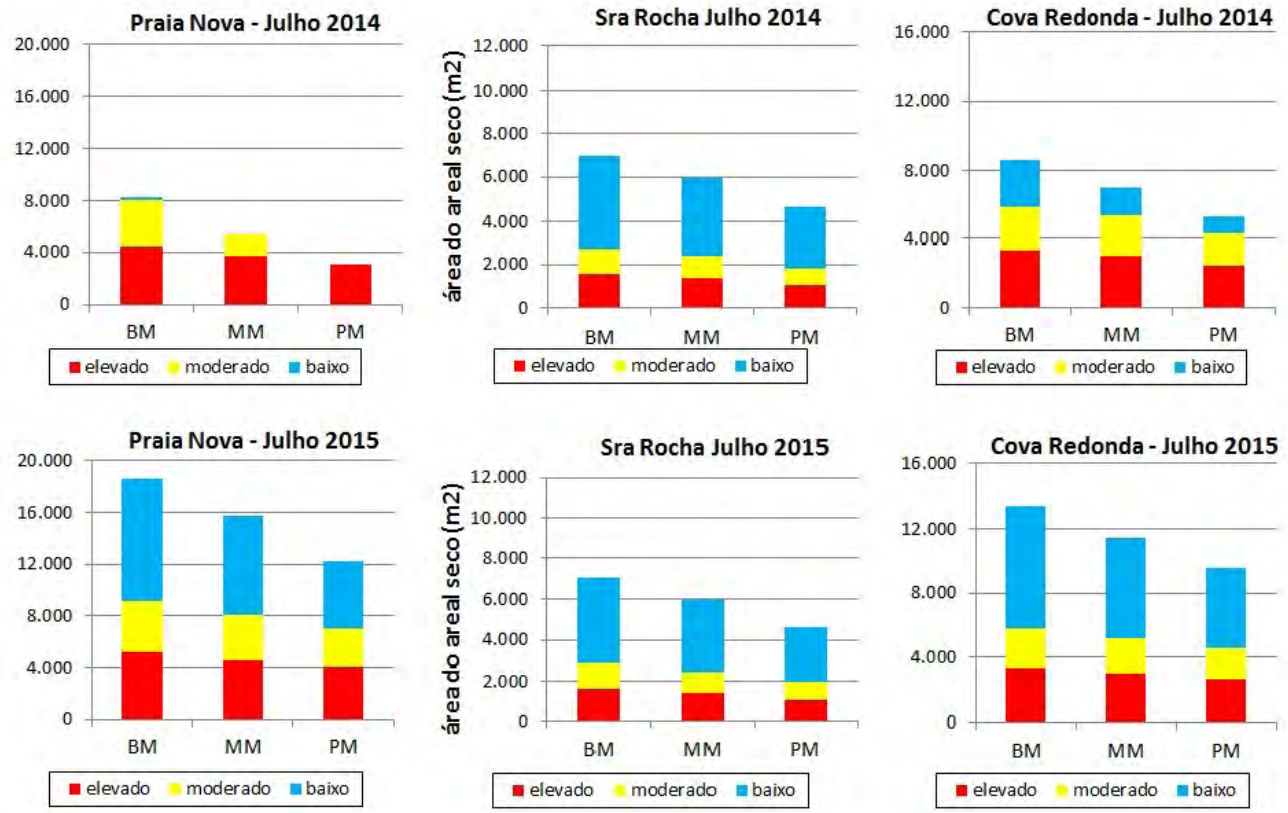

Figura 7- Variação da área de areal seco, antes (painel superior) e após (painel inferior) a alimentação artificial, em função do estado da maré em condições de agitação marítima médias do verão. BM – baixa-mar média; MM – meia maré; PM – preia-mar média. Áreas do areal seco contidas na faixa de perigo máximo (vermelho), na faixa de perigo moderado (amarelo) e na faixa de perigo baixo (azul),

Figure 7 - Dry beach area, before (upper panel) and after (lower panel) beach nourishment, depending on the state of the tide, under average summer wave conditions. BM - average low tide; MM – half-tide; PM - average high tide. Dry sand areas on the maximum hazard zone (red), moderate hazard zone (yellow) and low hazard zone (blue).

reduzia para 18% em condições de preia-mar média. Na praia da Senhora da Rocha, face à largura da praia, existe fração significativa do areal permanentemente fora das faixas de perigo máximo e moderado. Neste caso, estas faixas de perigo estão sobretudo dispostas em redor dos promontórios que limitam o areal e ocupam 40% do areal disponível.

Os resultados ilustrados na figura 7 mostram que, do incremento da largura da praia associado à intervenção de alimentação artificial das praias Nova e Cova Redonda, resultou a ampliação muito significativa do areal seco disponível fora das faixas de risco máximo e moderado. Em condições de agitação e maré média de verão, na praia Nova, anteriormente à alimentação artificial, não havia qualquer porção do areal seco fora daquelas faixas de risco. Após a intervenção, a área contida na faixa de risco baixo ocupava já mais de 48% do areal existente. Na praia da Cova Redonda, em situação de preia-mar média no verão, a fração do areal na faixa de risco baixo era apenas de 18%, antes da intervenção, valor que aumentou para 52% após a alimentação artificial.

6.2. Ocupação global das praias

Tal como seria de esperar, a ocupação das três praias apresenta padrão de ocupação com forte componente sazonal, acompanhando a variação anual da temperatura e da ocupação turística. O pico da ocupação em qualquer das três praias está concentrado no mês de agosto coincidindo com o mês de maior procura turística da região (fig. 8). Sob o mesmo clima mediterrânico que o do Algarve, no sul da Califórnia o mês de maior ocupação é julho (Dwight *et al.*, 2007). Já nas praias mediterrâneas, como na Catalunha, (Guillén *et al.*, 2008) ou na Riviera francesa (Balouin *et al.*, 2014) o pico da ocupação ocorre em agosto. Nas praias do Algarve verifica-se ainda um pico secundário na ocupação coincidente com o período da Páscoa, mais pronunciado quando esta festividade ocorre na segunda quinzena de abril (caso dos anos de 2006, 2011 e 2014).

Os resultados da distribuição anual da ocupação das três praias (fig. 8) mostram que na praia da Senhora da Rocha, em que não houve qualquer intervenção de

alimentação artificial e que serve como praia de controlo, não houve alterações significativas na ocupação da praia, à exceção do ligeiro incremento de ocupação no trimestre entre agosto e outubro. Em termos globais anuais, o incremento de ocupação na praia da Senhora da Rocha foi 13%. Também na praia da Cova Redonda, os resultados mostram estabilidade quer no padrão de distribuição anual da ocupação, quer na magnitude da mesma, com ligeiro incremento da ocupação anual (11%) após a alimentação artificial. Este incremento de ocupação nestas duas praias é equivalente ao incremento da procura turística (fig.4), pelo que pode ser atribuído à melhoria da atividade económica pós 2014, traduzida num aumento da procura da praia pelos turistas. Já na praia Nova, no período após a intervenção de alimentação artificial, verificou-se incremento muito significativo da procura do areal, registando-se aumento da ocupação da ordem de 4 vezes (fig.8), concentrado no período entre maio e outubro. Estes resultados mostram que, nesta praia, a alimentação artificial produziu efeito muito relevante no incremento de atração turística, ao contrário do registado na praia da Cova Redonda. Sem ter havido qualquer alteração nos acessos ou estacionamento automóvel que fomentasse o aumento da procura da praia Nova, a razão mais plausível para o incremento da utilização desta praia deverá estar associada a alteração do comportamento dos hóspedes dos empreendimentos mais próximos, que usualmente não utilizavam a praia. Uma praia recentemente ampliada, localizada a curta distância do alojamento turístico onde estão hospedados terá sido motivo suficiente para a procurarem, seja como alternativa a outras praias mais distantes ou às próprias piscinas dos empreendimentos.

6.3. A ocupação das faixas de perigo

A informação cartográfica sobre a distribuição espacial das faixas de perigo das arribas está disponível em todos os acessos às praias (fig. 5), alertando para o risco associado à geodinâmica das arribas. A figura 9 sintetiza a distribuição anual (com valores médios mensais) da ocupação das três faixas dos areais (perigo elevado-vermelho, perigo moderado-amarela e perigo baixo- azul) nas três praias nos períodos antes e após a intervenção de alimentação artificial nas praias Nova, Senhora da Rocha e Cova Redonda.

Na praia da Senhora da Rocha, a variação da distribuição da ocupação das faixas de perigo revela alterações muito pouco significativas, verificando-se que, no período 2014/2016, a ocupação das faixas de perigo elevado e moderado é apenas 2% inferior à que se verificava no período anterior à intervenção nas praias contíguas. Este resultado indicia que o efeito da colocação da sinalização na redução da ocupação das faixas de perigo é muito residual, demonstrando que a sinalização reforçada em 2014 não teve ainda efeito significativo na alteração do comportamento dos utentes face ao perigo, apesar de publicitado em todos os acessos às praias. No entanto, verifica-se que a densidade de ocupação do areal nas faixas de perigo baixo é muito superior (cerca do dobro) do que a densidade de ocupação nas áreas abrangidas pelas faixas de risco elevado e moderado (quadro II na SI-II). Este resultado indicia que os utentes tendem a utilizar áreas de menor perigo, em detrimento das áreas assinaladas como mais perigosas.

Na praia da Cova Redonda, a alteração do padrão de ocupação das faixas de perigo é notória, com a diminuição muito significativa da ocupação das faixas de perigo elevado e moderado (quadro II na SI-III). Em termos médios anuais, no período anterior à alimentação artificial da praia, 44% dos seus utentes permaneciam naquelas faixas, valor que reduziu para 12% após a intervenção. Este resultado deve ser atribuído ao aumento do areal disponível e ao consequente afastamento dos utentes da base das arribas em direcção ao plano de água. Apesar do aumento do areal, ainda se registam utentes com comportamentos de risco, verificando-se que, em média, 3% dos utentes permanecem na faixa de perigo elevado (faixa vermelha) e 9% utilizam o areal contido na faixa de perigo moderado (faixa amarela).

Na praia Nova, à semelhança do registado na praia da Cova Redonda, após a alimentação artificial verifica-se alteração de comportamento dos seus utentes, com a migração da ocupação rumo ao plano de água e consequente afastamento da base das arribas (fig. C da SI-I). Nesta praia, em que antes da alimentação artificial 92% dos seus utentes permaneciam nas faixas de perigo (71% na faixa vermelha e 21% na faixa amarela), após a intervenção essa percentagem reduziu muito significativamente para 17% (7% na faixa vermelha e 9% na faixa amarela). Em termos percentuais, a ocupação da faixa de perigo elevado reduziu para 1/10 da ocupação registada antes da intervenção. Apesar de a ocupação da praia Nova ter quadruplicado na sequência da intervenção, mesmo em termos absolutos se verifica uma redução de utentes em zonas de risco potencial. O número de utentes que no pico da ocupação no mês de agosto era de 91 nas faixas de perigo (65 na faixa vermelha e 24 na faixa amarela) passou a 67 após a intervenção (30 na faixa vermelha e 37 na faixa amarela).

