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

M. Camino Martín-Torre, Eva Cifrian, Gema Ruiz, Berta Galán, Javier R. Viguri*

Green Engineering & Resources Research Group (GER), Department of Chemistry and

Process & Resources Engineering, ETSIIT, University of Cantabria, Avda. de los

Castros s/n, 39005 Santander, Cantabria, Spain

* Corresponding author. Tel.: +34 942 201583; fax: +34 942 206706

E-mail address: vigurij@unican.es (Javier R. Viguri)

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.

2

Graphical Abstract
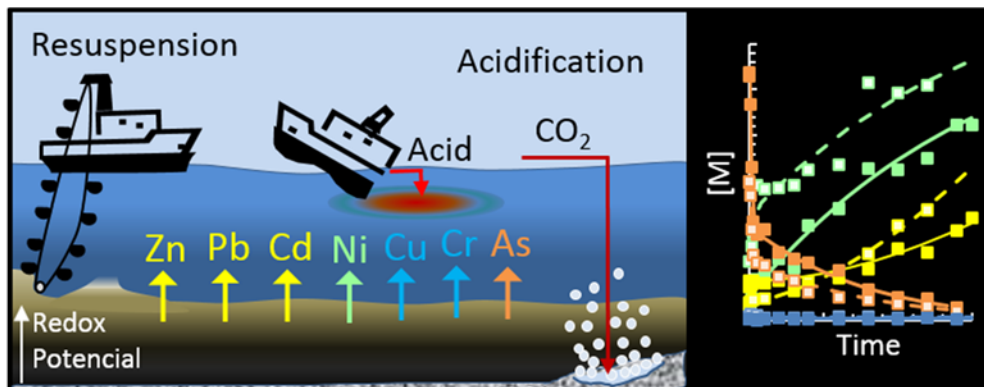
1. INTRODUCTION

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

121   oxidation level within sediments might vary over short periods of time, the redox

122   potential of the sediment matrix is expected to influence the release behaviour of

123   contaminants (Cappuyns and Swennen, 2005; Kalnejais et al., 2015; Lions et al., 2014).

124   In this way, the redox potential and pH are the two primary factors controlling the

125   release of trace metals from sediments (Frohne at al., 2011; Fonti et al., 2013; Choppala

126   et al., 2017).

127

128   The pH dependence leaching test with continuous pH control (CEN/TS 14997: 2006

129   standard, superseded by EN14997: 2015) has been previously used to assess

130   contaminant release from sediment under different types of acidification (Martín-Torre

131   et al., 2015b and Martín-Torre et al., 2016). Moreover, and owing to the huge number of

132   complex reactions involved in contaminant mobilisation from sediment matrices, a

133   general mathematical model has been proposed to fit experimental release over time

134   (Martín-Torre et al., 2015b). However, a comparative analysis and modelling of element

135   release under different types of acidification conditions and sediments with different

136   levels of oxidation has not been addressed, to the best of our knowledge.

137

138   The main purpose of this article is the analysis and modelling of the release of As, Cd,

139   Cr, Cu, Ni, Pb and Zn under different conditions of acidification and oxidation levels

140   from estuarine contaminated sediment. Hence, the release of trace elements from anoxic

141   and oxic sediment is addressed under resuspension conditions in order to analyse the pH

142   range of variation and the trace element mobilisation. Afterwards, the comparative

143   leaching behaviour of contaminants from anoxic and oxic sediment is assessed using

144   HNO_3 or CO_2 at pH = 6.5. Finally, the leaching behaviour of the trace elements from

145   anoxic sediment is compared under resuspension and acidification situations obtained

146   by the addition of HNO_3 or CO_2 at the minimum pH value achieved by the resuspension

147   experiments (pH = 7.0).

148

149   **2. EXPERIMENTAL METHODOLOGY**

150   The sediment samples were collected in the Suances estuary, inside a potential site for

151   CO_2 storage in the Cantabrian region (Northern Spain) (BOE, 2008). Shallow sediment

152   (0-5 cm) with its initial water content was sampled using a plastic paddle, sieved

153   through a 2-mm plastic mesh, homogenised and frozen until use.

154

155   When the leaching tests were performed with anoxic sediment (-168 ± 7.00 mV), the

156   selected sediment samples were used the day after being unfrozen. Oxic sediment

157   samples (27.0 ± 37.0 mV) were achieved after some weeks stored in the fridge. In this

158   period of time, the initially anoxic sediment was oxidised leading to a pH reduction and

159   an increase in redox potential. Upon oxidation, among other changes in the speciation

160   and binding of metals, sulphides were partially converted to sulphate and to

161   intermediary oxidised sulphur compounds (Calmano et al., 1993; Cappuyns and

162   Swennen, 2006; Tack et al., 1997). Therefore, the colour of the sediment also changed

163   (from very dark brown to brownish). It is important to highlight that the terms 'anoxic'

164   and 'oxic' refer to the initial state of the sediment, because the oxidation of the sediment

165   was allowed over the time of assay.

