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Assessing the influence of ocean acidification to marine amphipods: A comparative study

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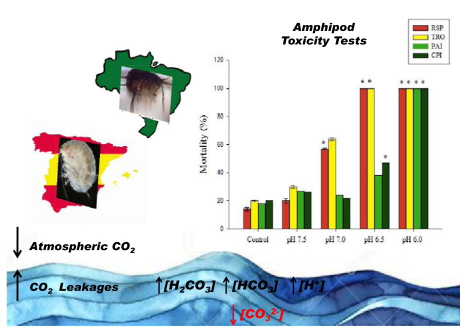
HIGHLIGHTS

- CO_2-induced acidification may changes the metal mobility from sediments;
- The tropical amphipod *Hyale youngi* shows to be more tolerant to ocean acidification than *Ampelisca brevicornis;*
- The Zn dissolved in overlying water was strongly correlated with the pH reduction and toxicity of the sediment;

GRAPHICAL ABSTRACT



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ABSTRACT

CO_2 increases in the ocean may occur both by the capacity of CO_2 exchanges with its dissolved form between atmosphere and surface seawater as well by CO_2 leaks during the carbon capture and storage (CCS) process. The decrease in seawater pH may result in a reduction in the concentration of both hydroxide and carbonate (OH^- and CO_3^{2-}). The main aim of this work is to conduct an ecotoxicology comparative survey using two amphipod species from Europe and Brazil exposed to different acidification (CO_2) scenarios. For it, an integrative approach based on the weight of evidence was used for comparative proposes to identify the effects on the amphipods association with the acidification and with the related mobility of metals. The results demonstrate that the *Ampelisca brevicornis* species is more sensitive to pH reductions than the *Hyale youngi* species. Furthermore, this study has demonstrated that the CO_2 enrichment in aquatic ecosystems would cause changes on the mobility of certain metals (Zn, Cu and As). The results of Principal Component Analysis (PCA) showed that the dissolved Zn in overlying water was strongly correlated with the decrease in the pH and was associated with increased toxicity of the sediment to the exposed organisms, mainly for the *A. brevicornis* species from Spain. Nevertheless, similar results were found in relation to the mortality of amphipods in low pH values for all sediment tested. Concluding, it is highlighted the importance of comparative studies in different types of environment and improve the understood of the risks associated with the ocean acidification.

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1. Introduction

The climate change phenomenon has been widely studied in recent years in order to analyze the impacts to the environment (Covey et al., 2003; IPCC, 2013; Komatsu et al., 2014; Vinagre et al., 2016). The increasing of anthropogenic emissions such as the use of fossil fuel, electric power plants, and automobiles, caused a result the CO_2 increase in the atmosphere (IPCC, 2013). It is estimated that CO_2 concentrations in the atmosphere have been raised from 280 ppm, dated in preindustrial time, to the current 401 ppm (Tans and Keeling, 2015). Additionally, it was registered that the surface waters of the ocean have taken up about 25% of carbon generated by human activities since 1800 (Sabine et al., 2004).

CO_2 increases in the ocean may occur both by the capacity of CO_2 exchanges with its dissolved form between atmosphere and surface seawater as well as by CO_2 leaks during the carbon capture and storage (CCS) process. Regarding the first way mentioned, previous studies have been reported that the pH in seawater surface is estimated to a reduction of around 0.4 units by 2100 and 0.77 units by 2300 (Caldeira and Wickett, 2005; IPCC, 2007). Briefly, this reaction occurs because there is a natural equilibrium between the ocean and the atmosphere. When there is an excess of atmospheric CO_2 concentrations in the atmosphere resulting from human activity, the gas is absorbed by the ocean as a sink (Sabine et al., 2004). It then reacts with the seawater and decreases the ocean's pH (Millero, 1995).

On other hand, the CCS is considered one of the best choices for the reduction of atmospheric CO_2 emissions to 15% and 60% of current emissions by 2025 and 2050, respectively, as required by the United Nations Framework Convention on Climate Change, or UNFCCC (UNFCC, 1992). However, the environmental risk related to this technique is needed to be fully understood the potential impact of a large scale leak and still remains largely unexplored hampered by complex ecological relationships (Blackford et al., 2015).