A capacidade de carga das praias é um parâmetro usualmente utilizado, como indicador da disponibilidade física da praia em acomodar a sua utilização, havendo certo consenso nos valores padrão. Nas praias urbanas o valor guia para a área mínima aceitável por utente anda pelos 5 m^2/utente, podendo chegar a valores da ordem de 25 m^2/utente em praias naturais com custos de alojamento mais elevado (Roca, 2008 e referências aí incluídas). As praias em análise são do tipo intermédio entre aqueles extremos guia. O próprio Plano de Ordenamento da Orla Costeira vigente aponta para valores guia de capacidade

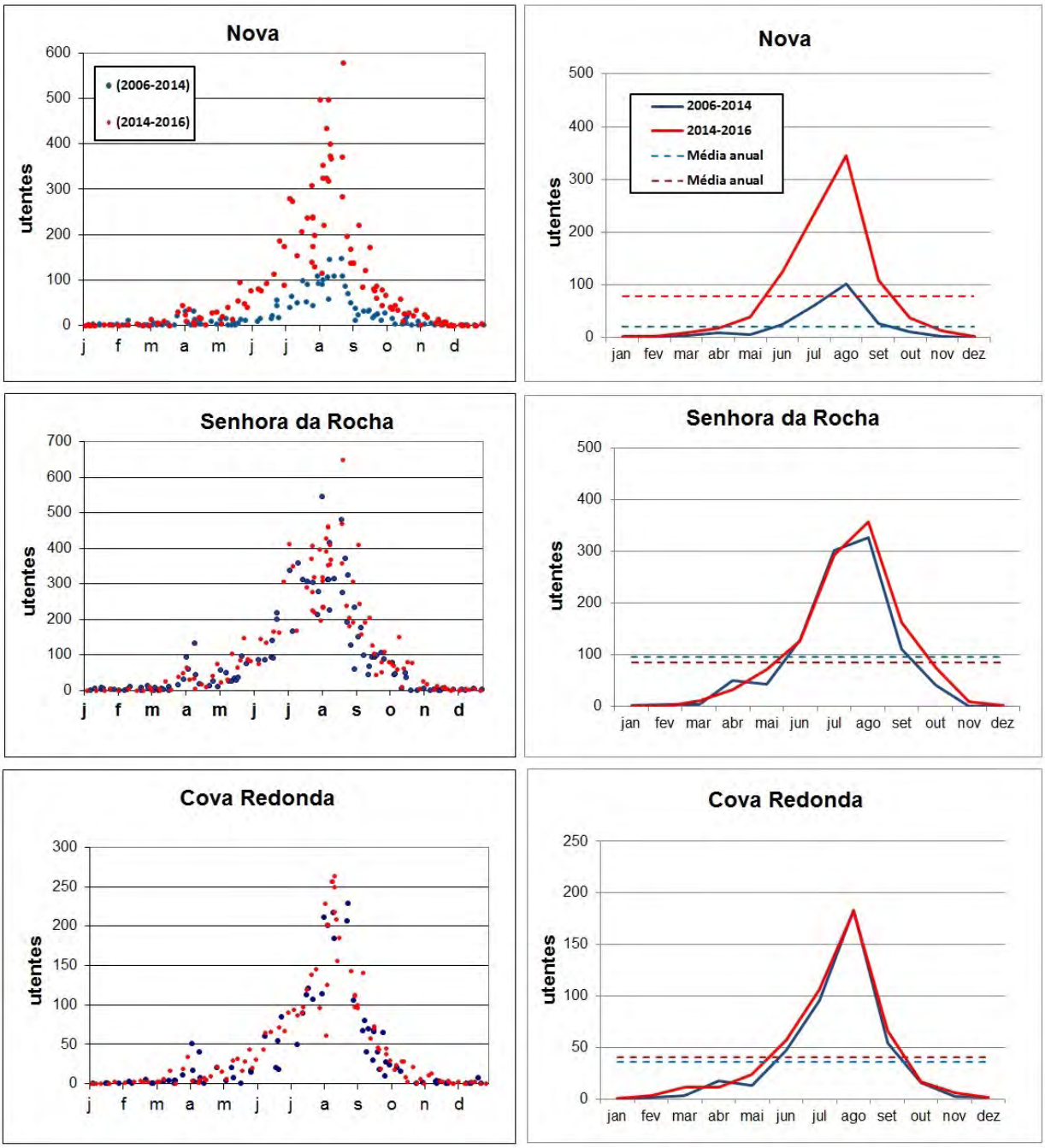

Figura 8 – Dados de ocupação das praias ao longo do ano entre maio de 2006 e maio de 2016, antes e após a alimentação artificial. Valores brutos (painel da esquerda) e médias mensais (painel da direita).

Figure 8 – Annual beach occupation data within the decade May 2006 – May 2016, before and after beach nourishment. Daily (left panel) and monthly average (right panel) beach occupation.

de carga de 15 m^2/utente para as praias em análise. Com base nos levantamentos topográficos de 2014 e 2015 e nos valores médios da ocupação das praias em Agosto para condições de agitação média a meia-maré (quadro II na SP-II), verifica-se que na praia da Senhora de Rocha o espaço real ocupado pelos utentes ronda 17-20 m^2/utente, sendo inferior na área da faixa de perigo baixo (13-16 m^2/utente). Na praia da Cova Redonda, a carga da praia antes da alimentação artificial na área da faixa de perigo baixo era de 17 m^2/utente.

Após a alimentação artificial das praias, a capacidade real de ocupação das praias na faixa de perigo baixo sofreu incremento muito significativo, tendo em consideração os valores guia de 15 m^2/utente. A densidade de ocupação quer da praia Nova, quer da praia da Cova Redonda tem agora valores superiores a 25 m^2/utente nas áreas das faixas de perigo baixo. Apesar do incremento do espaço disponível em ambas as praias, a utilização das faixas de perigo elevado e moderado continua a ocorrer, embora já de forma muito mais reduzida.

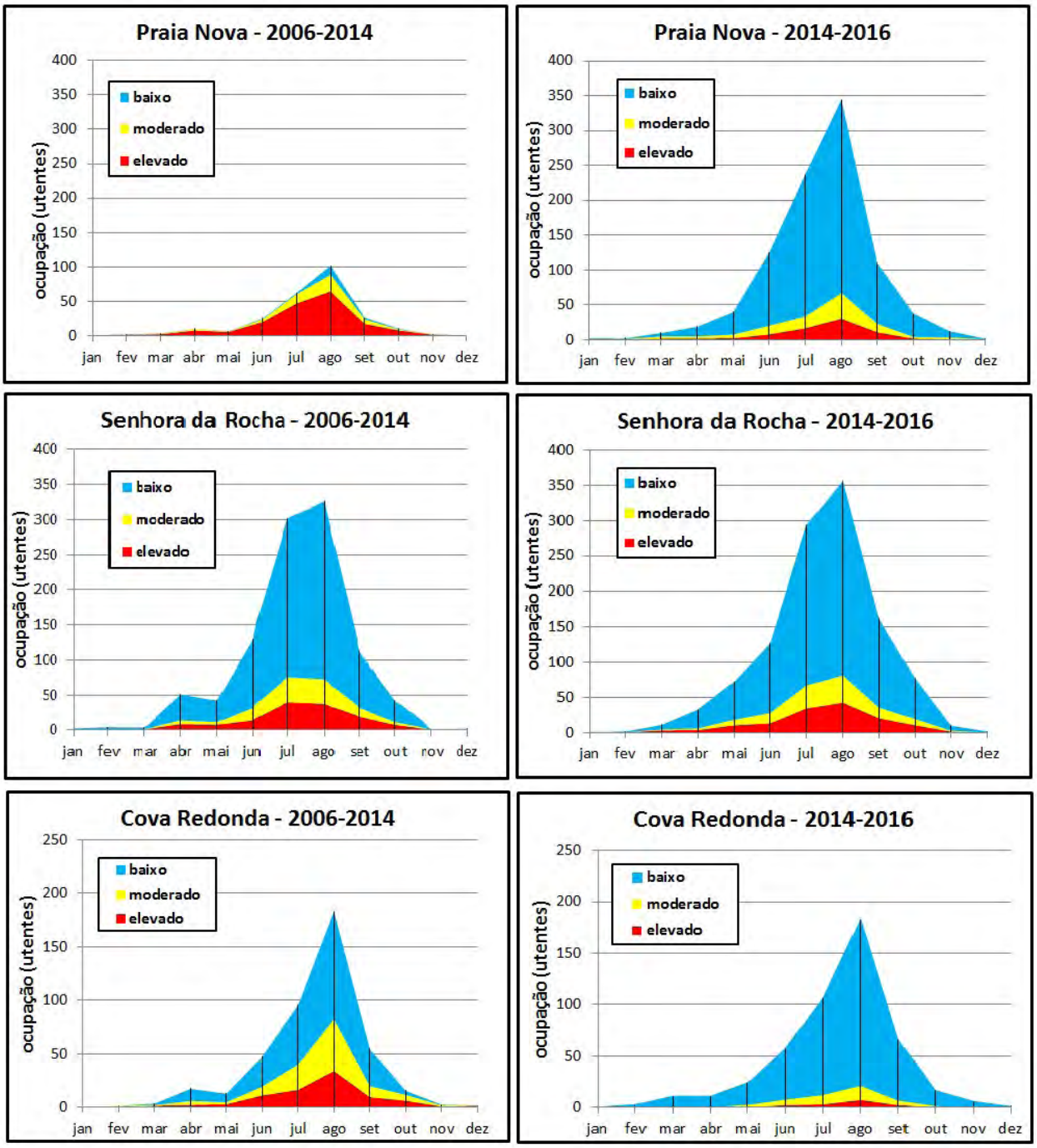

Figura 9 - Ocupação média mensal das praias, distribuídas pelas áreas de perigo elevado, moderado e baixo, antes (painel da esquerda) e após (painel da direita) a alimentação artificial.

Figure 9 - Monthly average beach occupation distributed by high (red), moderate (yellow) and low (blue) hazard areas, before (left panel) and after (right panel) beach nourishment.

7. Conclusões

A geodinâmica natural das arribas determina a existência de perigo para os utentes das praias encaixadas suportadas por arribas rochosas do litoral do Algarve. Para diminuir a frequência da ação direta das ondas na base da arriba e promover a utilização das praias fora das faixas de perigo das arribas, em 2014 foi executada alimentação artificial da zona subaérea das praias Nova e Cova Redonda, onde a área do areal seco a meia maré em condições de agitação média do verão na faixa de perigo baixo era respetivamente de 0% e 24%. A alimentação artificial das praias executada na fração subaérea permitiu o alargamento do areal em 50 m nas praias Nova e da Cova Redonda. Após o primeiro inverno, na sequência do ajuste natural do perfil de praia, a largura das praias foi reduzida em 19% e 40% respetivamente.

Contagens sistemáticas das pessoas presentes nas praias durante a década 2006-2016 no período antes e após a intervenção de alimentação artificial atestam inequivocamente a reação natural dos utentes ao enchimento da praia, traduzindo-se na sua migração instintiva e natural no sentido do plano de água, resultando no seu afastamento relativamente às faixas de perigo. Na sequência da intervenção, a ocupação das faixas de perigo elevado e moderado reduziu muito significativamente, de 92% para 17% na praia Nova e de 44% para 12% na praia da Cova Redonda. Esta redução contrasta com a baixa redução de 2% da ocupação das faixas de risco elevado e moderado medida na praia da Senhora da Rocha, não submetida a qualquer alimentação, que foi associada ao efeito do reforço da sinalização executado no mesmo ano.

Os resultados da evolução da ocupação das praias após a alimentação artificial mostram que enquanto na praia Nova a ocupação quadruplicou, na praia da Cova Redonda a ocupação sofreu ligeiro incremento, similar ao verificado na praia da Senhora da Rocha, atribuído ao aumento da procura associado à melhoria regional da atividade económica. Esta diferença de reação em duas praias contíguas mostra que, previamente à intervenção, não é possível antecipar a amplitude do incremento da utilização associado ao facto de a área disponível aumentar.

Os resultados apresentados e discutidos no presente trabalho demonstram que a alimentação artificial é medida eficaz na redução do risco para os utentes das praias suportadas por arribas rochosas, sendo no caso do Algarve, medida adequada na gestão do risco.

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Referências bibliográficas

Agência Portuguesa do Ambiente – www.ambiente.pt. Faixas de risco das arribas. Placas disponíveis em http://www.apambiente.pt/index.php?ref=16&subref=7&sub2ref=10&sub3ref=923

Anthony, E. J., Cohen, O. Sabatier, F. (2011) - Chronic offshore loss of nourishment on Nice beach, French Riviera: A case of over-nourishment of a steep beach? Coastal Eng. 58, 374-383. doi:10.1016/j.coastaleng.2010.11.001

Balouin, Y, Rey-Valette, H., Picand.-A. (2014) - Automatic assessment and analysis of beach attendance using video images at the Lido of Sète beach, France. Ocean & Coastal Manag. Vol.102, 114-122. doi:10.1016/j.ocecoaman.2014.09.006

Costa, M. , Silva, R., Vitorino, J. (2001) – Contribuição para o estudo do clima de agitação marítima na costa portuguesa. Com. 2ª Jornadas Portuguesas de Engenharia Costeira e Portuária. Associação Nacional de Navegação. Sines. CD-ROM, 20p.

Direção Regional de Agricultura e Pescas do Algarve. Estações meteorológicas automáticas. http://www.drapalg.min-agricultura.pt.

Dwight, R. H., Brinks, M. V., Kumar, G, S., Semenza, J. C. (2007) - Beach attendance and bathing rates for Southern California beaches. Ocean & Coast. Manag., Vol.50, 847-858. doi:10.1016/j.ocecoaman.2007.04.002

Guillén, J., García-Olivares, A., Ojeda, E., Osorio, A. Chic, O., González, R. (2008) - Long-Term Quantification of Beach Users Using Video Monitoring. Journ. Coast. Research, Vol.24, Issue 6, pp.1612-1619. doi:10.2112/07-0886.1

Instituto Português do Mar e da Atmosfera (IPMA). Daily weather forecast. www page, http://www.ipma.pt.

Instituto Hidrográfico – Bóia ondógrafo de Faro Costeira, disponíveis em http://www.hidrografico.pt/boias-ondografo.php.