166

167   As explained in Martín-Torre et al. (2015b), the main crystalline phases of the used

168   sediment are quartz, aluminium oxide, calcite and dolomite. The total concentrations of

169   Zn, Pb, Cd, Ni, Cr, Cu and As are 5220 ± 140, 564 ± 2.22, 12.6 ± 0.732, 36.0 ± 1.86,

170   72.0 ± 5.31, 48.0 ± 3.13 and 59.0 ± 1.39 mg/kg, respectively.

171   The modified pH dependence leaching tests performed in this work were based on the

172   CEN/TS 14997: 2006 standard although some modifications such as the particle size,

173   the leaching agent and the duration of the experiment were undertaken. The

174   experimental equipment consisted of a glass-made 2-L jacketed vessel and a

175   temperature controller (Polyscience) in order to perform all the assays at a temperature

176   of 20 ºC. The operation of the equipment when HNO_3 was used to acidify the medium

177   is already published in Martín-Torre et al., 2015b. When the acidification was provoked

178   by the addition of CO_2, the pH controller (AT Control systems) injected pure CO_2

179   bubbles as needed to maintain the set point pH of the assay, with a hysteresis of 0.1 pH

180   units (Martín-Torre et al., 2016). In the resuspension assays, the pH was measured

181   continuously but without any control. A schematic figure of the three possibilities of the

182   experimental equipment is shown in Fig. 1. In all the cases, the pH electrode used was

183   suitable for samples with suspended solids and calibrated against standard solutions.

184
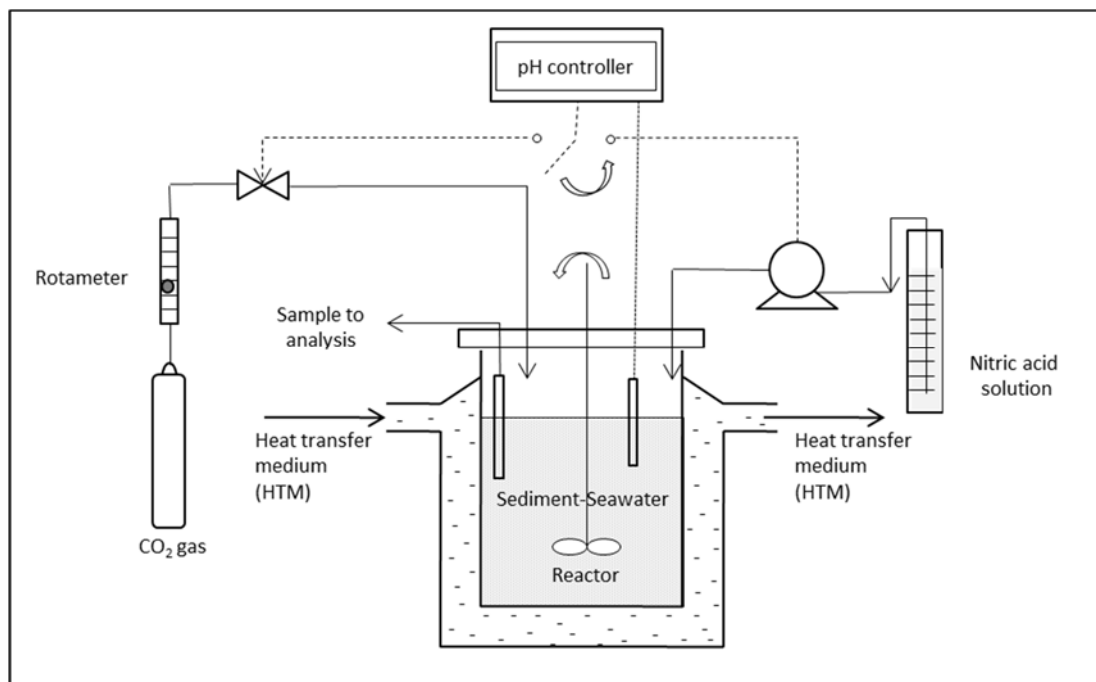
185

186   Fig. 1. Experimental equipment used in the pH-static leaching tests with continuous pH

187   control. Depending on the position of the switch, the addition of CO_2, HNO_3 or of none

188   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.

214

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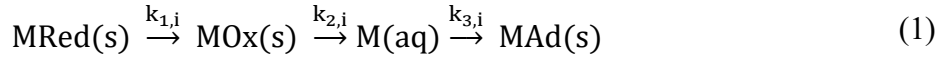
$$\begin{aligned}
\frac{LS}{1000}[M]_i = & \left(\frac{k_{1,i}\, k_{2,i}\, [MRed]_{i,0}}{\left(k_{2,i} - k_{1,i} \right)\left(k_{3,i} - k_{1,i} \right)} \right) \exp\left(-k_{1,i}t \right) \\[2mm]
& + \left(\frac{k_{1,i}\, k_{2,i}\, [MRed]_{i,0}}{\left(k_{1,i} - k_{2,i} \right)\left(k_{3,i} - k_{2,i}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

215

216   where LS corresponds to the Liquid/Solid ratio of the experiment, $[M]_{i,0}$ is the

217   concentration of element i in the liquid phase at $t = 0$ expressed in units of µg/L,

218    $[MRed]_{i,0}$ and $[MOx]_{i,0}$ are the maximum concentration (mg/kg) of the element i that

219   can be released in the proposed leaching test from the reduced and oxidised fractions of

220   the sediment respectively, and t is the reaction time. It should be noted that these

221   concentrations are those available in the experimental conditions under study and do not

222   have to match with the maximum extractable concentrations in each fraction.

