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

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Highlights

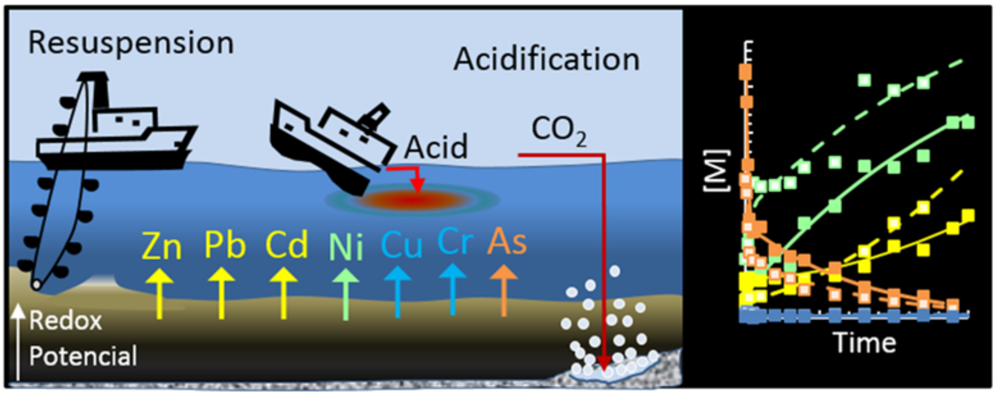
- Trace element release under resuspension conditions from anoxic and oxic sediment
- Experimental and modelled release under HNO_3 and CO_2 conditions at pH = 6.5
- CO_2 acidification enhances contaminant mobility under slightly acidic scenarios
- The sediment resuspension mobilises more Pb than acidification at pH = 7.0

Keywords: Kinetic modelling; HNO_3 and CO_2 acidification; contaminant release; resuspension; pH-static leaching; oxic and anoxic sediment.

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.

Graphical Abstract



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; PTECO$_2$, 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; 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., 2009; 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 at 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 EN14997: 2015) has been previously used to assess contaminant release from sediment under different types of acidification (Martín-Torre et al., 2015b and 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 anoxic sediment is compared under resuspension and acidification situations obtained by the addition of HNO_3 or CO_2 at the minimum pH value achieved by the resuspension experiments (pH = 7.0).

2. EXPERIMENTAL METHODOLOGY

The sediment samples were collected in the Suances estuary, inside a potential site for CO_2 storage in the Cantabrian region (Northern Spain) (BOE, 2008). Shallow sediment (0-5 cm) with its initial water content was sampled using a plastic paddle, sieved through a 2-mm plastic mesh, homogenised and frozen until use.

When the leaching tests were performed with anoxic sediment (-168 ± 7.00 mV), the selected sediment samples were used the day after being unfrozen. Oxic sediment samples (27.0 ± 37.0 mV) were achieved after some weeks stored in the fridge. In this period of time, the initially anoxic sediment was oxidised leading to a pH reduction and an increase in redox potential. Upon oxidation, among other changes in the speciation and binding of metals, sulphides were partially converted to sulphate and to intermediary oxidised sulphur compounds (Calmano et al., 1993; Cappuyns and Swennen, 2006; Tack et al., 1997). Therefore, the colour of the sediment also changed (from very dark brown to brownish). It is important to highlight that the terms 'anoxic' and 'oxic' refer to the initial state of the sediment, because the oxidation of the sediment was allowed over the time of assay.

As explained in Martín-Torre et al. (2015b), the main crystalline phases of the used sediment are quartz, aluminium oxide, calcite and dolomite. The total concentrations of Zn, Pb, Cd, Ni, Cr, Cu and As are 5220 ± 140, 564 ± 2.22, 12.6 ± 0.732, 36.0 ± 1.86, 72.0 ± 5.31, 48.0 ± 3.13 and 59.0 ± 1.39 mg/kg, respectively.

The modified pH dependence leaching tests performed in this work were based on the CEN/TS 14997: 2006 standard although some modifications such as the particle size, the leaching agent and the duration of the experiment were undertaken. The experimental equipment consisted of a glass-made 2-L jacketed vessel and a temperature controller (Polyscience) in order to perform all the assays at a temperature of 20 ºC. The operation of the equipment when HNO_3 was used to acidify the medium is already published in Martín-Torre et al., 2015b. When the acidification was provoked by the addition of CO_2, the pH controller (AT Control systems) injected pure CO_2 bubbles as needed to maintain the set point pH of the assay, with a hysteresis of 0.1 pH units (Martín-Torre et al., 2016). In the resuspension assays, the pH was measured continuously but without any control. A schematic figure of the three possibilities of the experimental equipment is shown in Fig. 1. In all the cases, the pH electrode used was suitable for samples with suspended solids and calibrated against standard solutions.

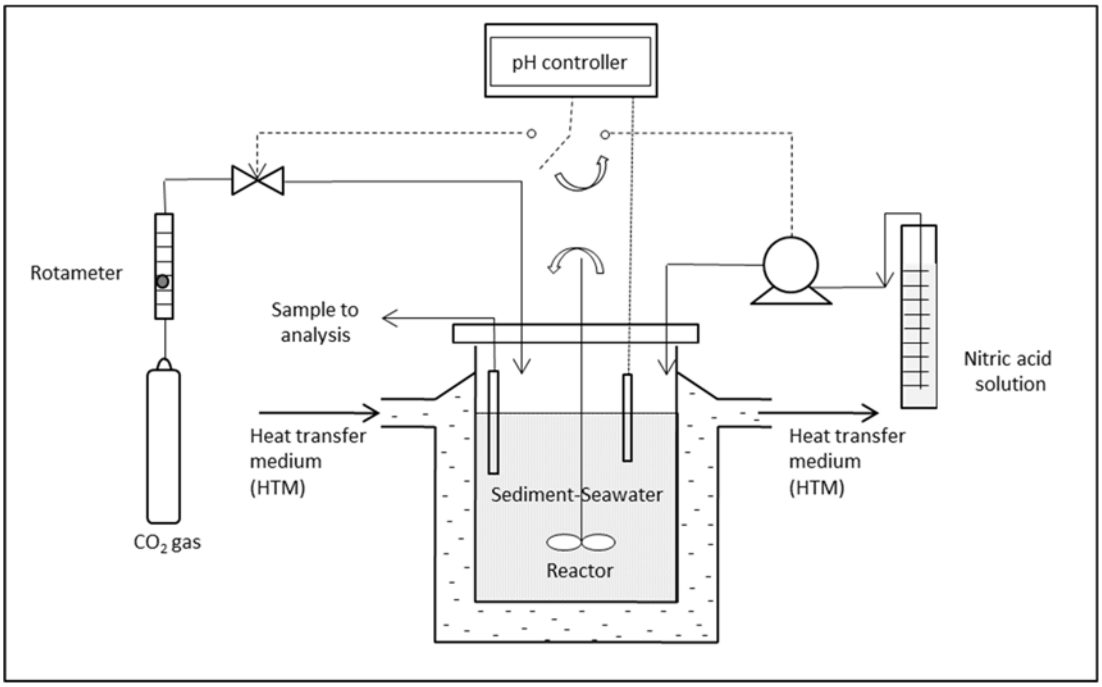


Fig. 1. Experimental equipment used in the pH-static leaching tests with continuous pH control. Depending on the position of the switch, the addition of CO_2, HNO_3 or of none of them (resuspension assay) was allowed.