Gallien, T.W, O'Reilly, W.C, Flick, R.E., Guza, R.T. (2015) - Geometric properties of anthropogenic flood control berms on southern California beaches. Ocean & Coast. Manag., Vol.105, 35-47. doi:10.1016/j.ocec.oaman.2014.12.014

Gomes, N. A., Weinholtz, M. B. (1971) - Evolução da embocadura do estuário do Arade (Portimão) e das praias adjacentes. Influência da construção dos molhes de fixação do canal de acesso ao Porto de Portimão. Emagrecimento da Praia da Rocha e sua reconstituição por deposição de areias dragadas no anteporto. Com. 3ªs Jornadas Luso-Brasileiras de Engenharia Civil, Lourenço Marques, Vol. III, p. III-4-1/27.

Hanson, H., Brampton, A. Capobianco, M., Dette, H.H., Hamm, L., Laustrup, C., Lechuga, A., Spanhoff, R. (2002) – Beach nourishment projects, practices, and objectives – a European overview. Coast. Engineering, 47, 81-11.

Marques, F.M.S.F. (1994) - Sea cliff evolution and related hazards in miocene terranes of Algarve (Portugal). 7th Int. Cong. of the I.A.E.G. Lisbon, Proc., V.4, 3109-3118.

Marques, F.M.S.F. (1997) – As arribas do Algarve, Dinâmica, Processos e Mecanismos, PhD. Thesis., Universidade de Lisboa, 556p. (não publicado).

Marques,F.M.S.F., Andrade, C. (2009) - Parecer sobre risco associado às arribas do Algarve. Fac. Ciências Univ. Lisboa Parecer para Administração da Região Hidrográfica do Algarve, Faro, Portugal, 25 pp., 2009. Disponível em biblioteca.turismodoalgarve.pt/getmedia.aspx?guid.0047.pdf

Pinto, C. A., Silveira, T., Taborda, R. (2015) – Alimentação artificial das praias da Costa da Caparica: síntese dos resultados de monitorização (2007 a 2014). Proc. 3ª Conf. Morf. Estuar. Cost., Faro, 47-48.

Pires, H. O. (1989) - Alguns aspectos do clima de agitação marítima de interesse para a navegação da costa de Portugal. O Clima de Portugal. Fasc. XXXVII, vol. 2. Instituto Nacional de Meteorologia e Geofísica, Lisboa, 34p.

Roca, E. Riera, C. Villares, M., Fragell, R., Junyent, R. (2008) - A combined assessment of beach occupancy and public perceptions of beach quality: A case study in the Costa Brava, Spain. Ocean & Coast. Manag. 51, 839-846. doi:10.1016/j.ocecoaman.2008.08.005.

Teixeira, S.B. (2006) - Slope mass movements on rocky sea-cliffs: A power-law distributed natural hazard on the Barlavento Coast, Algarve, Portugal. Cont. Shelf Research 26, 1077-1091. doi: 10.1016/j.csr.2005.12.013.

Teixeira, S.B. (2009a) - Geodinâmica, ocupação e risco na praia María Luísa (Albufeira), Administração da Região Hidrográfica do Algarve. Relatório, Faro, Portugal, 24 p. disponível em biblioteca.turismodoalgarve.pt/getmedia.aspx?guid. 0047.pdf

Teixeira, S. B. (2009b) - Demarcação do leito e da margem das águas do mar no litoral sul do Algarve, Administração da Região Hidrográfica do Algarve. 207p. Disponível em: http://pt.scribd.com/doc/306900059/Demarcacao-Do-Leito-e-Da-Margem-Das-Aguas-Do-Mar-No-Litoral-Sul-Do-Algarve#scribd

Teixeira, S. B. (2011) - A alimentação artificial de praias com dragados no Algarve. In: Coelho, C., Silva, O. A., Pinheiro, L. M. Gonçalves, D. S. (Eds). Dragagens – Fundamentos, Técnicas e Impactos. Universidade de Aveiro, Lusoimpress, pp. 221-240. ISBN 978-972-789-346-1.

Teixeira, S. B. (2014) - Coastal hazards form slope mass movements: Analysis and management approach on the Barlavento Coast, Algarve, Portugal. Ocean & Coast. Manag. 102, 285-293. http://dx.doi.org/10.1016/j.ocecoaman.2014.10.008.

Turismo de Portugal. Estatísticas do Turismo. http://www.turismodeportugal.pt

Van de Graaff, J. Niemeyer, H. D., Van Overeem, J. (1991) - Beach nourishment, philosophy and coastal protection policy. In: L. van de Graaff, H. D. Niemeyer and J. van Overeem (Eds), Artificial Beach Nourishments. Coastal Eng., 16: 3-22..

Van Rijn, L. C. (2011) - Coastal erosion and control. Ocean & Coast. Manag. 54, 867-887. doi:10.1016/j.ocecoaman.2011.05.004.

Vera-Cruz, D. (1972) - Artificial nourishment of Copacabana beach. Proceedings 13th Coastal Engineering Conference. New York: ASCE, 141-163.

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Nonlinear and dispersive wave effects in coastal processes*

José Simão Antunes do Carmo [a]

ABSTRACT

Numerical models are useful instruments for studying complex superposition of wave-wave and wave-current interactions in coastal and estuarine regions, and to investigate the interaction of waves with complex bathymetries or structures built in near-shore areas. The ability of the standard Boussinesq and Serre or Green and Naghdi equations to reproduce these nonlinear processes is well known. However, these models are restricted to shallow water conditions, and addition of other terms of dispersive origin has been considered since the 90's, particularly for approximations of the Boussinesq-type. Using the general wave theory in shallow water conditions, the different approaches commonly used in hydrodynamics studies in river systems, estuaries and coastal zones are initially addressed. Then, to allow applications in a greater range of shallow waters, namely in intermediate water conditions, a new set of extended Serre equations, with additional terms of dispersive origin, is presented and tested with available data in the literature. The hydrodynamic module, composed of the extended Serre equations, is then used as part of a morphodynamic model, which incorporates two more equations taking into account various processes of sediment transport. The wave velocity-skewness and the acceleration-asymmetry are taken into account and discussed based on numerical results and physical considerations.

Keywords: Wave theory in shallow waters, extended Serre equations, sediment transport, Bailard model, wave acceleration-asymmetry, wave velocity-skewness.

RESUMO

Efeitos não-lineares e dispersivos da onda nos processos costeiros

Os modelos numéricos são instrumentos úteis para estudar a propagação de ondas em meios com diferentes características, desde águas profundas (ao largo) até condições de água pouco profunda, e investigar a interação de ondas com batimetrias complexas ou estruturas construídas em regiões costeiras e estuarinas. As capacidades de modelos do tipo Boussinesq e as equações de Serre, ou de Green e Naghdi, para reproduzir os processos não-lineares de diversas interações são bem conhecidas. No entanto, estas aproximações clássicas restringem-se a condições de águas pouco profundas. Desde meados da década de 90 têm sido desenvolvidas formulações que modificam ou acrescentam termos de origem dispersiva para aplicações mais generalizadas, particularmente em aproximações do tipo Boussinesq. Recorrendo à teoria geral das ondas em condições de águas pouco profundas, são aqui apresentadas, em primeiro lugar, as aproximações comumente usadas em estudos da hidrodinâmica em meios fluviais, estuários e zonas costeiras. Tendo como objetivo alargar o campo de aplicação a outros domínios, em particular a condições de águas intermédias, é em seguida apresentada e testada com dados experimentais uma formulação das equações clássicas de Serre com melhores características dispersivas lineares. Por fim, é proposto um modelo morfodinâmico 1DH composto por um módulo hidrodinâmico, que resolve as equações expandidas de Serre, e por duas equações que incorporam vários processos de transporte sedimentar. Em particular, são avaliados e discutidos termos de transporte induzidos pelo enviesamento (skewness) e pela assimetria da onda.

***Paravras-chave**: Teoria da onda em água pouco profunda, equações expandidas de Serre, transporte sedimentar, modelo de Bailard, enviesamento e assimetria da onda.*

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1. Introduction

Knowledge of the flow characteristics associated with surface waves and currents, and their dependency on the bathymetry and coastal geometry, is of considerable importance when designing structures commonly found in the coastal environment, like groynes and breakwaters. Such knowledge also helps to predict the modifications thereby introduced into sea disturbance and into transport and deposition of sediments.

By the end of the 70's linear models were used to simulate the refraction effect produced by depth variation along the direction of the wave crest propagation, and the diffraction effect produced by the gradient of the wave amplitude along its crest. In the 80's other models, that take into account not only de refraction but also the diffraction process, have been proposed and commonly used by Berkhoff *et al*. (1982), Kirby & Dalrymple (1983), Booij (1983), Kirby (1984) and Dalrymple (1988), among many others. However, as they are based on the linear theory, those models should not be utilized in shallow water conditions.

Even at that time, models based on the Saint-Venant equations were frequently used in practical applications. However, as has been widely demonstrated, in shallow water conditions and for some types of waves, models based on a non-dispersive theory, of which the Saint-Venant model is an example, are limited and are not usually able to compute satisfactory results over long periods of analysis (Santos, 1985). Nowadays, it is generally accepted that for practical applications the combined gravity wave effects in shallow water conditions must be taken into account. In addition, the refraction and diffraction processes, the swelling, reflection and breaking waves, all have to be considered.

A number of factors has made it possible to employ increasingly complex mathematical models. Not only our theoretical knowledge of the phenomena involved has improved greatly, but also the numerical methods have been used more efficiently. The great advances made in computer technology, especially since the 1980s, improving information processing and enabling large amounts of data to be stored have made possible the use of mathematical models of greater complexity and with fewer restrictions.

Therefore, only models of order σ^2 ($\sigma = h_0/\lambda$), where h_0 and λ represent, respectively, depth and wavelength characteristics) or greater, of the Boussinesq or Serre types (Boussinesq, 1872; Serre, 1953), are able to reproduce several phenomena in addition to the dispersive effects, including the non-linearities resulting from wave-wave and wave-current interactions, and the waves resulting from sudden time-bed-level changes that cause tsunamis, wherein submerged landslides in reservoirs, or landslides on reservoir banks, are examples of such changes.

In the past few years, the possibility of using more powerful computational facilities along with the technological evolution and sophistication of control systems have required a thorough theoretical and experimental research designed to improve the knowledge of coastal hydrodynamics. Numerical methods aimed to applications in engineering fields more sophisticated and with a higher degree of complexity have also been developed.

In Section 2, the general shallow water wave theory is used to develop different mathematical approaches, which are nowadays the basis of the most sophisticated models in hydrodynamics and sedimentary dynamics. An extension of the Serre equations for applications in intermediate water conditions and comparisons of numerical results with physical data available in the literature are presented in Sections 3 and 4. Then, a morphodynamic model composed of this hydrodynamic module and a sediment transport model is proposed and discussed in Section 5. The sediment transport model consists on a sediment conservation equation and a dynamic equation. An improved version of Bailard model, incorporating various sediment transport processes, is used as the dynamic equation of the solid-phase model. It is shown that both the skewness and the wave asymmetry lead to an increase of the sediment transport in the wave direction.

2. Mathematical formulations

We start from the fundamental equations of the Fluid Mechanics, written in Euler's variables, relating to a three-dimensional and *quasi*-irrotational flow of a perfect fluid [Euler equations, or Navier-Stokes equations with the assumptions of non-compressibility ($d\rho/dt = div\ \vec{v} = 0$), irrotationality (rot $\vec{v} = 0$) and perfect fluid (dynamic viscosity $\mu = 0$)]:

$$
\begin{aligned}
& u_x + v_y + w_z = 0 \\
& u_t + uu_x + vu_y + wu_z = -p_x/\rho \\
& v_t + uv_x + vv_y + wv_z = -p_y/\rho \\
& w_t + uw_x + vw_y + ww_z = -p_z/\rho - g \\
& u_z = w_x;\ v_z = w_y;\ v_x = u_y
\end{aligned}
\tag{1}
$$

with $p = 0$ at $z = \eta(x,y,t)$, $w = \eta_t + u\eta_x + v\eta_y$ at $z = \eta(x,y,t)$, and $w = \xi_t + u\xi_x + v\xi_y$ at $z = -h_0 + \xi(x,y,t)$.

In these equations ρ is density, t is time, g is gravitational acceleration, p is pressure, η is free surface elevation, ξ is bottom, and (u, v, w) are velocity components.