223

224   The modelling of this study and the estimation of the corresponding parameters were

225   completed using the Aspen Custom Modeler software which solves rigorous models and

226   simultaneously estimates parameters. The adjustment of the model parameters was

227   performed using the NL2SOL algorithm for the least-square minimization of the

228   deviation between the experimental results and simulated data.

229

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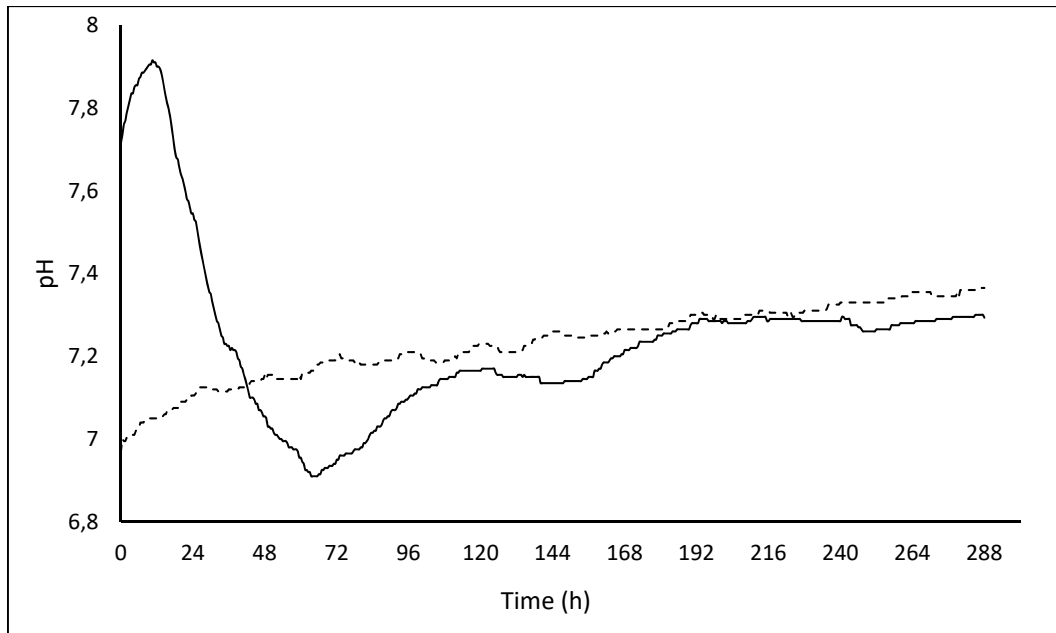
Fig. 3. Experimental pH evolution over time under resuspension conditions using anoxic and oxic sediment: ⎯ anoxic sediment; ---oxic sediment

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

12

273   t = 0 h and when oxic sediment is used, all the Ni that can be leached from the sediment

274   is already in the liquid phase. As a consequence of this rapid release, it is not possible to

275   determine the kinetic parameters of the mathematical model. Zn shows a similar release

276   behaviour from both sediments, although leached concentrations from oxic sediment are

277   higher during the whole assay. On the contrary, the release of As and Pb does not

278   present a clear trend.