Seawater and sediment were placed in the reactor at the Liquid to Solid (L/S) ratio of 10 and taking into consideration the moisture of the sediment, according to the standard. In all the assays, the mixture was shaken for 15 minutes before the beginning of the assay in order to homogenise it. Resuspension assays lasted 288 hours, when the value of the pH was almost constant. Assays conducted at pH = 6.5 using HNO_3 lasted 96 hours whereas assays acidified by CO_2 lasted between 288 and 360 hours, depending on the oxidation level of the sediment, until reaching constant pH. Samples of the mixture were taken at 0, 0.5, 1, 3, 6, 12, 24, 48, 72, 96 h and afterwards for every 48 hours without interrupting the shaking of the medium. The redox potential was measured continuously during the experiment by a Basic 20 pH metre (Crison) with a special electrode for samples with suspended solids. Samples were filtered through a 0.45-µm pore size nitrocellulose filtration membrane and HNO_3-acidified to analyse the dissolved concentrations of the selected trace elements by an Agilent 7500CE ICP-MS equipment in helium-collision mode. The detection limits for the elements under study (Zn, Pb, Cd, Ni, Cr, Cu and As) were 0.750; 0.0200; 0.0600; 0.230; 0.0300; 0.210 and 0.160 µg/L, respectively. Before the experiments, all the used material was precleaned, acid washed (10 % HNO_3) and rinsed with Milli-Q water (Direct-Q 5 UV, Merck Millipore). All the experiments were performed in duplicate.

In this study, the kinetic model proposed by Martín-Torre et al. (2015b) was used. The model considers that the contaminant (M) is associated with an oxidised fraction of the sediment (MOx) and with a reduced fraction (MRed), that must be oxidised before the release of the element. It also considers an adsorption/precipitation (MAd) reaction in series. The reaction scheme and the integral expression of the mass balance assuming first order reactions are shown in Eqs. 1 - 2, respectively.

$$\mathrm{MRed(s)} \xrightarrow{k_{1,i}} \mathrm{MOx(s)} \xrightarrow{k_{2,i}} \mathrm{M(aq)} \xrightarrow{k_{3,i}} \mathrm{MAd(s)} \tag{1}$$

$$\begin{aligned}\frac{LS}{1000}[M]_i = & \left(\frac{k_{1,i}\,k_{2,i}\,[MRed]_{i,0}}{(k_{2,i}-k_{1,i})\,(k_{3,i}-k_{1,i})}\right)\exp(-k_{1,i}t) \\ & + \left(\frac{k_{1,i}\,k_{2,i}\,[MRed]_{i,0}}{(k_{1,i}-k_{2,i})\,(k_{3,i}-k_{2,i})} - \frac{k_{2,i}\,[MOx]_{i,0}}{(k_{2,i}-k_{3,i})}\right)\exp(-k_{2,i}t) \\ & + \left(\frac{LS\,[M]_{i,0}}{1000} + \frac{k_{2,i}\,[MOx]_{i,0}}{(k_{2,i}-k_{3,i})}\right. \\ & \left. + \frac{k_{2,i}\,k_{1,i}\,[MRed]_{i,0}}{(k_{1,i}-k_{3,i})\,(k_{2,i}-k_{3,i})}\right)\exp(-k_{3,i}t)\end{aligned} \tag{2}$$

where LS corresponds to the Liquid/Solid ratio of the experiment, $[M]_{i,0}$ is the concentration of element i in the liquid phase at $t = 0$ expressed in units of μg/L, $[MRed]_{i,0}$ and $[MOx]_{i,0}$ are the maximum concentration (mg/kg) of the element i that can be released in the proposed leaching test from the reduced and oxidised fractions of the sediment respectively, and t is the reaction time. It should be noted that these concentrations are those available in the experimental conditions under study and do not have to match with the maximum extractable concentrations in each fraction.

The modelling of this study and the estimation of the corresponding parameters were completed using the Aspen Custom Modeler software which solves rigorous models and simultaneously estimates parameters. The adjustment of the model parameters was performed using the NL2SOL algorithm for the least-square minimization of the deviation between the experimental results and simulated data.

3. RESULTS AND DISCUSSION

The average value of the experimental results obtained for the release of Zn, Pb, Cd, Ni, As, Cu and Cr from the different experiments carried out in this work and the error bars between both replicates are shown in Fig. 2a, 2b and 2c. The relative error between both replicates under the same leaching conditions is lower than 20 % for any of the studied elements. Errors lower than 10 % are shown for the near half (49.56 %) of the experimental results obtained from assays with pH control; under resuspension conditions higher experimental variability is shown because the slight different behaviour of pH with time in each replicate.

3.1. Resuspension conditions

Under sediment-seawater resuspension conditions the pH is allowed to vary over time (Fig. 3). When anoxic sediment is used, the initial pH of the sediment-seawater mixture is 7.72. During the first 10.5 hours of the assay the pH increases and reaches a maximum value of 7.92. Afterwards, the pH decreases likely because the acid producing capacity resulting from the oxidation of reduced compounds is higher than the acid neutralising capacity of the mixture (Cappuyns and Swennen, 2005; Eggleton and Thomas, 2004; Ho et al., 2012; Hwang et al., 2011). The minimum value (pH = 6.91) occurs at t = 64 h. There is a subsequent increase of the pH value likely because there are not more oxidation reactions and there are still buffer components, like $CaCO_3$, in the medium; at t = 288 h the pH reaches a value of 7.30. The mixture of oxic sediment-seawater has an initial pH of 6.97. The pH increases over time, being the final measured pH value of 7.37. In both cases (anoxic and oxic sediment) the final pH of the sediment-seawater mixture takes a similar value (7.34 ± 0.0350).