Defining the dimensionless quantities $\varepsilon = a/h_0$ and $\sigma = h_0/\lambda$, in which a is a characteristic wave amplitude, h_0 represents water depth, and λ is a characteristic wavelength, we proceed with suitable non-dimensional variables:

$$x' = x/\lambda\,,\; y' = y/\lambda\,,\; z' = z/h_0\,,\; \eta' = \eta/a\,,$$
$$\xi' = \xi/h_0\,,\; t' = t\sqrt{gh_0}/\lambda = tc_0/\lambda\,,\; p' = p/(\rho g h_0),$$
$$u' = u/\left(a\sqrt{g/h_0}\right) = uh_0/(ac_0),$$
$$v' = v/\left(a\sqrt{g/h_0}\right) = vh_0/(ac_0),$$
$$w' = w\lambda/\left(ah_0\sqrt{g/h_0}\right) = v\lambda/(ac_0),$$

where c_0 represents critical celerity, given by $c_0 = (gh_0)^{1/2}$, η is free surface elevation, ξ represents bathymetry, u, v and w are velocity components, and p is pressure.

In dimensionless variables, without the line on the variables, the fundamental equations and the boundary conditions are written (Carmo & Seabra-Santos, 1996):

A – Fundamental equations

$$\begin{aligned}
&\text{a)}\quad u_x + v_y + w_z = 0\\
&\text{b)}\quad \varepsilon u_t + \varepsilon^2 u u_x + \varepsilon^2 v u_y + \varepsilon^2 w u_z = -p_x\\
&\text{c)}\quad \varepsilon v_t + \varepsilon^2 u v_x + \varepsilon^2 v v_y + \varepsilon^2 w v_z = -p_y\\
&\text{d)}\quad \varepsilon\sigma^2 w_t + \varepsilon^2\sigma^2 u w_x + \varepsilon^2\sigma^2 v w_y + \varepsilon^2\sigma^2 w w_z = -p_z - 1\\
&\text{e)}\quad u_z = \sigma^2 w_x\,;\; v_z = \sigma^2 w_y\,;\; v_x = u_y
\end{aligned} \tag{2}$$

B – Boundary conditions

$$\begin{aligned}
&\text{a)}\quad w = (1/\varepsilon)\xi_t + u\xi_x + v\xi_y && ,\; z = -1 + \xi\\
&\text{b)}\quad w = \eta_t + \varepsilon u \eta_x + \varepsilon v \eta_y && ,\; z = \varepsilon\eta\\
&\text{c)}\quad p = 0 && ,\; z = \varepsilon\eta
\end{aligned} \tag{3}$$

Integrating the first equation 2.a) between the bed $-1+\xi$ and the free surface $\varepsilon\eta$, taking into account 3.a) and 3.b), yields the continuity equation (4):

$$\left[\eta - (1/\varepsilon)\xi\right]_t + \left[(1 - \xi + \varepsilon\eta)\bar{u}\right]_x + \left[(1 - \xi + \varepsilon\eta)\bar{v}\right]_y = 0 \tag{4}$$

where the bar over the variables represents the average value along the vertical. Then, accepting the fundamental hypothesis of the shallow water theory, $\sigma = h_0/\lambda << 1$, and developing the dependent variables in power series of the small parameter σ^2, that is

$$f = \sum_{i=0}^{\infty}\left(\sigma^2\right)^i f_i\,,\ \text{for}\ f = (u, v, w, p, \eta, \xi, A) \tag{5}$$

where $A = u_x + v_y$, from continuity 2.a) and with 3.a) and 3.b) we obtain:

$$w_0 = -(z + 1 - \xi_0)A_0 + w_0^* \tag{6}$$
$$w_0^{**} = -(1 + \varepsilon\eta_0 - \xi_0)A_0 + w_0^* \tag{7}$$

where the simple and double asterisk represent the variables values at the bottom and at the surface, respectively. Of 2.e) we obtain, successively (Santos, 1989):

$$\begin{aligned}
u_0 &= u_0(x,y,t)\\
v_0 &= v_0(x,y,t)
\end{aligned} \tag{8}$$

$$\begin{aligned}
u_1 &= -(1/2)(z + 1 - \xi_0)^2 A_{0x}\\
&\quad + (z + 1 - \xi_0)(\xi_{0x}A_0 + w_{0x}^*) + u_1^*\\
v_1 &= -(1/2)(z + 1 - \xi_0)^2 A_{0y}\\
&\quad + (z + 1 - \xi_0)(\xi_{0y}A_0 + w_{0y}^*) + v_1^*
\end{aligned} \tag{9}$$

so that the average values of the horizontal components of the velocity, on the vertical, are given by:

$$\begin{aligned}
\bar{u} &= u_0 + \sigma^2 u_1^* - (\sigma^2/6)(1 + \varepsilon\eta_0 - \xi_0)^2 A_{0x}\\
&\quad + (\sigma^2/2)(1 + \varepsilon\eta_0 - \xi_0)(\xi_{0x}A_0 + w_{0x}^*) + O(\sigma^4)\\
\bar{v} &= v_0 + \sigma^2 v_1^* - (\sigma^2/6)(1 + \varepsilon\eta_0 - \xi_0)^2 A_{0y}\\
&\quad + (\sigma^2/2)(1 + \varepsilon\eta_0 - \xi_0)(\xi_{0y}A_0 + w_{0y}^*) + O(\sigma^4)
\end{aligned} \tag{10}$$

On the other hand, taking into account that,

$$f = f_0 + O(\sigma^2)\ \text{for}\ f = (u, v, \eta, \xi, w^*) \tag{11}$$

from (5) and (9) we obtain:

$$\begin{aligned}
u^{**} &= \bar{u} - (\sigma^2/3)(1 + \varepsilon\eta - \xi)^2 \bar{A}_x\\
&\quad + (\sigma^2/2)(1 + \varepsilon\eta - \xi)(\xi_x\bar{A} + w_x^*) + O(\sigma^4)\\
v^{**} &= \bar{v} - (\sigma^2/3)(1 + \varepsilon\eta - \xi)^2 \bar{A}_y\\
&\quad + (\sigma^2/2)(1 + \varepsilon\eta - \xi)(\xi_y\bar{A} + w_y^*) + O(\sigma^4)
\end{aligned} \tag{12}$$

Representing by $\Gamma = w_t + \varepsilon u w_x + \varepsilon v w_y + \varepsilon w w_z$ the vertical acceleration of the particles, we get $\Gamma = w_{0t} + \varepsilon u_0 w_{0x} + \varepsilon v_0 w_{0y} + \varepsilon w_0 w_{0z} + O(\sigma^2)$, and from (6), (7) and (11) the following approach is obtained:

$$\begin{aligned}
\Gamma &= -(z + 1 - \xi)\left(\bar{A}_t + \varepsilon\bar{u}\bar{A}_x + \varepsilon\bar{v}\bar{A}_y - \varepsilon\bar{A}^2\right)\\
&\quad + \left(w_t^* + \varepsilon\bar{u}w_x^* + \varepsilon\bar{v}w_y^*\right) + O(\sigma^2)
\end{aligned} \tag{13}$$

in which the terms within the two first parentheses represent the vertical acceleration when the bottom is horizontal, and the terms inside the third parenthesis represent the vertical acceleration along the real bottom. It should be noted that equation 2.d) can be written:

$$\varepsilon\sigma^2\Gamma = -p_z - 1 \tag{14}$$

where, for vertical integration between the bottom and the surface, the pressure p on the surface is obtained:

$$\begin{aligned}
p_x^{**} &= \varepsilon\eta_x\left(\varepsilon\sigma^2\Gamma^{**} + 1\right)\\
p_y^{**} &= \varepsilon\eta_y\left(\varepsilon\sigma^2\Gamma^{**} + 1\right)
\end{aligned} \tag{15}$$

which, along with 2b) and 2c), allow us to obtain (Santos, 1989):

$$\begin{aligned}&\left(u_t+\varepsilon uu_x+\varepsilon vu_y+\varepsilon wu_z\right)^{**}+\eta_x\left(1+\varepsilon\sigma^2\Gamma^{**}\right)=0\\&\left(v_t+\varepsilon uv_x+\varepsilon vv_y+\varepsilon wv_z\right)^{**}+\eta_y\left(1+\varepsilon\sigma^2\Gamma^{**}\right)=0\end{aligned}\tag{16}$$

or even, given that $\left(f_s\right)^{**}=f_s^{**}-\varepsilon\left(f_z\right)^{**}\eta_s$, where $f=(u,v)$ and $s=(x,y,t)$:

$$\begin{aligned}&u_t^{**}+\varepsilon u^{**}u_x^{**}+\varepsilon v^{**}u_y^{**}+\eta_x\left(1+\varepsilon\sigma^2\Gamma^{**}\right)=0\\&v_t^{**}+\varepsilon u^{**}v_x^{**}+\varepsilon v^{**}v_y^{**}+\eta_y\left(1+\varepsilon\sigma^2\Gamma^{**}\right)=0\end{aligned}\tag{17}$$

By developing expressions (17) in second approach (order 2 in σ^2), the following equations of motion (18) are obtained (Santos, 1989; Carmo, 2015):

$$\begin{aligned}&\bar{u}_t+\varepsilon\bar{u}\bar{u}_x+\varepsilon\bar{v}\bar{u}_y+\eta_x\\&\quad+\sigma^2\left\{\left[(2/3)(\varepsilon\eta-\xi)_x+(1/2)\xi_x\right]P+(1/3)(1+\varepsilon\eta-\xi)P_x\right\}\\&\quad+\sigma^2\left[\varepsilon\eta_xQ+(1/2)(1+\varepsilon\eta-\xi)Q_x\right]+O\left(\sigma^4\right)=0\\&\bar{v}_t+\varepsilon\bar{u}\bar{v}_x+\varepsilon\bar{v}\bar{v}_y+\eta_y\\&\quad+\sigma^2\left\{\left[(2/3)(\varepsilon\eta-\xi)_y+(1/2)\xi_y\right]P+(1/3)(1+\varepsilon\eta-\xi)P_y\right\}\\&\quad+\sigma^2\left[\varepsilon\eta_yQ+(1/2)(1+\varepsilon\eta-\xi)Q_y\right]+O\left(\sigma^4\right)=0\\&P=(1+\varepsilon\eta-\xi)\left(\varepsilon\bar{A}^2-\varepsilon\bar{u}\bar{A}_x-\varepsilon\bar{v}\bar{A}_y-\bar{A}_t\right)\\&Q=w_t+\varepsilon\bar{u}w_x+\varepsilon\bar{v}w_y\\&w=(1/\varepsilon)\xi_t+\bar{u}\xi_x+\bar{v}\xi_y\\&\bar{A}=\bar{u}_x+\bar{v}_y\end{aligned}\tag{18}$$

where, likewise, the bar over the variables represents the average value along the vertical. In dimensional variables and with a solid/fixed bottom ($\xi_t=0$), the complete set of equations is written, in second approach:

$$\begin{aligned}&h_t+(h\bar{u})_x+(h\bar{v})_y=0\\&\bar{u}_t+\bar{u}\bar{u}_x+\bar{v}\bar{u}_y+g\eta_x+\left[(2/3)h_x+(1/2)\xi_x\right]P\\&\quad+(1/3)hP_x+h_xQ+(1/2)hQ_x=0\\&\bar{v}_t+\bar{u}\bar{v}_x+\bar{v}\bar{v}_y+g\eta_y+\left[(2/3)h_y+(1/2)\xi_y\right]P\\&\quad+(1/3)hP_y+h_yQ+(1/2)hQ_y=0\\&P=h\left(\bar{A}^2-\bar{u}\bar{A}_x-\bar{v}\bar{A}_y-\bar{A}_t\right)\\&Q=w_t+\bar{u}w_x+\bar{v}w_y\\&w=\bar{u}\xi_x+\bar{v}\xi_y\\&\bar{A}=\bar{u}_x+\bar{v}_y\end{aligned}\tag{19}$$

where $h=h_0-\xi+\eta$ is total water depth. The one-dimensional form (1HD) of the equation system (19) is written, also with a fixed bottom:

$$\begin{aligned}&h_t+(\bar{u}h)_x=0\\&h\bar{u}_t+h\bar{u}\bar{u}_x+gh\eta_x\\&\quad+\left[h^2(P/3+Q/2)\right]_x+\xi_xh(P/2+Q)=0\\&P=-h\left(\bar{u}_{xt}+\bar{u}\bar{u}_{xx}-\bar{u}_x^2\right)\\&Q=\xi_x\left(\bar{u}_t+\bar{u}\bar{u}_x\right)+\xi_{xx}\bar{u}^2\end{aligned}\tag{20}$$