279
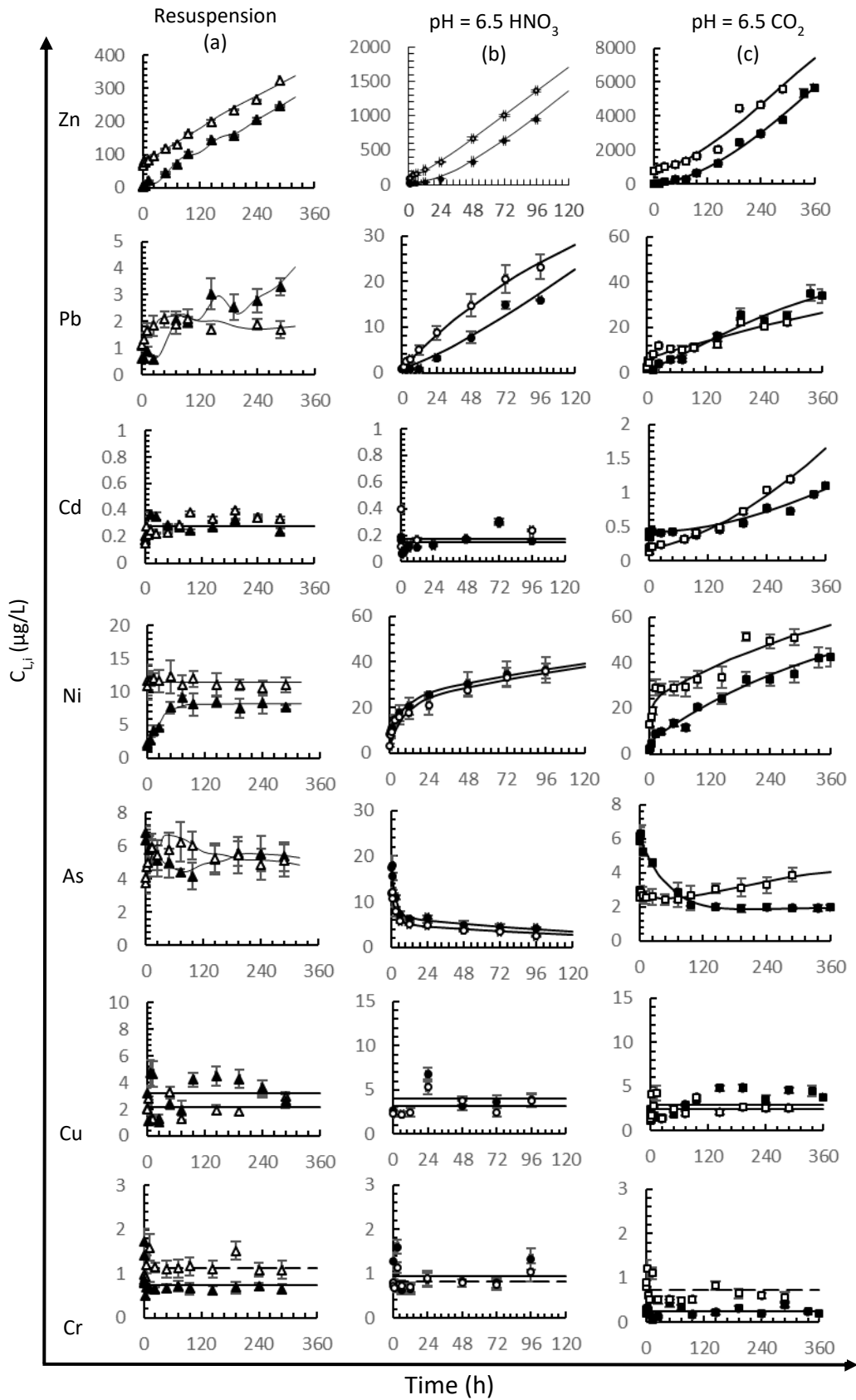
Fig. 2. Experimental and modelled concentration ($C_{L,i}$) over time under (a) resuspension, (b) HNO_3 and (c) CO_2 acidified at pH = 6.5 conditions using anoxic and oxic sediment: ▲ resuspension with anoxic sediment; △ resuspension with oxic sediment; ● pH = 6.5, HNO_3 acidified with anoxic sediment; ○ pH = 6.5, HNO_3

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

290 In Fig. 4 the maximum concentrations, under resuspension conditions, that can be

291 leached from the reduced ($[MRed]_0$) and oxidised ($[MOx]_0$) fraction of the sediment, as

292 well as the sum of the maximum concentrations that can be leached from both fractions

293 of the sediment ($C_{s,0} = [MRed]_0 + [MOx]_0$), are shown.

	Anoxic Sediment			Oxic Sediment		
	$[MRed]_0$	$[MOx]_0$	$[MRed]_0 + [MOx]_0$	$[MRed]_0$	$[MOx]_0$	$[MRed]_0 + [MOx]_0$
■ 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
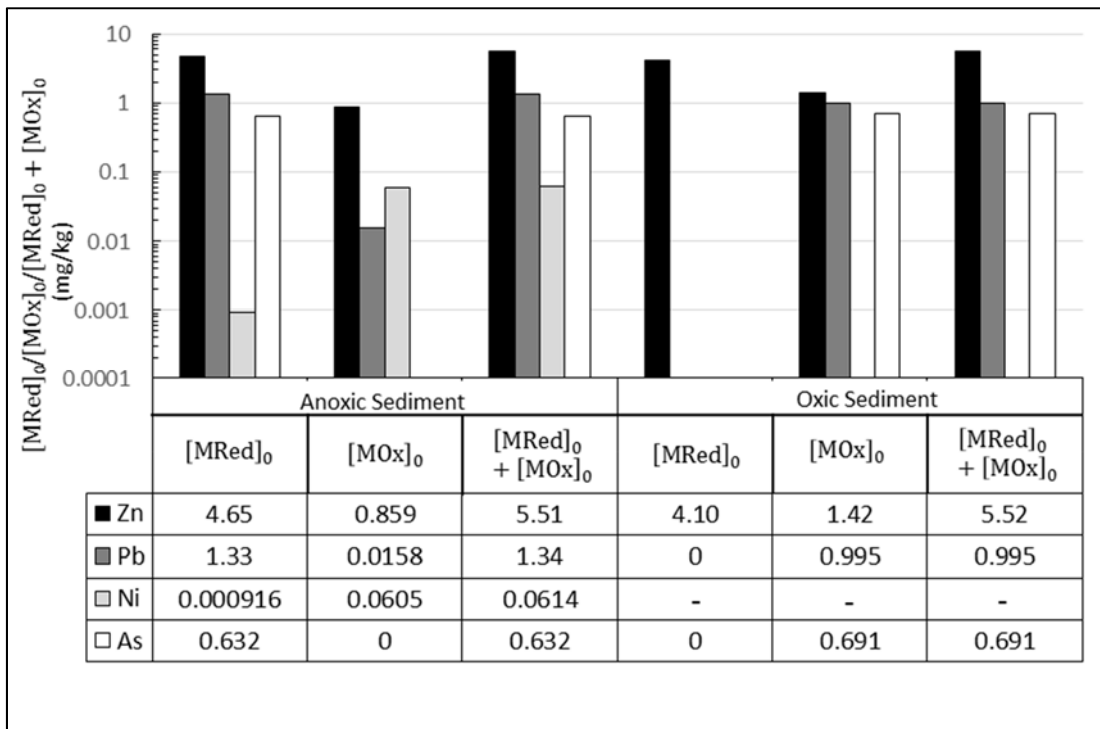
295 Fig. 4. Maximum concentrations that can be leached from the reduced and oxidised
296 fractions of the anoxic and oxic sediment under resuspension conditions. $[MRed]_0$ and
297 $[MOx]_0$ are the reduced and oxidised fractions of the sediment, respectively.