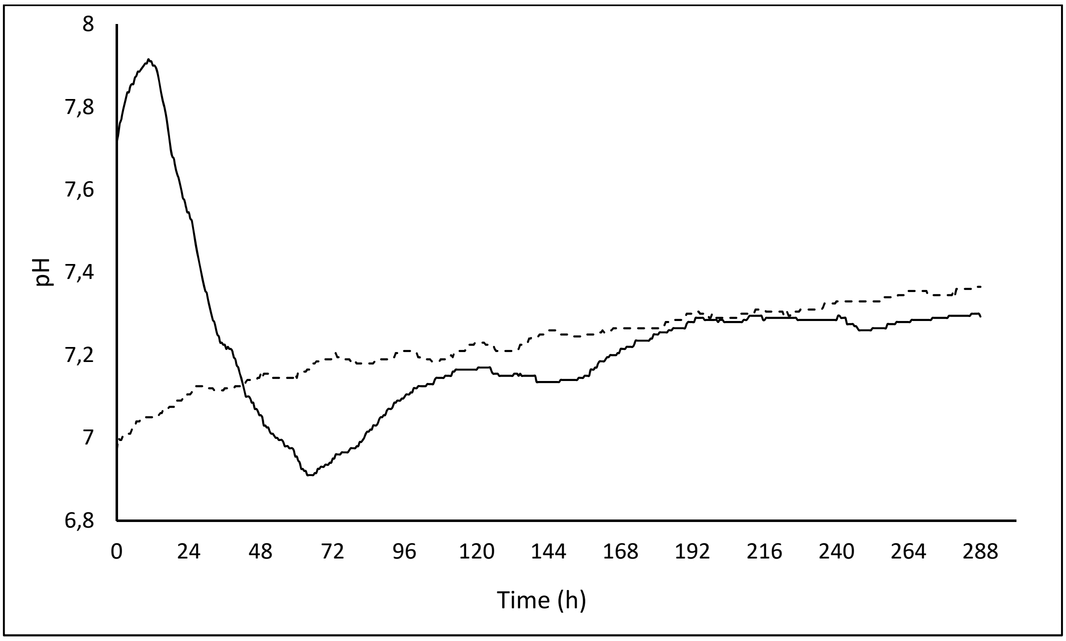


Fig. 3. Experimental pH evolution over time under resuspension conditions using anoxic and oxic sediment: ___ anoxic sediment; ---oxic sediment

Element release models that include pH instead of other explanatory variables such as the redox potential shows a slightly better explaining power (Schul-Zunkel et al., 2015). The pH of the resuspension assays varies over time so it has to be fitted to polynomial equations before being introduced in the kinetic model, as shown in the Section 1 of the Supplementary Information.

Fig. 2a shows the trace element experimental release ($C_{L,i}$) over time under resuspension conditions for assays with anoxic and oxic sediment. Considering the concentrations of Cd, Cu and Cr in the used seawater (0.481 ± 1.02, 1.62 ± 1.03 and 0.718 ± 0.418 µg/L, respectively) and their low release (0.149 - 0.394; 0.510 - 1.73 and 1.00 - 4.74 µg/L, respectively) independently of the sediment level of oxidation, their mobilisation from the sediment is considered negligible and these elements are not modelled. The main reason for this behaviour might be the high insolubility of their salts. In the case of Ni, there is a fast release, higher from the oxic sediment than from the anoxic one. Hence, at t = 0 h and when oxic sediment is used, all the Ni that can be leached from the sediment is already in the liquid phase. As a consequence of this rapid release, it is not possible to determine the kinetic parameters of the mathematical model. Zn shows a similar release behaviour from both sediments, although leached concentrations from oxic sediment are higher during the whole assay. On the contrary, the release of As and Pb does not present a clear trend.

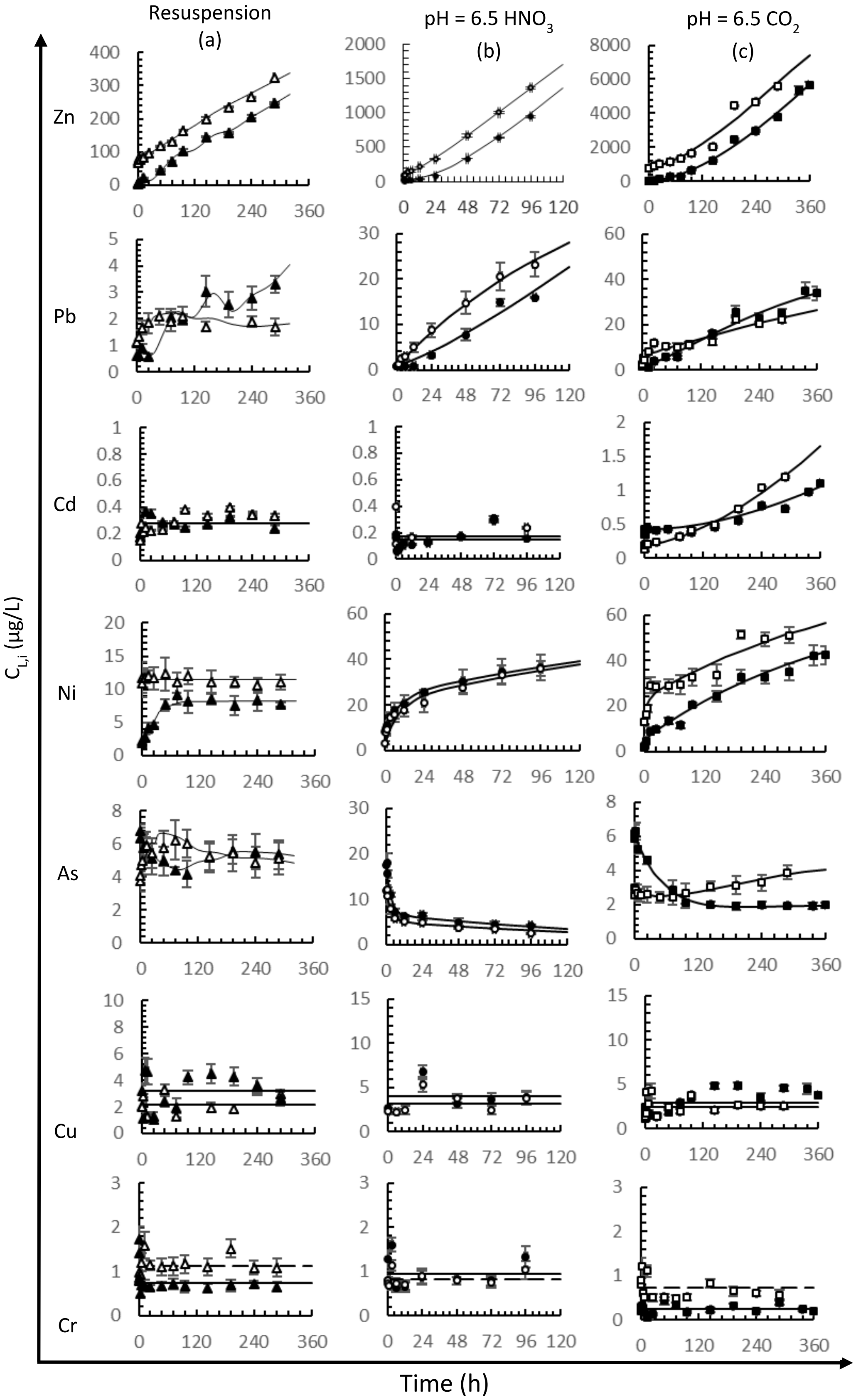
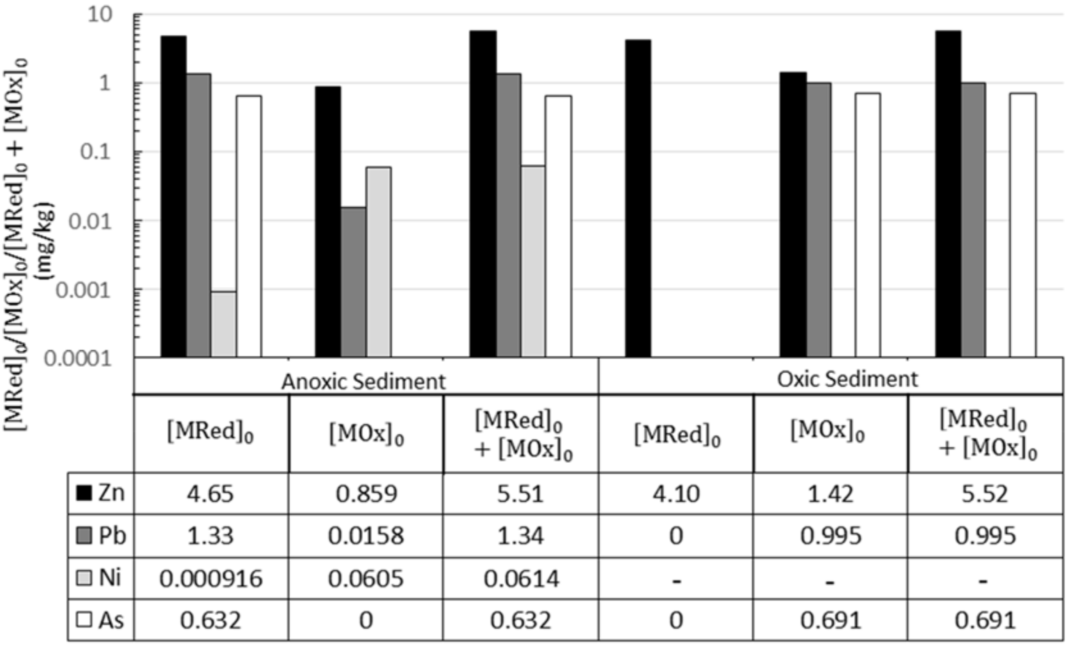