Assuming additionally a relative elevation of the surface due to the waves ($\varepsilon=a/h_0$) having a value close to the square of the relative depth ($\sigma=h_0/\lambda$), i.e. $O(\varepsilon)=O(\sigma^2)$, from the equation system (18), and at the same order of approximation, the following approach is obtained, in dimensional variables:

$$\begin{aligned}&h_t+(h\bar{u})_x+(h\bar{v})_y=0\\&\bar{u}_t+\bar{u}\bar{u}_x+\bar{v}\bar{u}_y+g\eta_x\\&\quad-(1/6)\xi_xP+(1/3)hP_x+(1/2)h_rQ_x=0\\&\bar{v}_t+\bar{u}\bar{v}_x+\bar{v}\bar{v}_y+g\eta_y\\&\quad-(1/6)\xi_yP+(1/3)h_rP_y+(1/2)h_rQ_y=0\end{aligned}\tag{21}$$

where $h_r=h_0-\xi$ is the water column height at rest, P and Q are given by $P=-(h_0-\xi)\left(\bar{u}_x+\bar{v}_y\right)_t$ and $Q=\left(\bar{u}\xi_x+\bar{v}\xi_y\right)_t$. The momentum equations are written:

$$\begin{aligned}&\bar{u}_t+\bar{u}\bar{u}_x+\bar{v}\bar{u}_y+g\eta_x+(1/6)h_r\xi_x\left(\bar{u}_x+\bar{v}_y\right)_t\\&\quad-(1/3)h_r^2\left(\bar{u}_x+\bar{v}_y\right)_{xt}+(1/3)h_r\xi_x\left(\bar{u}_x+\bar{v}_y\right)_t\\&\quad+(1/2)h_r\left(\bar{u}\xi_x+\bar{v}\xi_y\right)_{xt}=0\end{aligned}\tag{22}$$

$$\begin{aligned}&\bar{v}_t+\bar{u}\bar{v}_x+\bar{v}\bar{v}_y+g\eta_y+(1/6)h_r\xi_y\left(\bar{u}_x+\bar{v}_y\right)_t\\&\quad-(1/3)h_r^2\left(\bar{u}_x+\bar{v}_y\right)_{yt}+(1/3)h_r\xi_y\left(\bar{u}_x+\bar{v}_y\right)_t\\&\quad+(1/2)h_r\left(\bar{u}\xi_x+\bar{v}\xi_y\right)_{yt}=0\end{aligned}\tag{23}$$

with $\xi_t=0$, the complete system of equations (24) is obtained:

$$\begin{aligned}&h_t+(h\bar{u})_x+(h\bar{v})_y=0\\&\bar{u}_t+\bar{u}\bar{u}_x+\bar{v}\bar{u}_y+g\eta_x\\&\quad-(1/3)h_r^2\left(\bar{u}_{xxt}+\bar{v}_{xyt}\right)+h_r\xi_x\bar{u}_{xt}\\&\quad+(1/2)h_r\left(\xi_{xx}\bar{u}_t+\xi_y\bar{v}_{xt}+\xi_x\bar{v}_{yt}+\xi_{xy}\bar{v}_t\right)=0\\&\bar{v}_t+\bar{u}\bar{v}_x+\bar{v}\bar{v}_y+g\eta_y\\&\quad-(1/3)h_r^2\left(\bar{u}_{xyt}+\bar{v}_{yyt}\right)+h_r\xi_y\bar{v}_{yt}\\&\quad+(1/2)h_r\left(\xi_{yy}\bar{v}_t+\xi_y\bar{u}_{xt}+\xi_x\bar{u}_{yt}+\xi_{xy}\bar{u}_t\right)=0\end{aligned}\tag{24}$$

Further simplifying the equations of motion (18), retaining only terms up to order 1 in σ, i.e., neglecting all terms of dispersive origin, this system of equations is written in dimensional variables:

$$\begin{aligned} &h_t + (h\bar{u})_x + (h\bar{v})_y = 0 \\ &\bar{u}_t + \bar{u}\bar{u}_x + \bar{v}\bar{u}_y + g\eta_x = 0 \\ &\bar{v}_t + \bar{u}\bar{v}_x + \bar{v}\bar{v}_y + g\eta_y = 0 \end{aligned} \tag{25}$$

Approaches (19), (24) and (25) are known as Serre equations, or Green & Naghdi, Boussinesq and Saint-Venant, respectively, in two horizontal dimensions (2HD models). The classical Serre equations (19) (or Green & Naghdi, 1976) are fully-nonlinear and weakly dispersive. Boussinesq equations (24) only incorporate weak dispersion and weak non-linearity, and are valid only for long waves in shallow waters. As for the Boussinesq-type models, also Serre's equations are valid only for shallow water conditions.

3. Derivation and numerical formulation of higher order Serre equations

3.1. Mathematical derivation

To allow applications in a greater range of h_0/λ, other than shallow waters, a new set of extended Serre equations, with additional terms of dispersive origin, is developed and tested in Carmo (2013a,b) by comparisons with the available test data. The methodology used by Beji & Nadaoka (1996) and later by Liu & Sun (2005), to obtain an improved set of Boussinesq equations, was used to improve the dispersion characteristics of equations (20).

From the equation system (20), by adding and subtracting terms of dispersive origin, using the approximation $u_t = -g\eta_x$ and considering the parameters α, β and γ, with $\beta = 1.5\alpha - 0.5\gamma$, allows to obtain a new system of equations with improved linear dispersion characteristics:

$$\begin{aligned} &h_t + (uh)_x = 0 \\ &u_t + uu_x + g(h+\xi)_x + (1+\alpha)(\Omega u_t - hh_x u_{xt}) \\ &\quad - (1+\beta)\frac{h^2}{3}u_{xxt} + \alpha g\Omega(h+\xi)_x - \alpha g h h_x (h+\xi)_{xx} \\ &\quad - \beta g\frac{h^2}{3}(h+\xi)_{xxx} - hh_x uu_{xx} + \frac{h^2}{3}(u_x u_{xx} - uu_{xxx}) \\ &\quad + h(u_x)^2(h+\xi)_x + \xi_{xx}u^2(h+\xi)_x \\ &\quad + (\Omega + h\xi_{xx})uu_x + \frac{h}{2}\xi_{xxx}u^2 = 0 \end{aligned} \tag{26}$$

where $\Omega = \xi_x\eta_x + \frac{1}{2}h\,\xi_{xx} + (\xi_x)^2$.

After linearization of the equation system (26), the following dispersion relation is obtained, similar to the one obtained by Liu & Sun (2005) for an extended version of Boussinesq equations:

$$\frac{\omega^2}{gk} = \frac{kh_r\left[1 + (\alpha/2 - \gamma/6)(kh_r)^2\right]}{1 + \left[(1+\alpha)/2 - (1+\gamma)/6\right](kh_r)^2} \tag{27}$$

Comparing equation (27), written in terms of the phase speed (28)

$$C^2 = \frac{\omega^2}{k^2} = gh_r\left\{\frac{1 + (\alpha/2 - \gamma/6)(kh_r)^2}{1 + \left[(1+\alpha)/2 - (1+\gamma)/6\right](kh_r)^2}\right\} \tag{28}$$

with the linear dispersion relation $\omega^2/gk = tanh(kh_r)$, using the approach (29)

$$\begin{aligned} C_{Airy}^2 = \frac{\omega^2}{k^2} &= (gh_r)tanh(kh_r) \\ &= gh_r\left[\frac{1 + (1/15)(kh_r)^2}{1 + (2/5)(kh_r)^2}\right] + O\left[(kh)^6\right] \end{aligned} \tag{29}$$

allows to obtain values for the parameters α and γ. In a first approximation, we can suggest: $\alpha \approx 0.1308$ and $\gamma \approx -0.0076$ (Carmo, 2013a, b). It can be proven that a value of α within the interval $\alpha \in [0.13, 0.14]$ could be a good choice (Clamond *et al.*, 2015). Considering these boundaries for α, the parameter γ will be within the interval $\gamma \in [-0.01, +0.02]$. It should be noted that with $\alpha \approx 2/15 = 0.1333$, as proposed by Madsen *et al.* (1991) and Madsen & Sørensen (1992) for an extended version of the Boussinesq equations, the value $\gamma = 0$ is obtained.

Different approaches for the wave and group celerity, up to order σ^4, can be found in Simarro (2013) and Simarro *et al.* (2015). Through analyses of the wave shoaling in one-layer, and comparing the shoaling errors for different sets of Boussinesq-type equations, Simarro (2013) propose the following values: $\beta = 0.06219$ instead of $\beta = 0.06667$, as also proposed by Madsen & Sorensen (1992), or $\beta = 0.15278$ instead of $\beta = 0.20$, as suggested by Beji & Nodaoka (1996). Using $\beta = 0.15278$ and with $\bar{\alpha} = 0.1350$, a value of $\gamma = -0.5117$ is obtained. It is thus evident that further studies on this matter are needed, but this is not the goal of the present work. Values of $\alpha \approx 0.1308$ and $\gamma \approx -0.0076$ are used in this work.

3.2. Numerical solution

The equation system (26) is solved using an efficient finite-difference method, whose consistency and stability are tested in Carmo (2013a,b) by comparison with a closed-form solitary wave solution of the Serre

equations. For this purpose, the terms containing derivatives in time of u are grouped. The final system of three equations is re-written according to the following equivalent form (SERIMP model) (Carmo, 2013a,b):

$$h_t + (uh)_x = 0 \tag{30a}$$

$$\begin{aligned} q_t &+ \Big\{ uq - \frac{1}{2}\Big[u^2 + (1+2\alpha)h^2(u_x)^2 \\ &+ (1+2\alpha)(\xi_x)^2 u^2 - h\,\xi_x (u^2)_x \Big]\Big\}_x \\ &+ \big[g(1+\alpha\Omega) + \alpha h u u_{xx}\big]\eta_x - \alpha g h h_x \eta_{xx} - \beta g \frac{h^2}{3}\eta_{xxx} \end{aligned} \tag{30b}$$

$$\begin{aligned} &- \frac{\alpha}{2}\Big[(h\,\xi_{xx}u^2)_x + h_x\,\xi_{xx}u^2 - h\,\xi_{xx}u\,u_x\Big] \\ &+ \left(\alpha - \frac{\beta}{3}\right)h^2 u_x u_{xx} + \beta\frac{h^2}{3}u\,u_{xxx} + \tau_b/(\rho h) = 0 \end{aligned}$$

$$\big[1 + (1+\alpha)\Omega\big]u - (1+\alpha)h\,h_x u_x - (1+\beta)\frac{h^2}{3}u_{xx} = q \tag{30c}$$

$$\Omega = \xi_x \eta_x + \frac{1}{2}h\,\xi_{xx} + (\xi_x)^2 \tag{30d}$$

To compute the solution of equation system (30) (values of the variables h and u at time $t+\Delta t$) we use a numerical procedure based on the following scheme, itself based on the last equation system (30), for variables h, q and u. Knowing all values of h_i and u_i, $i = 1, N$, in the whole domain at time $n\Delta t$, the equations (30c) and (30d) are used to obtain the first values of q_i and Ω_i in the whole domain. Then, we continue with the following steps, in which the index p means predicted values (Carmo, 2013a,b):

(1) The first equation (30a) is used to predict the variable values h_{pi} at time $t+\Delta t$ ($h_{pi}^{t+\Delta t}$), in the whole domain.

(2) The second equation (30b) makes it possible to predict the variable values q_{pi} at time $t+\Delta t$ ($q_{pi}^{t+\Delta t}$), taking into account the values $\widetilde{h}_i^{t+\Delta t} = 0.5\left(h_i^t + h_{pi}^{t+\Delta t}\right)$, namely for Ω_i in the whole domain.

(3) The third equation (30c) makes it possible to compute the mean-averaged velocities $u_i^{t+\Delta t}$ at time $t+\Delta t$, taking into account the predicted values $h_{pi}^{t+\Delta t}$ and $q_{pi}^{t+\Delta t}$, namely for Ω_i in the whole domain.

(4) The first operation (step 1) is repeated in order to improve the accuracy of the variable values h_i at time $t+\Delta t$ ($h_i^{t+\Delta t}$), using the values $\overline{u}_i^{t+\Delta t} = 0.5\left(u_i^t + u_i^{t+\Delta t}\right)$ in the whole domain.

(5) Finally, the second operation (step 2) is repeated in order to improve the accuracy of the variable values q_i at time $t+\Delta t$ ($q_i^{t+\Delta t}$), taking into account the values $\overline{h}_i^{t+\Delta t} = 0.5\left(h_i^t + h_i^{t+\Delta t}\right)$ and $\overline{u}_i^{t+\Delta t} = 0.5\left(u_i^t + u_i^{t+\Delta t}\right)$ in the whole domain.