299 As expected, the element concentrations that can be leached from the oxidised fraction

300 are higher in assays using oxic sediment than when anoxic sediment is selected. In

301 addition, the contaminant concentrations leached from the reduced fraction of the

302 sediment are higher in assays using anoxic sediment. The maximum release ($C_{s,0}$) of Zn

303 and As is slightly higher when the oxic sediment is used likely because of the

304 transformation of the stable metal sulphides into more labile binding positions during

305   the oxidation process of the sediment (Calmano et al., 1993). On the contrary, Pb

306   mobilisation is higher from the anoxic sediment.

307   Considering that the pH is not constant in the resuspension assay, kinetic parameters

308   which depend on the pH ($k_{j,i}$) have to be correlated with this variable following a

309   second order polynomial equation, obtaining the kinetic and statistical parameters

310   shown in Table 1.

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

312

| 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

313

314

315

316 For all the trace elements under study and both types of sediment, the parameters to

317 correlate the kinetic rate of the oxidation reaction ($k_{1,i}$) take the same value than those

318 obtained in assays using HNO_3 (Martín-Torre et al., 2015b). The release kinetic

319 parameters ($k_{2,i}$) does not present a common trend for the elements under study likely

320 due to the ionic competition occurs in the sediment-seawater system. The oxyanion As

321 is the only trace element with an adsorption/precipitation reaction ($k_{3,i} \neq 0$). The

322 modelled curves under resuspension conditions, shown in Fig. 2a, correlate reasonably

323 well ($R^2 = 99.2$ %, RSD = 6.03 %) with the experimental results.

324

325 **3.2. Acidified conditions at pH = 6.5 with HNO_3 and CO_2**

326 As shown in Fig. 2b and 2c, the mobilisation of Cu and Cr at pH = 6.5 with both types

327 of acidification and the release of Cd in assays using HNO_3 are almost constant and

328 lower than 5 µg/L. Similarly to resuspension conditions, taking into account the initial

329 concentration in the seawater, their release is considered negligible.

330

331 Independently of the type of acidification, the initial delay of Zn, Pb and Cd is shorter

332 when the oxic sediment is used likely because there is a higher concentration of each

333 element in the oxidised fraction, which is released before that from the reduced fraction

334 of the sediment. The release of Ni seems not to be depend on the acid used due to the

335 similar leaching behaviour in both assays.

336

337 The initial release rate of Zn, Pb and Ni is higher from oxic sediments than from anoxic

338 sediments, except in the case of Ni in assays by using HNO_3, in which the mobilisation

339 rate from both types of sediment is similar. Initially, arsenic shows a higher release