Fig. 2. Experimental and modelled concentration ($C_{L,i}$) over time under (a) resuspension, (b) HNO_3 and (c) CO_2 acidified at pH = 6.5 conditions using anoxic and oxic sediment: ▲ resuspension with anoxic sediment; △ resuspension with oxic sediment; ● pH = 6.5, HNO_3 acidified with anoxic sediment; ○ pH = 6.5, HNO_3

acidified with oxic sediment; ■ pH = 6.5, CO_2 acidified with anoxic sediment; □ pH = 6.5, CO_2 acidified with oxic sediment, ___ modelled curve for anoxic sediment; _ _ modelled curve for oxic sediment. Error bars between both experimental replicates are also shown.

In Fig. 4 the maximum concentrations, under resuspension conditions, that can be leached from the reduced ($[\mathrm{MRed}]_0$) and oxidised ($[\mathrm{MOx}]_0$) fraction of the sediment, as well as the sum of the maximum concentrations that can be leached from both fractions of the sediment ($\mathrm{C}_{\mathrm{s},0} = [\mathrm{MRed}]_0 + [\mathrm{MOx}]_0$), are shown.



	Anoxic Sediment $[\mathrm{MRed}]_0$	Anoxic Sediment $[\mathrm{MOx}]_0$	Anoxic Sediment $[\mathrm{MRed}]_0 + [\mathrm{MOx}]_0$	Oxic Sediment $[\mathrm{MRed}]_0$	Oxic Sediment $[\mathrm{MOx}]_0$	Oxic Sediment $[\mathrm{MRed}]_0 + [\mathrm{MOx}]_0$
■ Zn	4.65	0.859	5.51	4.10	1.42	5.52
▨ Pb	1.33	0.0158	1.34	0	0.995	0.995
▒ Ni	0.000916	0.0605	0.0614	-	-	-
□ As	0.632	0	0.632	0	0.691	0.691

Fig. 4. Maximum concentrations that can be leached from the reduced and oxidised fractions of the anoxic and oxic sediment under resuspension conditions. $[\mathrm{MRed}]_0$ and $[\mathrm{MOx}]_0$ are the reduced and oxidised fractions of the sediment, respectively.

As expected, the element concentrations that can be leached from the oxidised fraction are higher in assays using oxic sediment than when anoxic sediment is selected. In addition, the contaminant concentrations leached from the reduced fraction of the sediment are higher in assays using anoxic sediment. The maximum release ($\mathrm{C}_{\mathrm{s},0}$) of Zn and As is slightly higher when the oxic sediment is used likely because of the transformation of the stable metal sulphides into more labile binding positions during the oxidation process of the sediment (Calmano et al., 1993). On the contrary, Pb mobilisation is higher from the anoxic sediment.

Considering that the pH is not constant in the resuspension assay, kinetic parameters which depend on the pH ($k_{j,i}$) have to be correlated with this variable following a second order polynomial equation, obtaining the kinetic and statistical parameters shown in Table 1.

Table 1. Coefficients of the second order equations that correlate kinetic rate coefficients with the pH under resuspension conditions.

Trace element	**Sediment**	$k_{1,i} = n_{1,i}\,pH^2 + m_{1,i}\,pH + p_{1,i}$			$k_{2,i} = n_{2,i}\,pH^2 + m_{2,i}\,pH + p_{2,i}$			$k_{3,i} = n_{3,i}\,pH^2 + m_{3,i}\,pH + p_{3,i}$		
		$n_{1,i}$	$m_{1,i}$	$p_{1,i}$	$n_{2,i}$	$m_{2,i}$	$p_{2,i}$	$n_{3,i}$	$m_{3,i}$	$p_{3,i}$
Zn	**Anoxic and oxic**	0.00323	-0.042	0.143	0.0175	-0.261	0.978	-	-	-
Pb	**Anoxic**	0.00332	-0.0431	0.143	0.00476	-0.0705	0.261	-	-	-
	Oxic				0.00484	-0.0711	0.261	-	-	-
Cd	**Oxic**	0.0037	-0.0457	0.148	0.0173	-0.0668	0.509	-	-	-
Ni	**Anoxic**	0.00332	-0.0435	0.147	0.0158	-0.263	1.11	-	-	-
As	**Anoxic**	0.00513	-0.0735	0.265	0.0105	-0.122	0.358	0.0237	-0.342	1.25
	Oxic				0.0428	-0.622	2.26	0.0869	-1.23	4.36
Percentage variation explained (R^2)							99.23			
Relative standard deviation (RSD in %)							6.03			

For all the trace elements under study and both types of sediment, the parameters to correlate the kinetic rate of the oxidation reaction ($k_{1,i}$) take the same value than those obtained in assays using HNO_3 (Martín-Torre et al., 2015b). The release kinetic parameters ($k_{2,i}$) does not present a common trend for the elements under study likely due to the ionic competition occurs in the sediment-seawater system. The oxyanion As is the only trace element with an adsorption/precipitation reaction ($k_{3,i} \neq 0$). The modelled curves under resuspension conditions, shown in Fig. 2a, correlate reasonably well ($R^2 = 99.2$ %, RSD = 6.03 %) with the experimental results.