At each interior point i, the first, second and third-order spatial derivatives are approximated through centered differences and the time derivatives are approximated using forward differences. The convective terms $(uh)_x$ and $(uq)_x$ in equations (30a) and 30b) are approximated through centered schemes in space and time for variables h and q. At each time t, these terms are written in the following form:

$$\begin{aligned} (uh)_x &= u_i^t\left(\frac{h_{i+1}^t - h_{i-1}^t + h_{i+1}^{t+\Delta t} - h_{i-1}^{t+\Delta t}}{4\Delta x}\right) \\ &+ \frac{1}{2}\left(h_i^t + h_i^{t+\Delta t}\right)\left(\frac{u_{i+1}^t - u_{i-1}^t}{2\Delta x}\right) \end{aligned} \tag{31}$$

$$\begin{aligned} (uq)_x &= u_i^t\left(\frac{q_{i+1}^t - q_{i-1}^t + q_{i+1}^{t+\Delta t} - q_{i-1}^{t+\Delta t}}{4\Delta x}\right) \\ &+ \frac{1}{2}\left(q_i^t + q_i^{t+\Delta t}\right)\left(\frac{u_{i+1}^t - u_{i-1}^t}{2\Delta x}\right) \end{aligned} \tag{32}$$

All finite-difference equations are implicit. Therefore, the solution of system (30) requires, in each time step, the computation of five three-diagonal systems of N-2 equations (steps 1 to 5), which are easily computed using the three-diagonal matrix algorithm (TDMA), also known as the Thomas algorithm. The stability condition to be observed can be expressed in terms of the Courant/CFL number, and is given by:

$$C_R = \sqrt{gh}\,\frac{\Delta t}{\Delta x} < 1.0 \tag{33}$$

More accurate results are obtained with a domain discretization comprising about 25 to 30 points per wavelength and the condition (33) much lesser than unity, even below 0.5.

This numerical model (SERIMP) was used and tested in Carmo (2013a). With $\alpha = \beta = 0$, a comparison is presented with a closed-form solitary wave solution of these equations for a wave with $a/h0 = 0.60$. As can be seen, *the agreement between the numerical results and the analytical solution is perfect as much in wave amplitude as in phase* (Carmo, 2013a).

3.3. Boundary conditions

If an incident wave elevation $\eta(0,t)$ is given on the boundary (at $x = 0$) and the wave height is small compared to the water depth, the linear wave theory can be used to obtain the velocity of the incident wave

$$u(0,t)=\frac{\omega}{kh_r\left[1+(\beta/3)(kh_r)^2\right]}\eta(0,t) \tag{34}$$

where $\beta/3=\alpha/2-\gamma/6$ and $h_r=h_0-\xi$ is the water column height at rest on the boundary. Different kinds of wave patterns may be used. For mono-chromatic waves, the water-surface elevation $\eta(0,t)$ is given by $\eta(0,t)=a\,sin(\omega t)$, where a, ω and k are, respectively, the wave amplitude, frequency and wave number.

In general, our goal at the output boundary is to avoid reflections of the wave. To do this, the domain is extended with a damping region of length L_{damp}. Terms like $-m(x)\eta$ and $-m(x)u$ may be added to the evolution equations for h and u, respectively. The length of the damped region is chosen such that we do not see any significant reflections. The implemented procedure is similar to that described in Zhang *et al*. (2014).

The terms $-m(x)\eta$ and $-m(x)u$ are added to the second member of *h*- and *u*-equations (26), respectively. As a first approximation, these terms can be written as:

$$-m(x)\eta=-\omega_1(x)\eta \tag{35}$$

$$-m(x)u=-\omega_1(x)u \tag{36}$$

where $\eta=h-h_0+\xi$ is the free surface elevation, $\omega_1(x)=(\tilde{\omega}_1/L_{damp})f(x)$, $\tilde{\omega}_1\approx 10\sqrt{gh}$, $L_{damp}\geq 10h$ is the sponge length, and

$$f(x)=\begin{cases}(n+1)(x/L_{damp})^n, & 0\leq x\leq L_{damp}\\ 0, & x<0\end{cases}, \; n=2.$$

4. Applications of the 1HD extended Serre equations

4.1. Solitary wave travelling up a slope and reflection on a vertical wall

Experimental data and numerical results are available for a solitary wave propagating on the bathymetry shown in Figure 1 (Carmo, 2013a,b). It shows a constant depth before x = 55 m and a slope 1:50 between x = 55 m and x = 75 m. An impermeable vertical wall is placed at x = 75 m, corresponding to fully reflecting boundary conditions. A solitary wave of amplitude 0.12 m is initially centered at x = 25 m. The computational domain was uniformly discretized with a spatial step $\Delta x=0.05$ m. A zero friction factor has been considered. Computations were carried out with a time step $\Delta t=0.010$ s. Figure 2 compares numerical time series of surface elevation and test data at x = 72.75 m.

Figure 2 shows two peaks; the first one corresponding to the incident wave, and the second to the reflected wave. As pointed out in Carmo (2013a), the extended Serre model predictions for both peaks agree well with the measurements. *RMSE* values equal to 0.0090 m and 0.0117 m were found in first and second peaks, respectively, for the wave height. Regarding the phase, there is a loss of approximately 0.05 s and of 0.10 s in those peaks.

Predictions of the extended Boussinesq equations for both peaks are less accurate. Particularly for the reflected peak, this is overestimated in about 20%. This result is not surprising, given the lower validity of the Boussinesq model for waves of higher relative amplitude. Indeed, this model assumes $O(\varepsilon)<<1$, contrary to the Serre model, which is $O(\varepsilon)=1$. We used the extended Boussinesq model developed by Liu & Sun (2005). However, a similar study performed by Walkley & Berzins (1999), using the extended Boussinesq model developed by Nwogu (1993), shows no relevant differences in the graphs.

4.2. Periodic wave over an underwater bar

Beji & Battjes (1993) conducted experiments in a flume of 0.80 m wide with a submerged trapezoidal bar. The up- and down-wave bottom slopes of the submerged bar are 1:20 and 1:10 respectively. Before and after the bar, the water depth is 0.40 m, with a reduction to 0.10 m

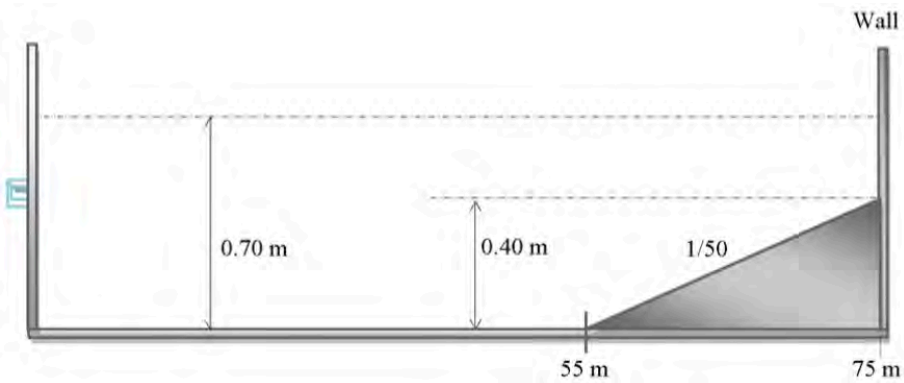

Figure 1 - Bathymetry for a solitary wave travelling up a slope and its reflection on a vertical wall (not in scale).

Figura 1 - Batimetria para a propagação de uma onda solitária sobre um trecho inclinado e sua reflexão numa parede vertical (fora de escala).

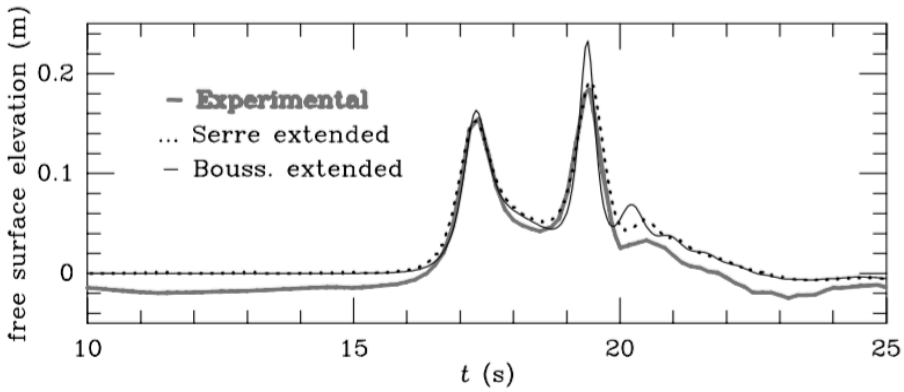

Figure 2 - Solitary wave travelling up a slope and its reflection on a vertical wall. Free surface elevation in a depth gauge located at x = 72.75 m. Experimental (▬▬); Serre extended (▪▪▪▪▪▪▪▪▪); Boussinesq extended (——) (adapted from Carmo, 2013a).

Figura 2 - Propagação de uma onda solitária sobre um trecho inclinado e sua reflexão numa parede vertical. Variação da superfície livre numa sonda localizada em x = 72.75 m. Experimental (▬▬); Serre com características dispersivas melhoradas (▪▪▪▪▪▪▪▪▪); Boussinesq com características dispersivas melhoradas (——) (adaptada de Carmo, 2013a).

above the bar, as shown in Figure 3. Experimental data obtained in this installation are available in the literature, and can be used for comparisons. The measured data are compared with numerical results of a 1HD extended version of the Boussinesq model (24), with $\alpha = 0.1308$ and $\gamma = -0.0076$, and the extended Serre equations (26) (SERIMP model) in Carmo (2013b), both improved with linear dispersive characteristics.

Comparisons are made in three wave gauges located at x = 10.5 m, x = 13.5 m and x = 17.3 m. For this purpose, a regular incident wave case with height 0.02 m, period T = 2.02 s and wavelength 3.73 m has been simulated. The computational domain was discretized with a uniform grid interval Δx = 0.025 m. A time step Δx = 0.0010s was used. Globally, numerical results of the improved Serre and Boussinesq models agree quite well with the measured data (Carmo 2013b).

Following is presented a comparison of the standard Serre's model (20) with the extended Serre equations (26) (SERIMP model). The standard Serre's model (20) is only valid for shallow waters, thus under conditions up to $h_0/\lambda = 0.05$. In this experiment, the dispersion parameter ($\sigma = h_0/\lambda$) is greater than 0.05 (about 0.11) in front and behind the bar, and therefore affects the validity of the numerical outcomes. Due to the fact that over the bar there are very shallow water conditions ($\sigma \approx 0.03$) the standard Serre equations are used considering the input boundary located at section x = 13.5 m, where the input signal is known (measured data). In this way, results of the Serre's standard model are not influenced, as would happen, by changes arising from the wave propagation before the bar, under intermediate water depths.

Figure 4 shows a comparison of numerical results of the standard Serre's model (20) with the extended Serre equations (26), considering, in the first case, the input boundary at x = 13.5 m (gauge signal) (Carmo, 2013b; 2015). The influence of additional terms of dispersive origin included in the extended Serre equations is clearly shown in Figure 4. The standard Serre model results (dashed line) are clearly of lesser quality. It should be noted that this application also demonstrates the good behavior of our numerical model to propagate a complex signal imposed at boundary.

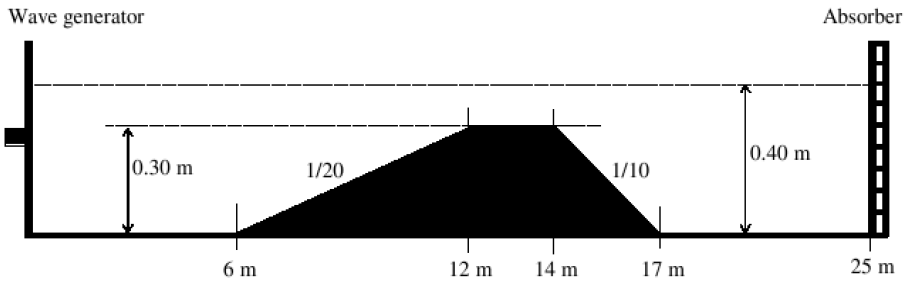

Figure 3 - Bathymetry for a periodic wave propagating over a bar (not in scale).

Figura 3 - Batimetria com barra sobre a qual se propaga uma onda periódica (fora de escala).

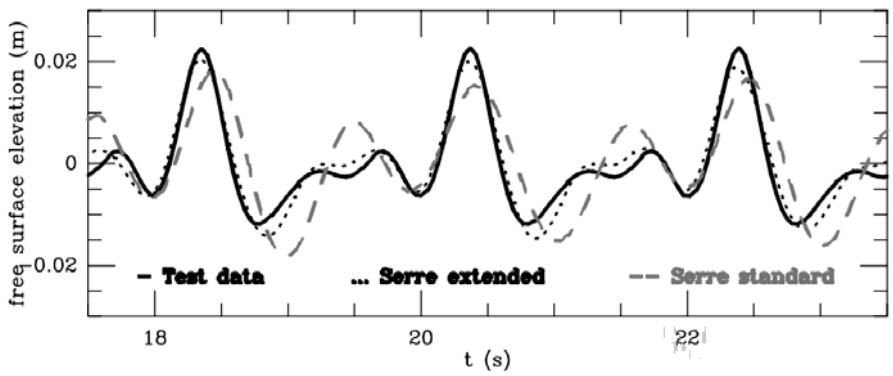

Figure 4 - Periodic wave propagating over a bar. Comparison of test data (——) with numerical results of the extended Serre model (26) (·····) and the standard Serre equations (20) (– – –) (adapted from Carmo, 2013b, 2015).