340 from the anoxic sediment. In the case of HNO_3 acidification, the mobilisation of As at
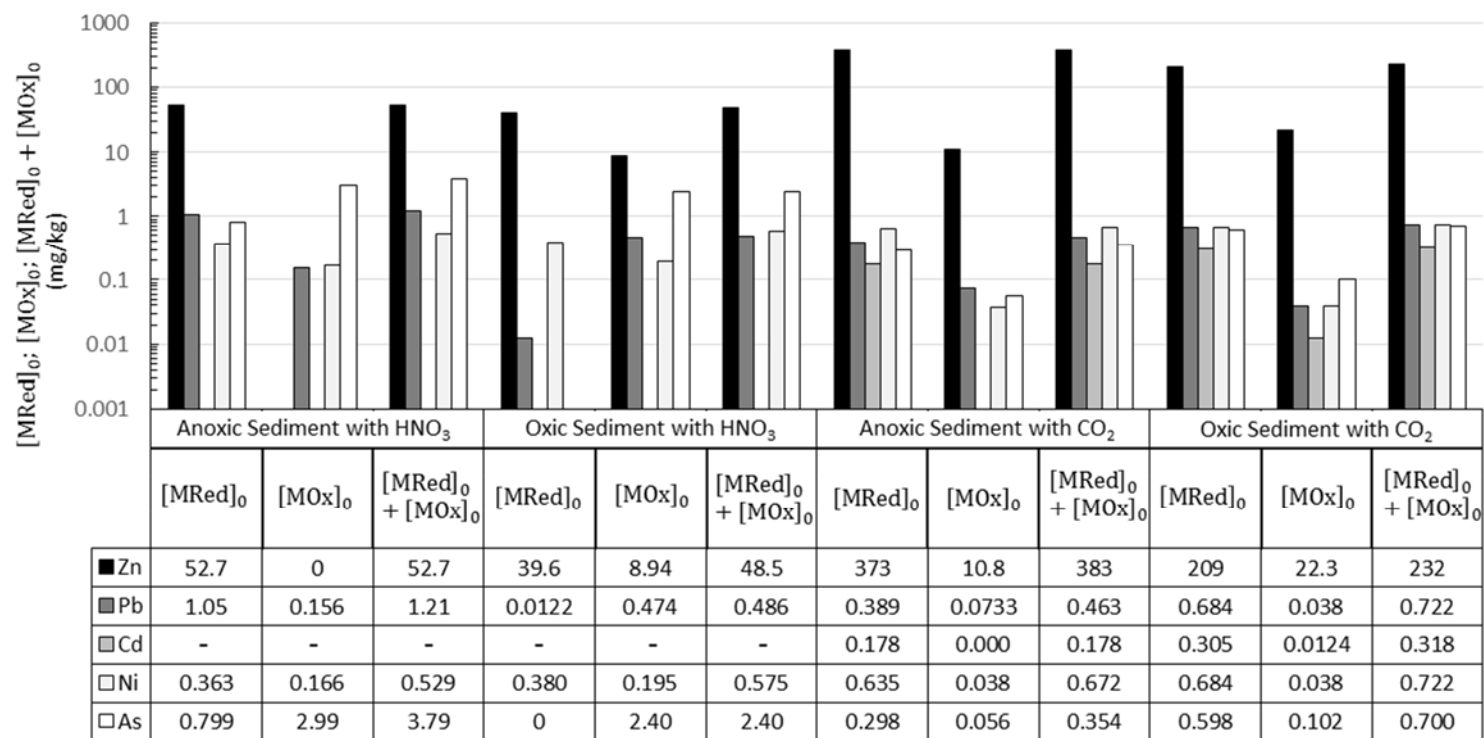
341   short times (t < 6 h) is higher than its release in CO_2 assays; however, as the following

342   adsorption is also higher, the final release of As is almost coincident in all the studied

343   cases (lower than 4.00 µg/L).

344

345   Regarding the acidification with HNO_3, the contaminant release patterns are similar

346   independently of the level of oxidation of the sediment although the release rates differ

347   significantly. In the case of CO_2 acidification, only the release of Zn and Ni follow the

348   same pattern for both sediments used (oxic and anoxic). At t = 96 h, there is a higher

349   release of Zn, Pb and Ni in assays acidified with HNO_3 whereas dissolved

350   concentrations of Cd are slightly higher in assays with CO_2. The application of the

351   mathematical model of Martín-Torre et al. (2015b) to the experimental results leads to

352   the modelled curves under pH = 6.5 acidification by HNO_3 and CO_2 shown in Fig. 2a

353   and b. The maximum released concentrations from the reduced and oxidised fractions

354   and the kinetic parameters ($k_{j,i}$) are obtained.

355

356

357

	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

358

359 Fig. 5. Maximum concentration of each studied trace element that can be leached from the sediment and from each fraction (oxidised fraction

360 and reduced fraction) in units of mg/kg.

361

362

363 Fig. 5 shows the maximum concentrations that can be leached from the reduced

364 ($[MRed]_0$) and oxidised ($[MOx]_0$) fractions of the sediment as well as the maximum

365 concentration that can be leached from the sediment ($C_{s,0} = [MRed]_0 + [MOx]_0$)). In

366 assays acidified by HNO_3, the maximum concentrations leached from the oxidised

367 fraction are higher in the assays which use the oxic sediment than those with the anoxic

368 sediment in the cases of Zn, Pb and Ni whereas this situation is shown for Zn, Cd and

369 As when CO_2 is added to the sediment-seawater mixture. When the acidification is

370 obtained by the addition of HNO_3, the concentration of As that can be leached from the

371 reduced fraction takes the value of zero. Under both studied acidic conditions (HNO_3

372 and CO_2) there is an increase in the percentage of the concentration that can be leached

373 from the oxidised fraction in the oxic sediment with respect to the anoxic sediment; this

374 implies a proportional decrease of the percentage of the potential leachable element

375 concentration from the reduced fraction of the oxic sediment in relation to the anoxic

376 sediment. Exceptions are found in the cases of Pb in assays with HNO_3 and Ni in assays

377 with CO_2.