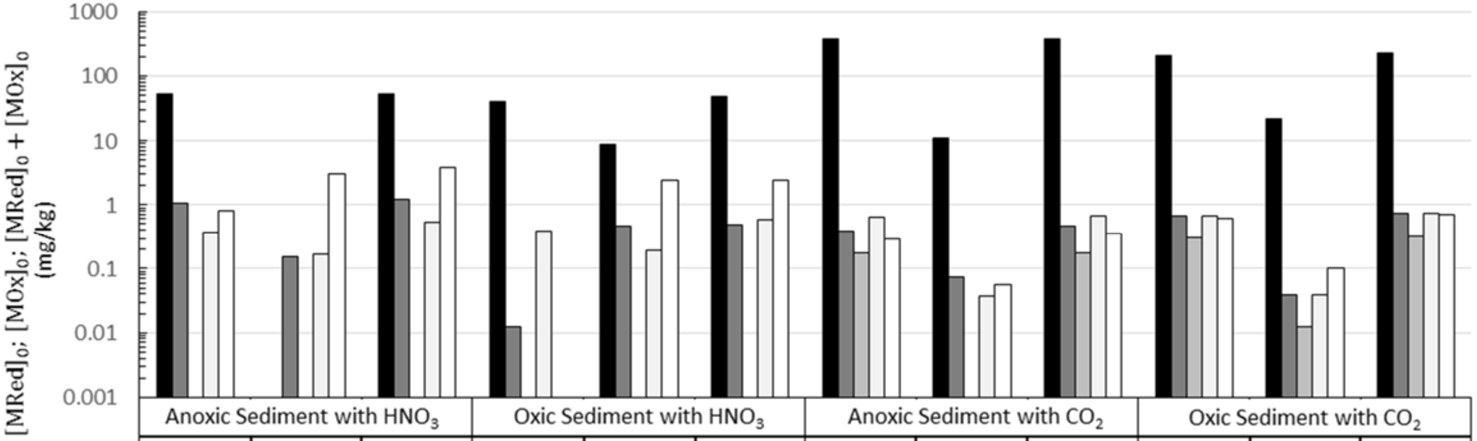
3.2. Acidified conditions at pH = 6.5 with HNO_3 and CO_2

As shown in Fig. 2b and 2c, the mobilisation of Cu and Cr at pH = 6.5 with both types of acidification and the release of Cd in assays using HNO_3 are almost constant and lower than 5 μg/L. Similarly to resuspension conditions, taking into account the initial concentration in the seawater, their release is considered negligible.

Independently of the type of acidification, the initial delay of Zn, Pb and Cd is shorter when the oxic sediment is used likely because there is a higher concentration of each element in the oxidised fraction, which is released before that from the reduced fraction of the sediment. The release of Ni seems not to be depend on the acid used due to the similar leaching behaviour in both assays.

The initial release rate of Zn, Pb and Ni is higher from oxic sediments than from anoxic sediments, except in the case of Ni in assays by using HNO_3, in which the mobilisation rate from both types of sediment is similar. Initially, arsenic shows a higher release from the anoxic sediment. In the case of HNO_3 acidification, the mobilisation of As at short times ($t < 6$ h) is higher than its release in CO_2 assays; however, as the following adsorption is also higher, the final release of As is almost coincident in all the studied cases (lower than 4.00 µg/L).

Regarding the acidification with HNO_3, the contaminant release patterns are similar independently of the level of oxidation of the sediment although the release rates differ significantly. In the case of CO_2 acidification, only the release of Zn and Ni follow the same pattern for both sediments used (oxic and anoxic). At $t = 96$ h, there is a higher release of Zn, Pb and Ni in assays acidified with HNO_3 whereas dissolved concentrations of Cd are slightly higher in assays with CO_2. The application of the mathematical model of Martín-Torre et al. (2015b) to the experimental results leads to the modelled curves under $pH = 6.5$ acidification by HNO_3 and CO_2 shown in Fig. 2a and b. The maximum released concentrations from the reduced and oxidised fractions and the kinetic parameters ($k_{j,i}$) are obtained.



