CO_2 leakage simulation; effects of the decreasing pH and the increasing dissolved metals to the fertilization and larval development of *Paracentrotus lividus*

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ABSTRACT

Carbon capture and storage has become a new mitigation option to reduce anthropogenic CO_2 emissions. The effects of the CO_2 related acidification, associated with unpredictable leaks of CO_2 during the operational phases were studied using the *Paracentrotus lividus* sea urchin liquid phase assays (Fertilization and embryo-larval development tests). The urchin larvae exposed to elutriate of sediments with different metals concentration, which were subjected to various pH treatments resulted in median toxic effect pH ranged from 6.33±0.02 and 6.91±0.01 for the egg fertilization, and between 6.66±0.03 and 7.16±0.01 for the larval development assays. The dissolved metals concentration measured in the elutriates were associated with acidification. For all the sediment elutriates tested the amount of the dissolved Zn increased in parallel with the pH reductions. Although correlated effects of acidification, biological response and the presence of dissolved metals were observed from this work, further research is required to properly explain the mechanisms associated with the increasing sediment toxicity because of CO_2 leakage.

INTRODUCTION

The Carbon Capture and Storage of CO_2 (CCS) has the potential to reduce the CO_2 emissions from fossil fuel combustion [1]. However, the CO_2 must be stored for at least hundreds of years if this technology intends to contribute efficiently to reduce the atmospheric CO_2 emissions. To date, 15 large-scale CCS projects are in operation around the world with the capacity to capture up to 28 million tones of CO_2 per annum (Mtpa) [2].

The underground storage of CO_2 is a relatively young technology; therefore it remains a lack of understanding of the behavior of the CO_2 under leaks. The increase of H^+ would be the effect of the mix and dissolution of CO_2 into seawater, which would lead to pH reductions, resulting in seawater acidification processes.

Accumulating on the sediment surface by adsorption and precipitation processes [3], the relevance of metals is related to their toxicity, persistence and potential bioaccumulation in marine organisms [4],[5]. Although metals can be strongly bound to the sediments without posing a threat to marine organisms, the remobilization of the unconsolidated sediments, together with the expected CO_2-induced acidification as a consequence of leaks of CO_2 could cause important changes to the form in which metals are present naturally in the environment increasing their bioavailability to the marine organisms.

The aims of this work were to observe the direct effect of decreasing pH, and whether CO_2 related acidification could affect the sediment metals behavior, increasing their toxicity to the sea urchin larvae. To this end, the sea urchin larvae were exposed to elutriates of sediments collected in different littoral areas and subjected to various pH treatments. Moreover, dissolved metal concentrations in the sediment elutriates were measured, intending to correlate sediment elutriates toxicity and pH reductions with the biological responses.

MATERIALS & METHODS

Test sediments were collected from two littoral areas in the Gulf of Cádiz, along the Southwestern Atlantic Coast of Spain: the Bay of Cádiz and the Ría of Huelva. The sediment sites were selected on the basis of the best available information to represent presumably low and high

levels of metals contamination [6]. Additionally, the sub-seafloor of the South West part of the Iberian Peninsula has been selected as one of the possible CO_2 storage sites in Europe [7].

A laboratory-scale-CO_2-injection system, designed to conduct ecotoxicological assays was used to work with sediment elutriates, employing a range of pH treatments [8]. The sediment elutriation procedure was performed according to modifications of the USEPA method (1998) [9] and Environment Canada (1994) [10], in 2 L test vessels. The pH treatments ranged from 8.0 to 6.0 (two replicates per treatment) for each one of the sediment tests.

The fertilization tests were adapted from Ghirardini et al. [11] and conducted in 25 mL polyethylene vessels containing 10 mL of the studied sediment elutriates. The embryo-larval development procedure was based on the methods developed by Fernandez and Beiras [12].

The median effect concentration (EC_{50}) was calculated for the toxic effects associated with pH reductions using the linear interpolation method. Statistical differences ($p < 0.05$, $p < 0.01$) in fertilization and developmental success between the sediment (MAZ, and ML) elutriates in reference to the TRO sediment (considered the relatively unpolluted sediment) were calculated. A multivariate analysis was conducted using principal component analysis (PCA) as the extraction procedure to describe the distribution of the data with the minimum loss of information.

RESULT AND DISCUSSION

According to the percentages of fines the sediment from MAZ was classified as muddy sand, while the sediments from TRO and ML sites were classified as sandy mud. The sediments from the Ría of Huelva, MAZ and ML, exhibited the highest metal concentrations.

As expected, the highest pCO_2 were recorded at pH 6.0, given that the highest amounts of CO_2 were injected to reach the lowest pH treatments. A similar pattern of CO_3^{2-} reduction as the pH decreased as well as the saturation states of aragonite (Ω_{Arag}) and calcite (Ω_{Cal}) were shown in all the elutriates tested. For the presented experiments, CO_2 gas was injected in order to modify and control the pH in the aquaria, then the balance between carbon species was altered. Since CO_2 concentration alters the TIC ($[CO_2]$, $[H_2CO_3]$, $[HCO_3^-]$ and $[CO_3^{2-}]$) in the system, the bicarbonate ions also vary, leading to an increase of the total alkalinity

The EC_{50} was estimated based on the fertilization failure and the abnormal larval development, for the larvae exposed to the sediment elutriates subjected to the pH treatments. The EC_{50} ranged from 6.33±0.00 to 6.91±0.01 for the egg fertilization assay. The EC_{50} calculated for the embryo-larval assay ranged between 6.66±0.03 and 7.16±0.01. According to our results, the acute sea urchin larvae test (egg fertilization) and the chronic test (embryo-larval development) are useful tests to study the effects of CO_2 induced acidification, with a slightly greater sensitivity observed with regard to acidification in the embryo-larval development assay.

Among the metals analyzed, Co, Zn, As, Cu, and Fe exhibited detectable concentrations in the sediment elutriates, passing from the sediment into the liquid phase. The dissolved metals may be easily available to aquatic organisms and therefore they could present more toxicity than particulate metals.

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