378

379 In assays with HNO_3, the maximum concentration that can be leached from the

380 sediment of all the modelled contaminants is higher in the anoxic sediment. In the case

381 of Ni, almost the same concentration (0.529 and 0.575 mg/kg) can be leached from oxic

382 and anoxic sediment in both type of assays. In the assays using CO_2, a higher release

383 from the anoxic sediment is shown in the case of Zn but not for the rest of the trace

384 elements under study. This different trend between HNO_3 and CO_2 acidified assays

385 might be caused by the influence of the acidic agent on the characteristics of the

386 medium: CO_2 gas modifies the chemical equilibria of the sediment-seawater mixture

387 whereas HNO_3 does not. Hence, acidification with CO_2 provokes higher leached
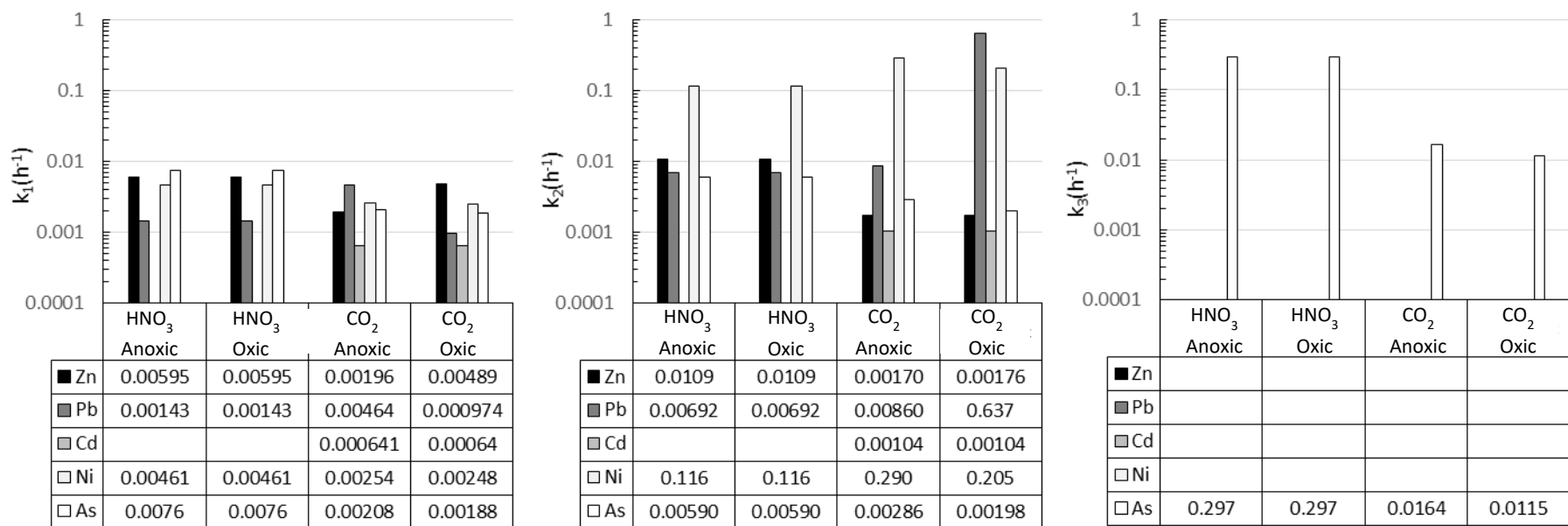
388 concentrations ($C_{s,0}$) from the oxic sediment than from the anoxic sediment, except in

389 the case of the major of the trace elements (Zn), which influences the release of the

390 other studied trace elements.

391

392 The kinetic parameters $k_{1,i}$ of the oxidation, $k_{2,i}$ of the release and $k_{3,i}$ of the

393 adsorption/precipitation reactions in assays at pH = 6.5 obtained from the mathematical

394 model are shown in Fig. 6. The kinetic parameters obtained in assays acidified by HNO_3

395 take the same value independently of the sediment level of oxidation. Hence, in HNO_3-

396 acidified assays, the mobilisation of the contaminants only depends on the maximum

397 concentrations that can be leached from the reduced and oxidised fractions. On the other

398 hand, the kinetic parameters from assays in which CO_2 is used for the acidification are

399 different depending on the oxidation level of the sediment. It might be provoked by the

400 changes which occurred in the sediment-seawater mixture due to the interaction of the

401 CO_2 with the ions present in the medium. HNO_3 is a strong and oxidant acid which

402 generates soluble salts whereas CO_2 is a weak acid that generates partially soluble salts

403 which influence the ionic competition and influence trace element release. Moreover,

404 the kinetic parameters vary differently for each trace element without a clear pattern due