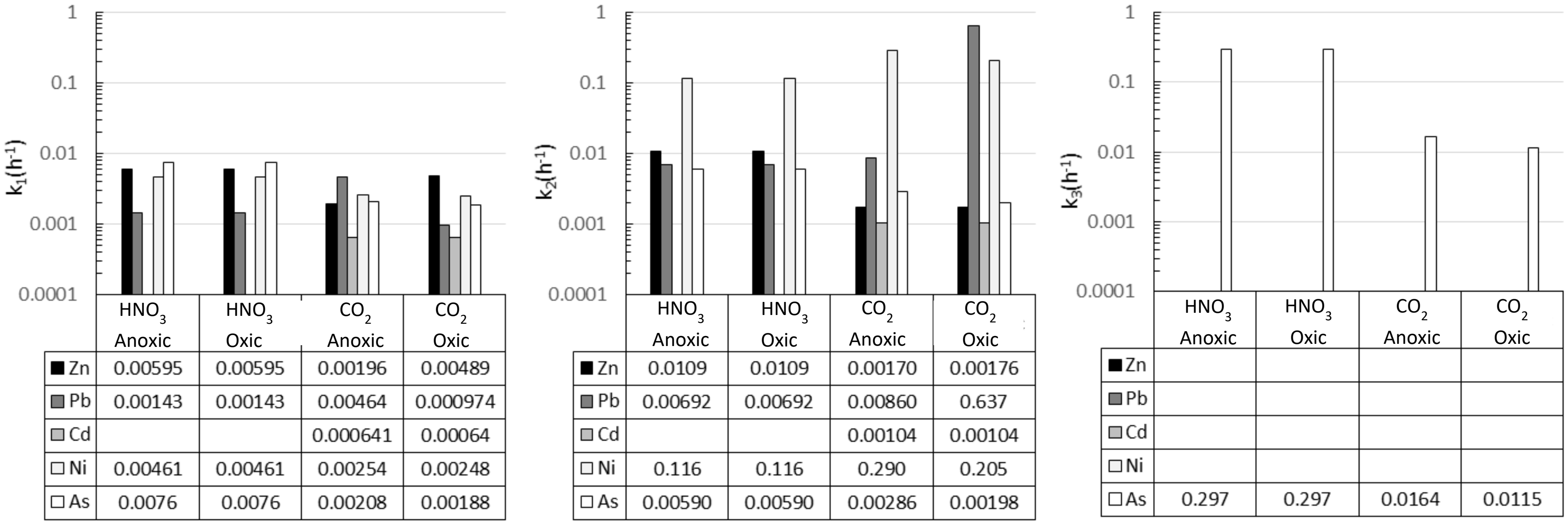
	Anoxic Sediment with HNO$_3$			Oxic Sediment with HNO$_3$			Anoxic Sediment with CO$_2$			Oxic Sediment with CO$_2$		
	[MRed]$_0$	[MOx]$_0$	[MRed]$_0$ + [MOx]$_0$	[MRed]$_0$	[MOx]$_0$	[MRed]$_0$ + [MOx]$_0$	[MRed]$_0$	[MOx]$_0$	[MRed]$_0$ + [MOx]$_0$	[MRed]$_0$	[MOx]$_0$	[MRed]$_0$ + [MOx]$_0$
■ Zn	52.7	0	52.7	39.6	8.94	48.5	373	10.8	383	209	22.3	232
▩ Pb	1.05	0.156	1.21	0.0122	0.474	0.486	0.389	0.0733	0.463	0.684	0.038	0.722
▨ Cd	-	-	-	-	-	-	0.178	0.000	0.178	0.305	0.0124	0.318
□ Ni	0.363	0.166	0.529	0.380	0.195	0.575	0.635	0.038	0.672	0.684	0.038	0.722
□ As	0.799	2.99	3.79	0	2.40	2.40	0.298	0.056	0.354	0.598	0.102	0.700

Fig. 5. Maximum concentration of each studied trace element that can be leached from the sediment and from each fraction (oxidised fraction and reduced fraction) in units of mg/kg.

Fig. 5 shows the maximum concentrations that can be leached from the reduced ($[\mathrm{MRed}]_0$) and oxidised ($[\mathrm{MOx}]_0$) fractions of the sediment as well as the maximum concentration that can be leached from the sediment ($\mathrm{C}_{\mathrm{s},0} = [\mathrm{MRed}]_0 + [\mathrm{MOx}]_0$)). In assays acidified by HNO_3, the maximum concentrations leached from the oxidised fraction are higher in the assays which use the oxic sediment than those with the anoxic sediment in the cases of Zn, Pb and Ni whereas this situation is shown for Zn, Cd and As when CO_2 is added to the sediment-seawater mixture. When the acidification is obtained by the addition of HNO_3, the concentration of As that can be leached from the reduced fraction takes the value of zero. Under both studied acidic conditions (HNO_3 and CO_2) there is an increase in the percentage of the concentration that can be leached from the oxidised fraction in the oxic sediment with respect to the anoxic sediment; this implies a proportional decrease of the percentage of the potential leachable element concentration from the reduced fraction of the oxic sediment in relation to the anoxic sediment. Exceptions are found in the cases of Pb in assays with HNO_3 and Ni in assays with CO_2.

In assays with HNO_3, the maximum concentration that can be leached from the sediment of all the modelled contaminants is higher in the anoxic sediment. In the case of Ni, almost the same concentration (0.529 and 0.575 mg/kg) can be leached from oxic and anoxic sediment in both type of assays. In the assays using CO_2, a higher release from the anoxic sediment is shown in the case of Zn but not for the rest of the trace elements under study. This different trend between HNO_3 and CO_2 acidified assays might be caused by the influence of the acidic agent on the characteristics of the medium: CO_2 gas modifies the chemical equilibria of the sediment-seawater mixture whereas HNO_3 does not. Hence, acidification with CO_2 provokes higher leached concentrations ($C_{s,0}$) from the oxic sediment than from the anoxic sediment, except in the case of the major of the trace elements (Zn), which influences the release of the other studied trace elements.

The kinetic parameters $k_{1,i}$ of the oxidation, $k_{2,i}$ of the release and $k_{3,i}$ of the adsorption/precipitation reactions in assays at pH = 6.5 obtained from the mathematical model are shown in Fig. 6. The kinetic parameters obtained in assays acidified by HNO_3 take the same value independently of the sediment level of oxidation. Hence, in HNO_3-acidified assays, the mobilisation of the contaminants only depends on the maximum concentrations that can be leached from the reduced and oxidised fractions. On the other hand, the kinetic parameters from assays in which CO_2 is used for the acidification are different depending on the oxidation level of the sediment. It might be provoked by the changes which occurred in the sediment-seawater mixture due to the interaction of the CO_2 with the ions present in the medium. HNO_3 is a strong and oxidant acid which generates soluble salts whereas CO_2 is a weak acid that generates partially soluble salts which influence the ionic competition and influence trace element release. Moreover, the kinetic parameters vary differently for each trace element without a clear pattern due to the characteristics of the medium, their concentration and the interactions among all the elements.



	HNO_3 Anoxic	HNO_3 Oxic	CO_2 Anoxic	CO_2 Oxic
■ Zn	0.00595	0.00595	0.00196	0.00489
▩ Pb	0.00143	0.00143	0.00464	0.000974
▨ Cd			0.000641	0.00064
□ Ni	0.00461	0.00461	0.00254	0.00248
□ As	0.0076	0.0076	0.00208	0.00188

	HNO_3 Anoxic	HNO_3 Oxic	CO_2 Anoxic	CO_2 Oxic
■ Zn	0.0109	0.0109	0.00170	0.00176
▩ Pb	0.00692	0.00692	0.00860	0.637
▨ Cd			0.00104	0.00104
□ Ni	0.116	0.116	0.290	0.205
□ As	0.00590	0.00590	0.00286	0.00198

	HNO_3 Anoxic	HNO_3 Oxic	CO_2 Anoxic	CO_2 Oxic
■ Zn				
▩ Pb				
▨ Cd				
□ Ni				
□ As	0.297	0.297	0.0164	0.0115

Fig.6. Kinetic rate coefficients of the generalised chemical reactions that occurred at pH = 6.5 using anoxic and oxic sediment.

Parity plots (Fig. 7) are useful for the validation of the model in terms of the released element concentration at any time and pH value. In the case of Cd, the results from the assays with CO_2 acidification are the only considered because they are the only which are modelled. Differences between experimental and simulated mobilisation are lower than 20% for 85.1 % of the data. Moreover, they are lower than 10 % for 74.7 % of the data. Considering all the trace elements at once, the data number (N) is 316, the percentage variation-explained value (R^2) takes a value of 99.2 % and the relative standard deviation (RSD) is 25.0 %. The high values of the global statistical parameters and the high individual R^2 (Fig. 7), show the good fit of the proposed model in all studied experiments.