Figura 4 - Propagação de uma onda periódica sobre um fundo com barra. Comparação de dados experimentais (——) com resultados numéricos do modelo de Serre melhorado (26) (·····) e com resultados das equações clássicas de Serre (20) (– – –) (adaptada de Carmo, 2013b; 2015).

5. Sediment transport model

5.1. Mathematical formulation

The Bailard model (Bailard, 1981) does not consider the contribution of the wave acceleration-asymmetry in the sediment transport. As outlined in Dubarbier *et al.* (2015), models frequently used to estimate the evolution of beach profiles are inefficient with regard to the simulation of bottom shapes and migration of bars. This may be attributed to the absence of transport induced by acceleration-asymmetry of the wave.

In the following we use a 1HD model to compute the sediment transport in a channel, over a sand pit, and examine its ability to generate and propagate ripples and other bottom shapes. The morphodynamic model consists of the hydrodynamic equations (26) and the following sediment conservation equation (37) and a dynamic equation (38), in which four sediment transport processes are incorporated (Carmo, 2015):

$$(1-p)\xi_t + \langle q_{st}\rangle_x = 0 \tag{37}$$

$$\langle q_{st}\rangle = \langle q_{sl}\rangle + \langle q_{ss}\rangle + \langle q_{sk}\rangle + \langle q_{sy}\rangle \tag{38}$$

where

$$\langle q_{sl}\rangle = \frac{c_{sl}}{g(s-1)}\frac{\varepsilon_a}{tan\,\phi}\left(\langle |u|^2 u\rangle - \frac{1}{tan\,\phi}\xi_x\langle |u|^3\rangle\right) \tag{39}$$

$$\langle q_{ss}\rangle = \frac{c_{ss}}{g(s-1)}\frac{\varepsilon_s}{w_s}\left(\langle |u|^3 u\rangle - \frac{\varepsilon_s}{w_s}\xi_x\langle |u|^5\rangle\right) \tag{40}$$

$$\langle q_{sk}\rangle = c_{sk}\left(T_p U_{orb}^2 A_{sk}\right) \tag{41}$$

$$\langle q_{sy}\rangle = -c_{sy}\left(T_p U_{orb}^2 A_{asy}\right) \tag{42}$$

In equations (37) and (38), $\langle ...\rangle$ represents mean values of the arguments in the wave period, q_{st} is the net sediment transport, which is composed of the bedload transport, q_{sl}, the suspended load transport, q_{ss}, the *skewness* related transport, q_{sk}, and the transport related to wave asymmetry, q_{sy}; u is the wave velocity, p is the sediment porosity, ϕ is the internal angle of friction, $\varepsilon_a \in [0.10, 0.30]$ and $\varepsilon_s \in [0.01, 0.03]$ are efficiency coefficients, w_s is the sediment fall velocity, c_{sl} and c_{ss} are global rugosity coefficients, c_{sk} and c_{sy} are calibration coefficients. $U_{orb} = \pi H_{rms}/(T_p\, sinh\,(kh))$ is the orbital velocity amplitude, $A_{sk} = \langle u^3\rangle / \langle u^2\rangle^{3/2}$ is a measure of orbital velocity-*skewness*, and $A_{asy} = \langle \{\mathbf{H}[u(t)]\}^3\rangle / \langle u^2\rangle^{3/2}$ is the velocity asymmetry coefficient, where $\mathbf{H}[u(t)]$ is the Hilbert transform of u. The asymmetry coefficient is here approximated by $A_{asy} = \langle a^3\rangle / a_{rms}^3$, with $a_{rms} = \langle a^2\rangle^{1/2}$, being a the wave acceleration.

All calibration coefficients, in particular the efficiencies (ε_a, ε_s) and (c_{sk}, c_{sy}), which represent the incomplete knowledge in our understanding of these processes, require a site-specific morphodyamic calibration. Once properly calibrated a comprehensive cross-shore profile model may predict the bar dynamics on the time-scale of days (at least). However, it must be noted that this calibration process is non-trivial since a large number of model coefficients is involved, typically requiring a large number of computations and optimization strategies. At a first approach, coefficients c_{sk} and c_{sy} are of the order of 10^{-6} to 10^{-5}, and are not necessarily equal. This work shows comparisons of numerical results considering $c_{sk} = c_{sy} = 5\text{x}10^{-6}$ and $c_{sk} = c_{sy} = 10^{-5}$. Anyway, it should be noted that the effects are in a significant part determined by the calibration coefficient settings that have been kept constant.

Bed slope-related transport is included according to the Bailard equation increasing (decreasing) the down-slope

(up-slope) sediment transport. Equation (37) is easily computed using the Weighted Essentially Non-Oscillatory (WENO) scheme, as is presented in Long *et al*. (2008).

5.2. Numerical applications

Gardin (2004) compares the evolution of a bed profile with a pit using measurements and Delf3D computations. The sediment transport, especially cross-shore, was evaluated according to Bailard in the TRAN module of Delft3D software, which takes into account the effects of slope and wave asymmetry. According to the measurements, an important sedimentation offshore the pit is noted. Gardin (2004) concluded that the numerical model allows to obtain the pit evolution in agreement with the observations, with however a slight shift of the pit in the offshore direction.

The wave asymmetry effect is clearly shown in Groot (2005). Two transport formulas implemented in LOMOR model were applied in the prediction of the morphological behavior of a sandpit. The sediment transport due to wave asymmetry is neglected in both formulas. Numerical results of LOMOR using both formulas were compared with Delft3D computations. Delft3D takes into account velocity skewness and asymmetry. In all cases, the pit showed migration, damping and evolution of the slopes. However, contrary to LOMOR, Delft3D showed sedimentation downstream the pit.

Measured and modeled results of an offshore and onshore sandbar migration are shown in Zheng *et al.* (2014). The authors noted that the velocity skewness decreases from the seaward boundary toward the seaward flank of the initial bar, and then it increases over the initial bar and decreases over the area of final bar position, which is the region of active sandbar migration. After the final bar, velocity skewness increases toward the shoreline. The measured velocity asymmetry continuously increases from offshore and reaches its maximum shoreward of the final bar crest and then decreases toward the shoreline. Zheng *et al.* concluded that the onshore transport mainly appears where both velocity skewness and asymmetry are relatively high.

Based on 41 experiments, Berni *et al*. (2012) obtained a large range of values for the free-stream skewness and large values of the asymmetry. The authors analyzed numerically and experimentally the asymmetry transformation process to skewness within the boundary layer. They concluded that this transformation results in skewed velocities near the bed that lead directly to net sediment transport.

The dominant hydrodynamic processes governing cross-shore sandbar behavior have been discriminated by Dubarbier *et al*. (2015) using four modes of sediment transport driven by wave skewness and asymmetry, mean current and slope effects. They concluded that acceleration–skewness-induced transport systematically results in a slow onshore sandbar migration together with a slow bar growth. They also concluded that velocity–skewness-induced transport can drive onshore and offshore bar migrations with substantially larger rates.

A morphodynamic model (MORSYS) was used by Rosa *et al*. (2011) to study the evolution of a sand pit offshore Vale do Lobo (Algarve, Portugal). The authors conclude that the simulations performed for a whole period of 2.5 years and during one month encompassing two storm events show similar trends for the morphological evolution of the sandpit. The obtained results allowed to evaluate the good performance of the numerical model.

Sand extractions and formation of sand pits is a common activity in coastal zones. Therefore, the sand pit evolution, and in particular its migration and rate of replenishment should be reproduced with sufficient accuracy. Following, the evolution of a sand pit is studied using the morphodynamic model described above.

In our numerical experiment, a wave with the following characteristics is considered: height H = 0.20 m, period T = 8 s, and wavelength λ = 24.8 m. This wave is introduced at the upstream boundary and propagated along a horizontal channel 1.0 m depth in the first 28.75 m. From this point there is a sand pit, with the upstream face having a slope 9.82% down to a minimum $\xi = -0.275$ and left constant between 31.55 m and 32.175 m. Then the pit increases up to $\xi = 0$, having this face a positive slope 18.64%. A median diameter $d_{50} = 1.0$ mm is representative of the bottom grain size.

Figure 5 shows the simulated wave along the channel with a sand pit, between 15 m and 45 m. The wave transformations that occurred are evident, increasing the *skewness* and asymmetry of the wave. Figure 6 shows bottom configurations obtained 450 waves after, corresponding to a simulation time of 60 minutes, considering the first two terms $\mathbf{q}_{sl}$, and $\mathbf{q}_{ss}$ of equation (38) (dashed line) and all terms of this equation with $c_{sk} = c_{sy} = 5\text{x}10^{-6}$ (dotted line). Figure 7 shows bottom configurations obtained 450 waves after, corresponding to a simulation time of 60 minutes, considering all terms of equation (38) with $c_{sk} = c_{sy} = 5\text{x}10^{-6}$ (dotted line) and with $c_{sk} = c_{sy} = 10^{-5}$ (bold line), respectively.

Although lacking experimental evidence, the presented results seem to translate the physical phenomena. Indeed, they exhibit identical behavior to that shown in the measured and simulated examples in the literature above. Observing Figures 6 and 7, a preliminary conclusion can be drawn. Excluding the transport associ-

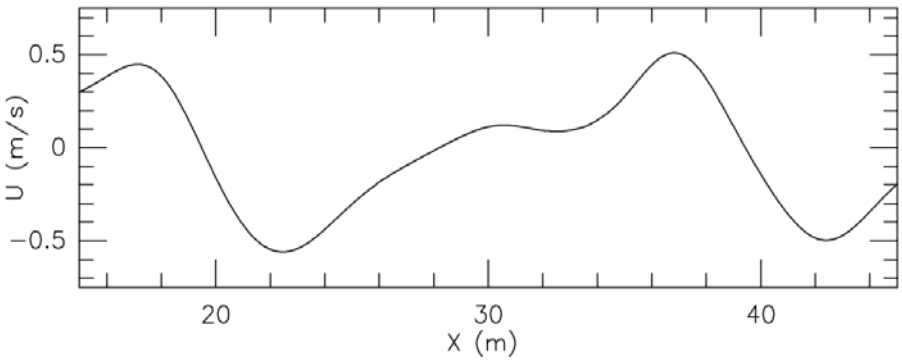

Figure 5 - Initial velocity of the wave propagating over a sandpit.

Figura 5 - Velocidade inicial da propagação de uma onda sobre uma cova de areia.

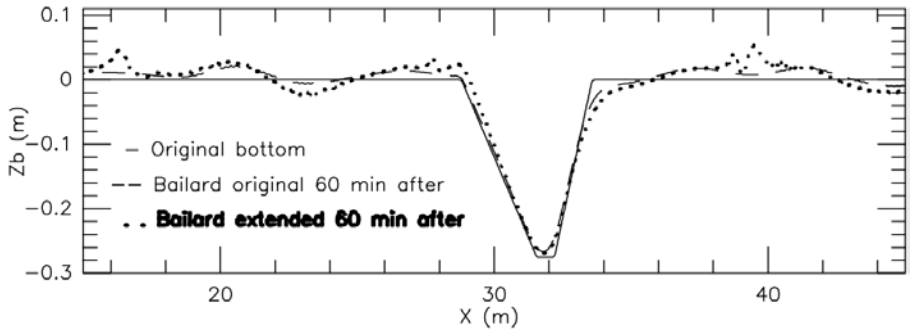

Figure 6 - Bottom profiles after 60 minutes of simulation, considering terms $\mathbf{q}_{sl}$ and $\mathbf{q}_{ss}$ of equation (38) (dashed line), and all terms $\mathbf{q}_{sl}$, $\mathbf{q}_{ss}$, $\mathbf{q}_{sk}$ and $\mathbf{q}_{sy}$ of this equation with $c_{sk} = c_{sy} = 5\text{x}10^{-6}$ (dotted line).

