Research article

Estuarine sediment resuspension and acidification: Release behaviour of contaminants under different oxidation levels and acid sources

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ABSTRACT

Carbon dioxide (CO_2) Capture and Storage (CCS) is a technology to reduce the emissions of this gas to the atmosphere by sequestering it in geological formations. In the case of offshore storage, unexpected CO_2 leakages will acidify the marine environment. Reductions of the pH might be also caused by anthropogenic activities or natural events such as acid spills and dredging operations or storms and floods. Changes in the pH of the marine environment will trigger the mobilisation of elements trapped in contaminated shallow sediments with unclear redox boundary. Trace element (As, Cd, Cr, Cu, Ni, Pb and Zn) release from anoxic and oxic estuarine sediment is analysed and modelled under different laboratory acidification conditions using HNO_3 (l) and CO_2 (g): acidification at pH = 6.5 as worst-case scenario in events of CO_2 leakages and acid spills, and acidification at pH = 7.0 as a seawater scenario under CO_2 leakages, acid spills, as well as sediment resuspension. The prediction of metal leaching behaviour appear to require sediment specific and site specific tools. In the present work it is demonstrated that the proposed three in-series reactions model predicts the process kinetics of the studied elements under different simulated environmental conditions (oxidation levels and acid sources). Differences between HNO_3 and CO_2 acidification are analysed through the influence of the CO_2 gas on the ionic competition of the medium. The acidification with CO_2 provokes higher released concentrations from the oxic sediment than from the anoxic sediment, except in the case of Zn, which influences the release of the other studied elements. Slight acidification can endanger the aquatic environment through an important mobilisation of contaminants. The obtained prediction of the contaminant release from sediment (kinetic parameters and maximum concentrations) can contribute to the exposure assessment stage for risk management and preincidental planning in accidental CO_2 leakages and chemical spills scenarios.

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1. Introduction

The Carbon dioxide (CO_2) Capture and Storage (CCS) technology will play an important role in climate change mitigation while the global economy continues based on fossil fuels (IEA, 2013; Sheppard and Socolow, 2007). However, it is still perceived as technically and economically risky. Cost reduction can be achieved through innovation, exploitability of economies of scale and sharing infrastructures. This scenario would allow this technology for helping to meet the climate change targets into the 2030s and beyond. However, the CCS can enter to the market only once the overall risk involved is reduced (Gammer, 2016; IEA, 2013).

During the injection stage of CCS, potential CO_2 leakages from the storage sites would expose the ecosystem to unprecedented changes. In addition to the potential negative effects on health and environment, the public perception of the implementation of this technology might highly condition its industrial application (Benson and Cole, 2008; IPIECA, 2003; PTECO2, 2014). In order to establish a risk management procedure which contributes to the safety of the CCS projects, the determination of contaminant mobility (kinetic) and availability (maximum released concentration from the solid matrix in contact as caprock formations, sediment or marshes) under different acidification events need to be assessed.

Coastal and estuarine sediments are an essential part of the aquatic systems and can act as a sink for contaminants discharged to the environment (Kalnejais et al., 2015). Unexpected CO_2 leakages from CCS offshore storage sites will acidify the marine environment and trigger the mobilisation of contaminants previously trapped within sediments, endangering the aquatic medium (De Orte et al., 2014; Martín-Torre et al., 2015a; Roberts et al., 2013;

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Rodríguez-Romero et al., 2014).

Additionally, the resuspension of sediments also reduces the pH of the medium due to the oxidation process, causing the mobilisation of contaminants (Calmano et al., 1993; Cappuyns et al., 2014). These resuspension conditions, which are usually uncontrolled and unavoidable (Pourabadehei and Mulligan, 2016; Simpson et al., 1998), might be caused by natural events or human activities (Eggleton and Thomas, 2004; Xu et al., 2015).

Seawater acidification processes enhance the solubility of most trace metals and increase their bioavailability for uptaking by organisms because of the influence of pH on the dissolved organic matter, dissolution of carbonate, sulphide and iron (oxy)hydroxide minerals, adsorption/desorption surface reactions and ion exchange (Dooley et al., 2006; Kharaka et al., 2010; Millero et al., 2009; Zheng et al., 2009).

Sequential extraction procedures which are designed to differentiate between fractions, have been commonly applied to evaluate the redistribution of metals in their (operationally defined) binding phases and can give an indication of the 'pools' of heavy metals that are potentially available under changing environmental conditions. However, the metal-binding phases are defined operationally, so real chemical species of metals cannot be clearly determined and sequential extraction procedures generally possess a low reproducibility (Ho et al., 2012); In addition, significant discrepancies have been observed between extractable pools of different element due to the differences in extraction procedures and natural conditions (Cappuyns et al., 2007; Cai et al., 2016; Choppala et al., 2017).