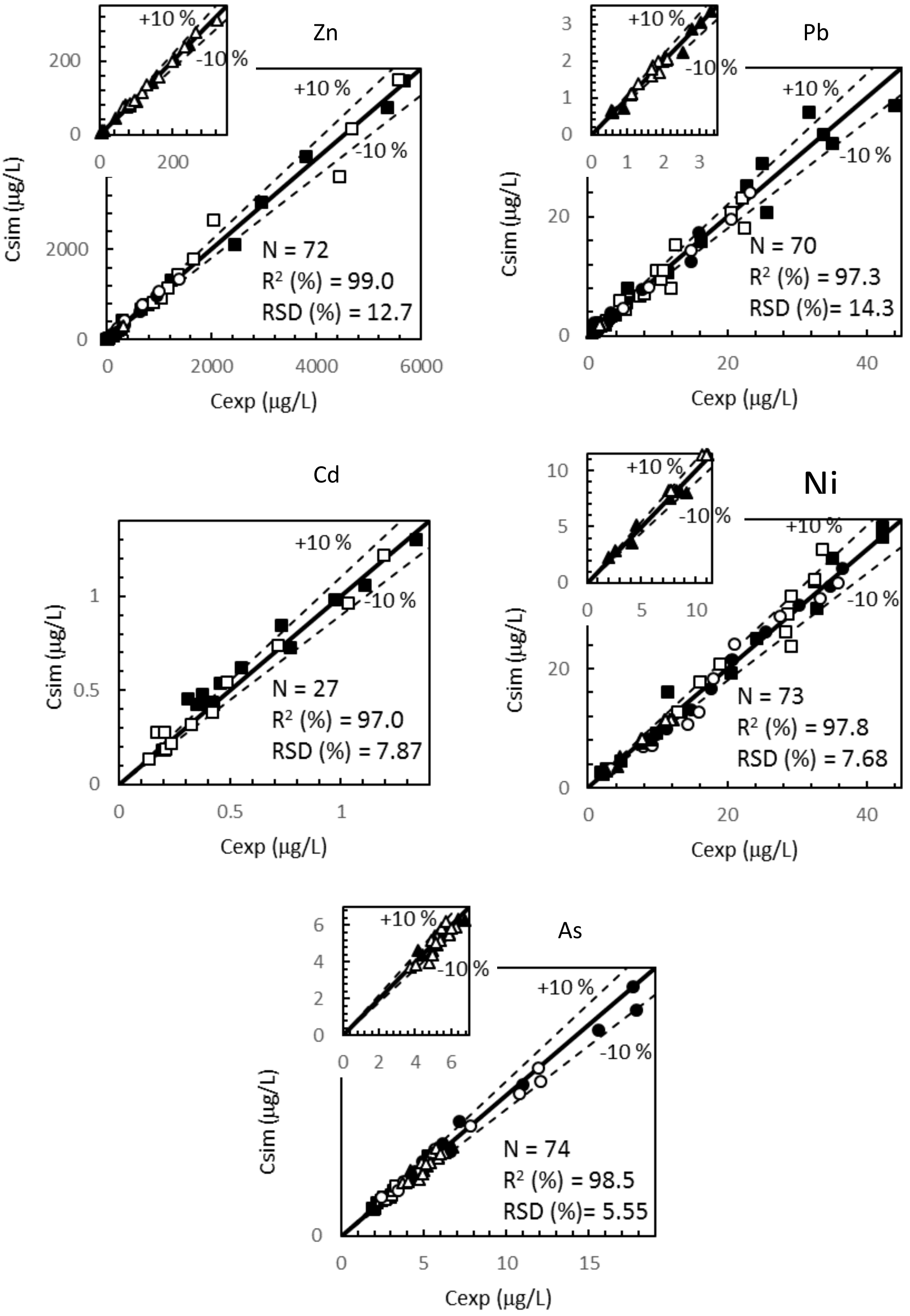


Fig. 7. Parity plots of the element concentrations from the experimental (Cexp) and simulated (Csim) results of the elements under study. ▲ resuspension with anoxic sediment; △ resuspension with oxic sediment; ● pH = 6.5, HNO_3 acidified with anoxic sediment; ○ pH = 6.5, HNO_3 acidified with oxic sediment; ■ pH = 6.5, CO_2 acidified with anoxic sediment; □ pH = 6.5, CO_2 acidified with oxic sediment. Additionally, the data number (N), percentage variation-explained value (R^2) and relative standard deviation (RSD) are shown.

3.3. Simulation of the trace element release at pH = 7.0 (resuspension, HNO_3 and CO_2 acidification)

During the resuspension experiment using anoxic sediment, the mixture reaches a pH value of 7.0 ± 0.30 for more than 260 h, beyond the initial 24 h. For this reason, it would be useful to compare the mobilisation of elements under resuspension conditions against acidification conditions achieved by HNO_3 and CO_2 at pH = 7.0 (Fig. 8). This comparative analysis highlights how small changes in the natural pH increase highly the release of the studied elements. Modelled data are obtained by applying the mathematical model of Martín-Torre et al. (2015b) to the experimental results.

In order to better compare the release of contaminants over time, we consider a 'release fraction' (x_i), defined as Eq. 8, which takes into consideration the maximum concentration that can be leached from the sediment, $C_{s,0}$. (Eq. 9).