Figura 6 - Configurações do fundo após 60 minutos de simulação, considerando os termos $\mathbf{q}_{sl}$ *e* $\mathbf{q}_{ss}$ *da equação (38) (linha tracejada), e todos os termos* $\mathbf{q}_{sl}$, $\mathbf{q}_{ss}$, $\mathbf{q}_{sk}$ *e* $\mathbf{q}_{sy}$ *desta equação com* $c_{sk} = c_{sy} = 5\text{x}10^{-6}$ *(linha ponteada).*

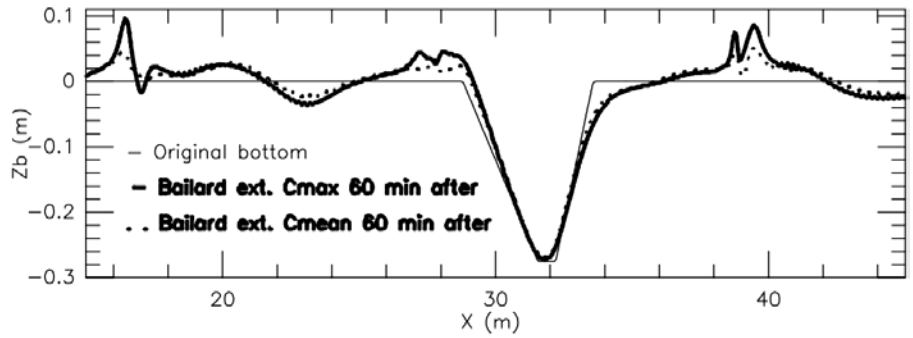

Figure 7 - Bottom profiles after 60 minutes of simulation, considering all terms $\mathbf{q}_{sl}$, $\mathbf{q}_{ss}$, $\mathbf{q}_{sk}$ and $\mathbf{q}_{sy}$ of equation (38) with $c_{sk} = c_{sy} = 5\text{x}10^{-6}$ (dotted line) and with $c_{sk} = c_{sy} = 10^{-5}$ (bold line).

Figura 7 - Configurações do fundo após 60 minutos de simulação, considerando os termos $\mathbf{q}_{sl}$, $\mathbf{q}_{ss}$, $\mathbf{q}_{sk}$ *e* $\mathbf{q}_{sy}$ *da equação (38) com* $c_{sk} = c_{sy} = 5\text{x}10^{-6}$ *(linha ponteada) e com* $c_{sk} = c_{sy} = 10^{-5}$ *(linha carregada).*

ated with the wave velocity-*skewness* and the acceleration-asymmetry reduces the onshore sediment transport (in the wave direction). Another evidence is the large difference in the bottom configurations considering relatively close values of c_{sk} and c_{sy}, thus showing great sensitivity to small variations of the involved constants.

6. Conclusions

Analytical developments and results of the numerical models presented in this work are promising enough to warrant further developments in both fields of the hydrodynamics and morphodynamics.

In hydrodynamic terms, extended versions of Boussinesq type models have shown a good performance. Less common are models of extended Serre equations, example of which is the model translated by equations (26); however, as is widely recognized, under certain conditions, the Serre equations more accurately simulate the behavior of the physical phenomena than Boussinesq type models.

In morphodynamic terms, it is known that the term $<|\boldsymbol{u}^2|\boldsymbol{u}>$ is associated with the short wave asymmetry and *skewness* in the surf zone. It is zero when there is no short wave *skewness* and a positively skewed wave results in an onshore directed transport. Consequently, as is reported in literature and this work also shows, the wave asymmetric oscillatory flow contributes to a shoreward directed net sediment transport.

The numerical results presented in this work, although qualitative, seem to translate the physical behavior of the processes involved. It is clearly shown that the *skewness* and wave asymmetry lead to an increase of the sediment transport in the wave direction.

An extended version of the two-dimensional equation system (19) with improved linear dispersion characteristics and using a finite element method is being developed and will be published soon. Also the experimental validation of the morphodynamic model will take place as quickly as possible.

Appendix

Supporting Information associated with this article is available online at **http://www.aprh.pt/rgci/pdf/rgci-660_Carmo_Supporting-Information.pdf**

References

Bailard, J.A. (1981) - An energetics total load sediment transport model for a plane sloping beach. *Journal of Geophysical Research*, 86(C11):10938-10954. DOI: 10.1029/JC086iC11p10938.

Beji, S.; Battjes, J.A. (1993) - Experimental investigations of wave propagation over a bar. *Coastal Engineering,* 19(1-2):151-162. DOI: 10.1016/0378-3839(93)90022-Z.

Beji, S.; Nadaoka, K., 1996. A formal derivation and numerical modelling of the improved Boussinesq equations for varying depth, *Ocean Engineering*, 23(8):691. DOI: 10.1016/0029-8018(96)84408-8.

Berkhoff, J.C.W.; Booij, N.; Radder, A.C. (1982) - Verification of numerical wave propagation models foe simple harmonic linear water waves. *Coastal Engineering,* 6:255-279. DOI: 10.1016/0378-3839(82)90022-9.

Berni, C.; Suarez, L.; Michallet, M.; Barthélemy, E. (2012) – Asymmetry and skewness in the bottom boundary layer: Small scale experiments and numerical model. 33rd International Conference on Coastal Engineering (25), Santander, Spain. Available online at https://icce-ojs-tamu.tdl.org/icce/index.php/icce/article/view/6637.

Booij, N. (1983) - A note on accuracy of the mild-slope equation. *Coastal Engineering*, 7(3):191-203. DOI: 10.1016/0378-3839(83)90017-0.

Boussinesq, J. (1872) - Théorie des ondes et des remous qui se propagent le long d'un canal rectangulaire horizontal. *Journal of Mathématiques Pures et Appliquées*, 2(17):55-108. Available online at https://eudml.org/doc/234248

Carmo, J.S. Antunes do ; Seabra-Santos, F.J. (1996) - On breaking waves and wave-current interaction in shallow water: A 2DH finite element model. *International Journal for Numerical Methods in Fluids,* 22:429-444. DOI: 10.1002/(SICI)1097-0363(19960315)22:5<429::AID-FLD388>3.0.CO;2-8

Carmo, J.S. Antunes do (2013a) - Boussinesq and Serre type models with improved linear dispersion characteristics: Applications. *Journal of Hydraulic Research*, IAHR, 51(6):719-727. DOI: 10.1080/00221686.2013.814090.

Carmo, J.S. Antunes do (2013b) - Extended Serre Equations for Applications in Intermediate Water Depths. *The Open Ocean Engineering Journal*, 6:16-25. DOI: 10.2174/1874835X01306010016.

Carmo, J.S. Antunes do (2015) - Sediment transport induced by *skewness* and asymmetry of the wave. In (*book*) *VIII Symposio sobre el Margen Continental Ibérico Atlántico*, 121-124, V. Díaz del Río, P.Bárcenas, L.M. Fernández-Salas, N. López-González, D. Palomino, J.L.Rueda, O.Sánchez-Guillamón e J.T.Vásquez (Editors). Ediciones Sia Graf, Málaga, Spain. Available online at https://www.researchgate.net/publication/282009789_Sediment_transport_induced_by_skewness_and_asymmetry_of_the_wave

Clamond, D.; Dutykh, D.; Mitsotakis, D. (2015) - *Conservative modified Serre-Green-Naghdi equations with improved dispersion characteristics*, 22 pages. Available online at http://arxiv.org/pdf/1511.07395.pdf

Dalrymple, R.A. (1988) - Model for refraction of water waves. *Journal of Waterway, Port, Coastal, and Ocean Engineering*, ASCE, 114(4):423-435. DOI: 10.1061/(ASCE)0733-950X(1988)114:4(423).

Dubarbier, B.; Castelle, B.; Marieu, V.; Ruessink, G. (2015) - Process-based modeling of cross-shore sandbar behavior. *Coastal Engineering*, 95:35–50. DOI: 10.1016/j.coastaleng.2014.09.004.

Gardin, B. (2004) - Numerical simulation of the impact of a sandpit on the shore stability, following Migniot and Viguier's experiments (1979). *VIIIèmes Journées Nationales Génie Côtier - Génie Civil*, Compiègne, France. Available online at http://wwz.ifremer.fr/gm_eng/content/download/18041/264573/file/dugardin_GCGC2004_uk.pdf

Green, A.E.; Naghdi, P.M. (1976) - A derivation of equations for wave propagation in water of variable depth. *Journal of Fluid Mechanics*, 78(2), 237-246. DOI: 10.1017/S0022112076002425.

Groot, P.J. (2005) - Modelling the morphological behaviour of sandpits. Influence sediment transport formula and verification of a 1DH model. Report carried out in the framework of the European project SANDPIT, University of Twente, The Netherlands. Available online at https://www.utwente.nl/ctw/wem/education/afstuderen/afstudeerverslagen/2005/de groot.pdf

Kirby, J.T. (1984) - A note on linear surface wave-current interaction over slowly varying topography. *Journal of Geophysical Research*, 89©:745-747. DOI: 10.1029/JC089iC01p00745.

Kirby, J.T.; Dalrymple, R.A. (1983) - A parabolic equation for the combined refraction-diffraction of stokes waves by mildly varying topography. *Journal of Fluid Mechanics*, 136:435-466. DOI: 10.1017/S0022112083002232.

Liu, Z.B.; Sun Z.C. (2005) - Two sets of higher-order Boussinesq-type equations for water waves. *Ocean Engineering* 32(11-12):1296-1310. DOI: 10.1016/j.oceaneng.2004.12.004.

Long, W.; Kirby, J.T.; Shao, Z. (2008) - A numerical scheme for morphological bed level calculations. *Coastal Engineering*, 55(2):167–180. DOI: 10.1016/j.coastaleng.2007.09.009.

Madsen, P.A.; Murray, R.; Sørensen, O.R. (1991) - A new form of the Boussinesq equations with improved linear dispersion characteristics. *Coastal Engineering*, 15(4):371-388. DOI: 10.1016/0378-3839(91)90017-B.

Madsen, P.A.; Sørensen, O.R. (1992) - A new form of the Boussinesq equations with improved linear dispersion

characteristics. Part 2. A slowly-varying bathymetry. *Coastal Engineering*, 18(3-4):183–204. DOI: 10.1016/0378-3839(92)90019-Q.

Nwogu, O. (1993) - Alternative form of Boussinesq equations for nearshore wave propagation. *Journal of Waterway, Port, Coastal, and Ocean Engineering*, 119(6):618-638. DOI: 10.1062/(ASCE)0733-950X(1993)119.6(618).

Rosa, J.; Gonçalves, D.; Silva, P.A.; Pinheiro, L.M.; Rebêlo, L.; Fortunato, A.; Bertin, X. (2011) - Sand Extraction Evolution Area offshore Vale do Lobo (Algarve, Portugal) - comparison between numerical results and bathymetric data. *Journal of Integrated Coastal Zone Management*, 11(3):369-377. DOI: 10.5894/rgci284.

Santos, F.J. Seabra (1985) - *Contribution a l'ètude des ondes de gravité bidimensionnelles en eau peu profonde*. Ph.D. thesis, Université Scientifique et Médicale et Institut National Polytechnique de Grenoble, France (*in French*). *Unpublished*.

Santos, F.J. Seabra (1989) - As aproximações de Wu e de Green & Naghdi no quadro geral da teoria da água pouco profunda. *Simpósio Luso-Brasileiro de Hidráulica e Recursos Hídricos* (4º SILUSBA), Lisboa, Portugal, 14-16 June, 209-219 (*in Portuguese*). *Unpublished*.

Serre, F. (1953) - Contribution à l'étude des écoulements permanents et variables dans les canaux. *La Houille Blanche*, 8(6):374–388. DOI: http://dx.doi.org/10.1051/lhb/1953058.

Simarro, G. (2013) - Energy balance, wave shoaling and group celerity in Boussinesq-type wave propagation models. *Ocean Modelling*, 72:74-79. DOI: 10.1016/j.ocemod.2013.08.004.

Simarro, G.; Orfila, A.; Mozos, C.M.; Pruneda, R.E. (2015) - On the linear stability of one- and two-layer Boussinesq-type equations for wave propagation over uneven beds. *Ocean Engineering*, 106:446-457. DOI: 10.1016/j.oceaneng.2015.07.022.

Walkley, M.A.; Berzins, M. (1999) - A finite element method for the one-dimensional extended Boussinesq equations. *International Journal for Numerical Methods in Fluids*, 29(2):143-157. DOI: 10.1002/fld.349.

Zhang Y.; Kennedy, A.B.; Panda, N.; Dawson, C.; Westerink, J.J. (2014) – Generating-absorbing sponge layers for phase-resolving wave models. *Coastal Engineering*, 84:1–9. DOI: 10.1016/j.coastaleng.2013.10.019.

Zheng, J.; Zhang, C.; Demirbilek, Z.; Lin, L. (2014) – Numerical study of sandbar migration under wave-undertow interaction. *Journal of Waterway, Port, Coastal, and Ocean Engineering*, 140(2):146-159. DOI: 10.1061/(ASCE)ww.1943-5460.0000231.