Considering that CO_2-induced acidification can provoke the disappearance of the macrobenthic community at pH = 6.0 (Almagro-Pastor et al., 2015) and that a pH value of 6.5 might be expected as the 'worst-case' scenario in cases of CO_2 leakages from storage sites, a pH value of 6.5 is chosen to address element release from a sediment with different levels of oxidation. This scenario has been previously studied in relation to the impact acidification assessment (Riba López et al., 2010; Wang et al., 2015).

Although the sediment redox potential can widely vary from −250 or −300 mV to 400−700 mV (Popenda, 2014; Ye et al., 2013), surface sediments (2−5 mm) are oxic (Kristensen, 2000; Williamson et al., 1999) and they become suboxic at greater depths due to the coexistence of mixtures of oxic and anoxic processes, bioturbation and seasonal variations that make the redox boundaries unclear (Atkinson et al., 2007; Burdige, 1993; Williamson et al., 1999). Considering that the upper layers of the sediment might be the first affected by changes in the aquatic environment and that the oxidation level within sediments might vary over short periods of time, the redox potential of the sediment matrix is expected to influence the release behaviour of contaminants (Cappuyns and Swennen, 2005; Kalnejais et al., 2015; Lions et al., 2014). In this way, the redox potential and pH are the two primary factors controlling the release of trace metals from sediments (Frohne et al., 2011; Fonti et al., 2013; Choppala et al., 2017).

The pH dependence leaching test with continuous pH control (CEN/TS 14997, 2006 standard, superseded by EN 14997, 2015) has been previously used to assess contaminant release from sediment under different types of acidification (Martín-Torre et al., 2015b; Martín-Torre et al., 2016). Moreover, and owing to the huge number of complex reactions involved in contaminant mobilisation from sediment matrices, a general mathematical model has been proposed to fit experimental release over time (Martín-Torre et al., 2015b). However, a comparative analysis and modelling of element release under different types of acidification conditions and sediments with different levels of oxidation has not been addressed, to the best of our knowledge.

The main purpose of this article is the analysis and modelling of the release of As, Cd, Cr, Cu, Ni, Pb and Zn under different conditions of acidification and oxidation levels from estuarine contaminated sediment. Hence, the release of trace elements from anoxic and oxic sediment is addressed under resuspension conditions in order to analyse the pH range of variation and the trace element mobilisation. Afterwards, the comparative leaching behaviour of contaminants from anoxic and oxic sediment is assessed using HNO_3 or CO_2 at pH = 6.5. Finally, the leaching behaviour of the trace elements from
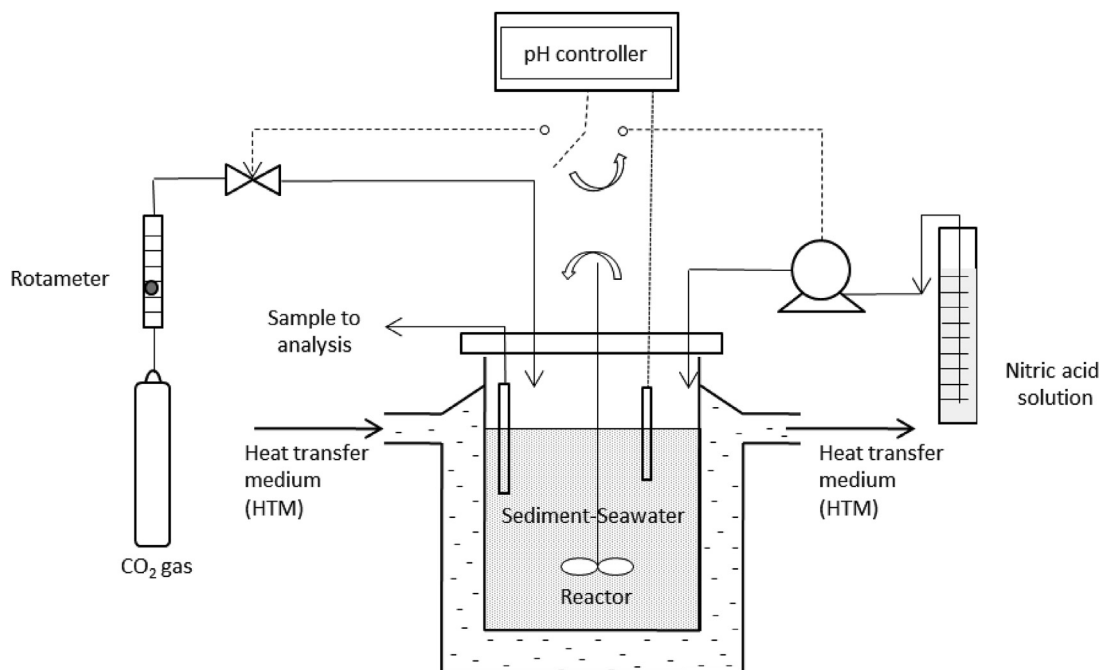

Fig. 1. Experimental equipment used in the pH-static leaching tests with continuous pH control. Depending on the position of the switch, the addition of CO_2, HNO_3 or of none of them (resuspension assay) was allowed.