$$x_i = \frac{C_i - C_{i,0}}{C_{s,0}} \qquad \text{(Eq. 8)}$$

$$C_{s,0} = [MRed]_0 + [MOx]_0 \qquad \text{(Eq. 9)}$$

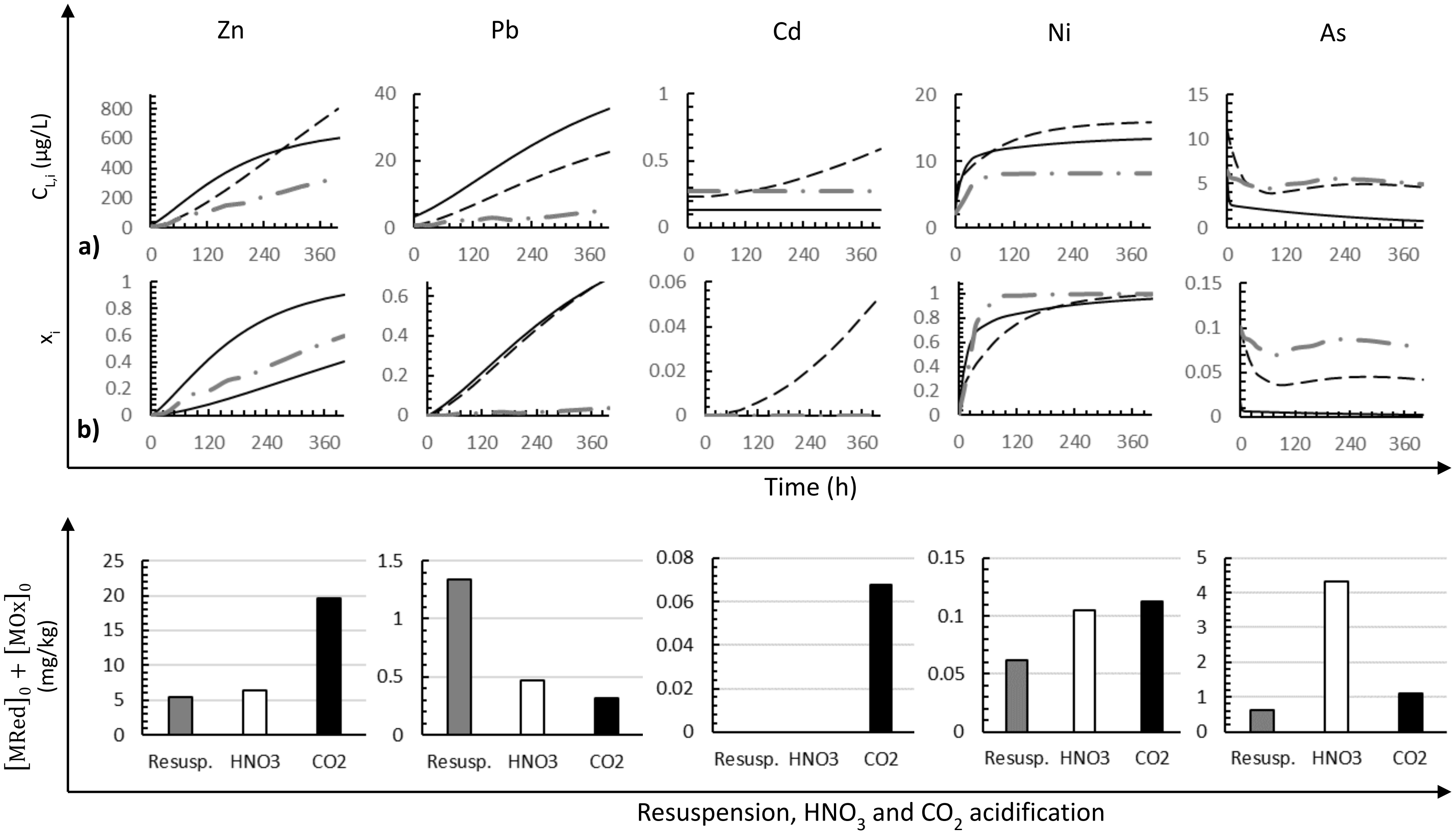


Fig. 8. a) Simulation over time of trace element released concentration ($C_{L,i}$) and release fraction (x_i) from anoxic sediment under resuspension (— ·); acidification at pH = 7.0 with CO_2 (— —) and HNO_3 (——) conditions; b) Maximum concentration that can be leached ($C_{s,0}$) from anoxic sediment under resuspension (— ·); acidification at pH = 7.0 with CO_2 (— —) and HNO_3 (——) conditions.

Fig. 8a shows the modelled curves for the trace element release over time under resuspension and acidification ($pH = 7.0$) conditions. The 'release fraction' (x_i) is shown in Fig. 8b in order to address in detail, and without the influence of the initial dissolved concentrations, the trace element mobilisation under each studied scenario. Moreover, the slope of these modelled curves indicates the release rate of each element. Hence, at short times, the most rapid release of Zn, Pb and Ni occurs in the assay acidified by HNO_3 (Fig. 8b).

In Fig. 8c the maximum concentrations that can be leached from the sediment ($C_{s,0} = [MRed]_0 + [MOx]_0$) are shown. In the cases of Zn, Pb, Cd and Ni, this maximum concentration is achieved at long times whereas in the case of As, it occurs at $t = 0$. The concentrations of As in the liquid phase at longer times are always lower than the initial one due to the adsorption process. The higher maximum dissolved concentrations of Zn, Cd and Ni that can be leached from the sediment are shown under CO_2-acidified conditions. However, the metal Pb releases the most under resuspension scenario. This fact highlights how anthropogenic activities or natural events might provoke higher risks than slight acidification conditions.

The oxyanion As is the only element which is adsorbed or precipitated after an initial release. Although the dissolved concentration of As at $t = 0$ is higher in HNO_3-acidified assays than in the other two cases, it is the lowest at long times (Fig. 8b). Higher initial dissolved concentrations of As, make the trace element more available to precipitate or adsorb when nitric acid is added to the sediment-seawater mixture.

4. CONCLUSIONS

This work analyses and models the release of Zn, Pb, Cd, Ni, Cu, Cr and As over time under resuspension and acidification (pH = 6.5 and 7.0) conditions using anoxic and oxic sediment. The kinetic parameters and the maximum concentrations that can be leached from the sediment allow for predicting the element release behaviour and the maximum concentrations in the seawater from anoxic (-168 ± 7.00 mV) and oxic (27.0 ± 37.0 mV) sediment under different conditions: acidification by HNO_3 (potential acid spills), acidification by CO_2 (mimicking potential leakages from CCS) and resuspension conditions due to natural or anthropogenic causes.

Acidification at pH = 6.5 is studied as worst-case scenario in events of CO_2 leakages. The kinetic coefficients obtained from assays acidified by HNO_3 present a clear trend whereas it does not happen in assays with CO_2, likely due to the influence of the CO_2 gas on the ionic competition of the medium. Acidification with CO_2 provokes higher leached concentrations from the oxic sediment than from the anoxic sediment, except in the case of Zn, the major of the trace elements which influences the release of the other studied elements. Independently of the external stress to the environment (resuspension, acidification with HNO_3 or with CO_2), sediment layers with different redox values, implies a release with different modelled contaminant speciation (oxidised or reduced element). Therefore, a distinct biodisponibility and potential effects in the marine environment would be expected.

Acidification at pH = 7.0 is studied as a seawater acidification scenario by CO_2 leakages from storage sites as well as sediment resuspension. The release of most trace elements from anoxic sediment, independently of the type of acidification (HNO_3 or CO_2), is higher than under resuspension conditions showing that even a slight acidification can endanger the aquatic environment through an important mobilisation of contaminants. However, resuspension conditions might mobilise some contaminants, like Pb, more than slight acidification levels.

In order to increase the range of applicability of the mathematical model used, additional steps should analyze the results studying sediments with different physico-chemical properties and the influence of organic matter under pH and redox environmental relevant conditions.

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