Many kinds of reactions may occur in the marine environment if there are changes in some parameters, such as temperature, dissolved oxygen, nutrients and pH. The decrease in seawater pH may result in a reduction in the concentration of both hydroxide and carbonate (OH^- and CO_3^{2-}). Millero et al. (2009) reported that the reduction in these concentrations could change the speciation of some metals, which could consequently have a higher fraction in their free forms at lower pH. Such increase could thus cause toxic effect to marine organisms, since these metals can become more available to water column. In this sense, many studies have been performed in the last few years in order to analyze the effect from ocean acidification (OA) to marine environment (De Orte et al., 2014a; Rodriguez-Romero et al., 2014a; Rodríguez-Romero et al., 2014b; Almagro-Pastor et al., 2015; Wang et al., 2016). Moreover, recently there has been a debate on whether the tropics or temperate zones are more vulnerable to climate warming (Ghalambor et al., 2006; Tewksbury et al., 2008) and the acclimation capacity of species that living in these zones (Vinagre et al., 2016). Considering that the ocean acidification would be one of the causes from the global warming, it is also very important to study its impacts on the organisms from different zones.

Amphipods are very sensitive to contaminants and have been used around the world to evaluate the quality of whole sediments (Environmental Canada, 1992; Cesar et al., 2002, 2004; Molisani et al., 2013). They are very sensitive to any changes in the environmental conditions and indicated as a well test organism to be applied in toxicity tests. Previous studies have been already showed the sensitivity of amphipods to OA (Musko et al., 1990; Taylor et al., 1994; Basallote et al., 2014; Goulding et al., 2017) that was associated to significant mortality in relation to pH reduction.

The use of integrated methods has been applied to the characterization of environmental quality in different ecosystems around the world (DelValls et al. 2002; Cesar et al., 2007; Choueri et al., 2009; Pereira et al., 2011, 2014; Baruarem et al., 2013; Torres et al., 2015). According to Cesar et al. (2014), such analysis allows a deeper understanding of the relationships between variables in the dataset with minimal loss of information, providing an objective procedure to achieve the final decision about the environmental risks assessment. In this sense, the use of an integrated approach could be thus an effective way to contribute with the studies of environmental risk related to CO_2 enrichment in the ocean, which would be employed different weight of evidence to analyze possible impacts associated with this acidification to marine ecosystem.

The main aim of this work is to conduct an ecotoxicology comparative survey using two amphipod species from Europe and Brazil exposed to different acidification (CO_2) scenarios. The selected amphipod species were *Ampelisca brevicornis* collected in Bay of Cádiz, SW, Spain and the tropical amphipod *Hyale youngi* collected in the Bay of Santos, SP, Brazil. An integrative approach based on the weight of evidence was used for comparative proposes to identify the effects associates with the acidification and with the related mobility of metals from the sediment samples used in this study and collected both at the SW, Spain and Brazil.

2. Methodology

2.1. Sampling

Sediment samples were collected from four sites in two different coastal areas. Two sampling sites are located in Bay of Cadiz, Spain (Fig. 1), and the others two sites in Santos Estuary and Bay, São Paulo – Brazil (Fig. 2).

The sampling sites in Spain are located in San Pedro River (RSP) and Trocadero (TRO) in Bay of Cádiz. Both are relatively protected areas connected to the Atlantic Ocean through intertidal channels and salt marshes. These areas are influenced by marine aquaculture, the shipbuilding industry, and urban discharges, among other human activities (DelValls et al., 1998; Silva et al. 2012). The RSP has a low metal concentration, while the TRO is considered an area with moderate metal concentration (Basallote et al., 2014).

The Santos Estuarine System is located on the central coast of the state of São Paulo, in southeastern Brazil. This region is of economic importance due to the industrial complex in the city of Cubatão, the Port of Santos, the potential for tourism, and the fisheries and natural resources provided by mangroves that occur within the estuary. The establishment of the sampling site in the Santos Estuary (CPI) is based on previous studies (Lamparelli et al., 2001; Abessa et al., 2005; Cesar et al., 2006, 2007; Torres et al., 2015) which show contamination gradients from the inner portions of the estuary to the external areas. In contrast, the site from Santos bay (PAI) is considered relatively clean and has been used as a reference site in this area (Szalaj et al., 2016; Goulding et al., 2017).

Collection procedures and sediment sample transport followed the recommendations of the USEPA (2001). After collection, all sediment samples were taken to the laboratory and sieved through a 2-mm plastic mesh to remove the gravel fraction and were then homogenized. The samples were stored at 4 °C in darkness until their use (no >2 weeks). Sub-samples were collected for the chemical quantification of organic carbon, organic matter content, and metals. Prior to sampling and storage, all material were thoroughly cleaned with acid (10% HNO_3), and rinsed in double-deionized (Milli-Q) water.

The water used in the experiments performed in Spain was collected from the surface (1 m depth) in RSP, during high tide (salinity 34 ± 1), transported to the laboratory. Already the water used in the experiments in Brazil was collected from Mar Casado, Bay of Santos – SP, and it was done by the same procedure described before. Both waters are considered as contamination free.

2.2. Test organisms

The amphipods *Ampelisca brevicornis* were collected from a non-contaminated area at Bay of Cádiz by sieving through a 0.5 mm mesh.