405 to the characteristics of the medium, their concentration and the interactions among all
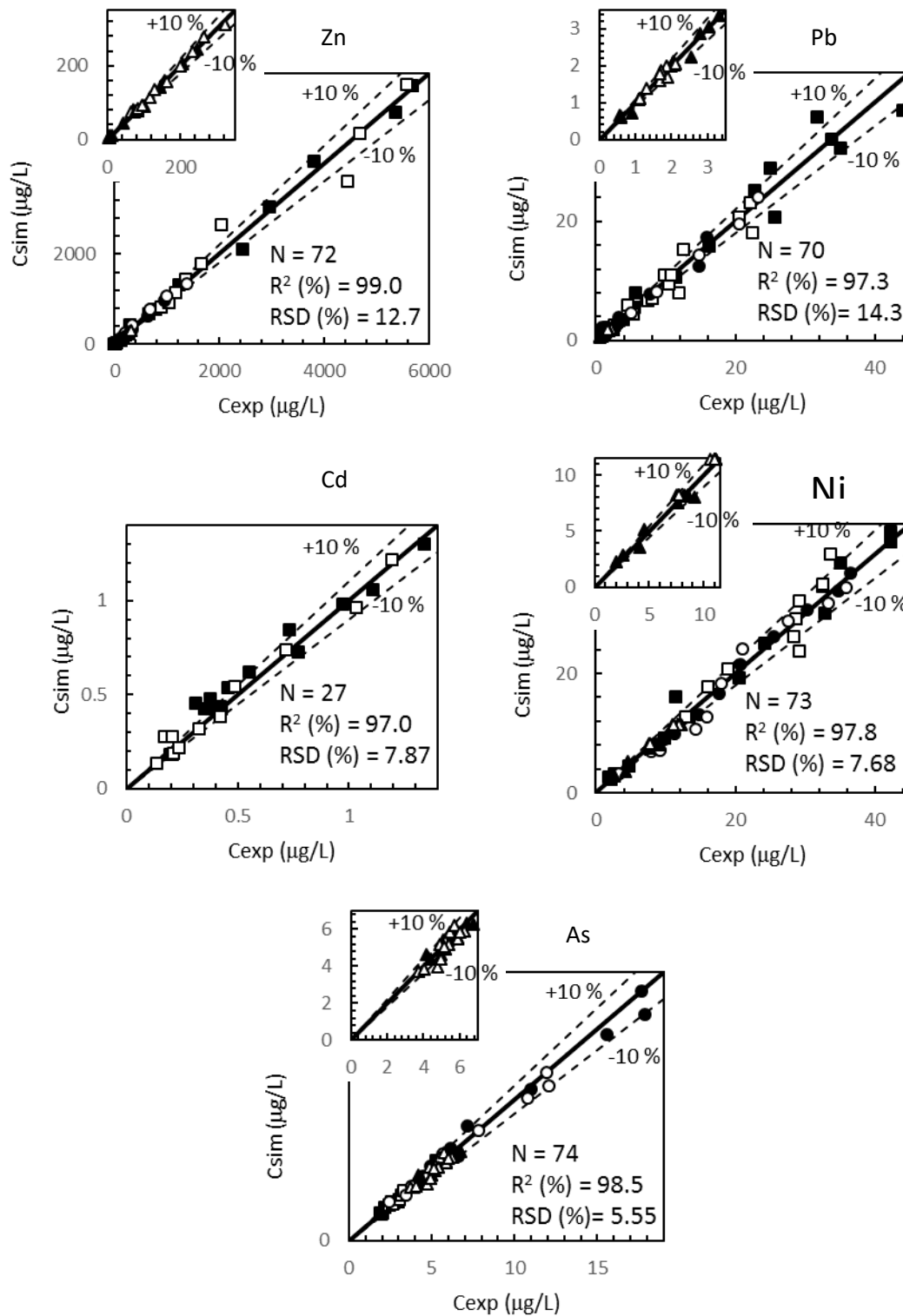
406 the elements.

407

408

	HNO₃ Anoxic	HNO₃ Oxic	CO₂ Anoxic	CO₂ 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

	HNO₃ Anoxic	HNO₃ Oxic	CO₂ Anoxic	CO₂ 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

	HNO₃ Anoxic	HNO₃ Oxic	CO₂ Anoxic	CO₂ Oxic
■ Zn				
■ Pb				
▣ Cd				
☐ Ni				
☐ As	0.297	0.297	0.0164	0.0115

409

410

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

412

23

413   Parity plots (Fig. 7) are useful for the validation of the model in terms of the released

414   element concentration at any time and pH value. In the case of Cd, the results from the

415   assays with CO_2 acidification are the only considered because they are the only which

416   are modelled. Differences between experimental and simulated mobilisation are lower

417   than 20% for 85.1 % of the data. Moreover, they are lower than 10 % for 74.7 % of the

418   data.   Considering all the trace elements at once, the data number (N) is 316, the

419   percentage variation-explained value (R^2) takes a value of 99.2 % and the relative

420   standard deviation (RSD) is 25.0 %. The high values of the global statistical parameters

421   and the high individual R^2 (Fig. 7), show the good fit of the proposed model in all

422   studied experiments.

423

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, HNO₃ acidified with anoxic sediment; ○ pH = 6.5, HNO₃ acidified with oxic sediment; ■ pH = 6.5, CO₂ acidified with anoxic sediment; □ pH = 6.5, CO₂ 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, HNO₃ and CO₂ 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).

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

$$C_{s,0} = [MRed]_0 + [MOx]_0 \qquad \text{(Eq. 9)}$$
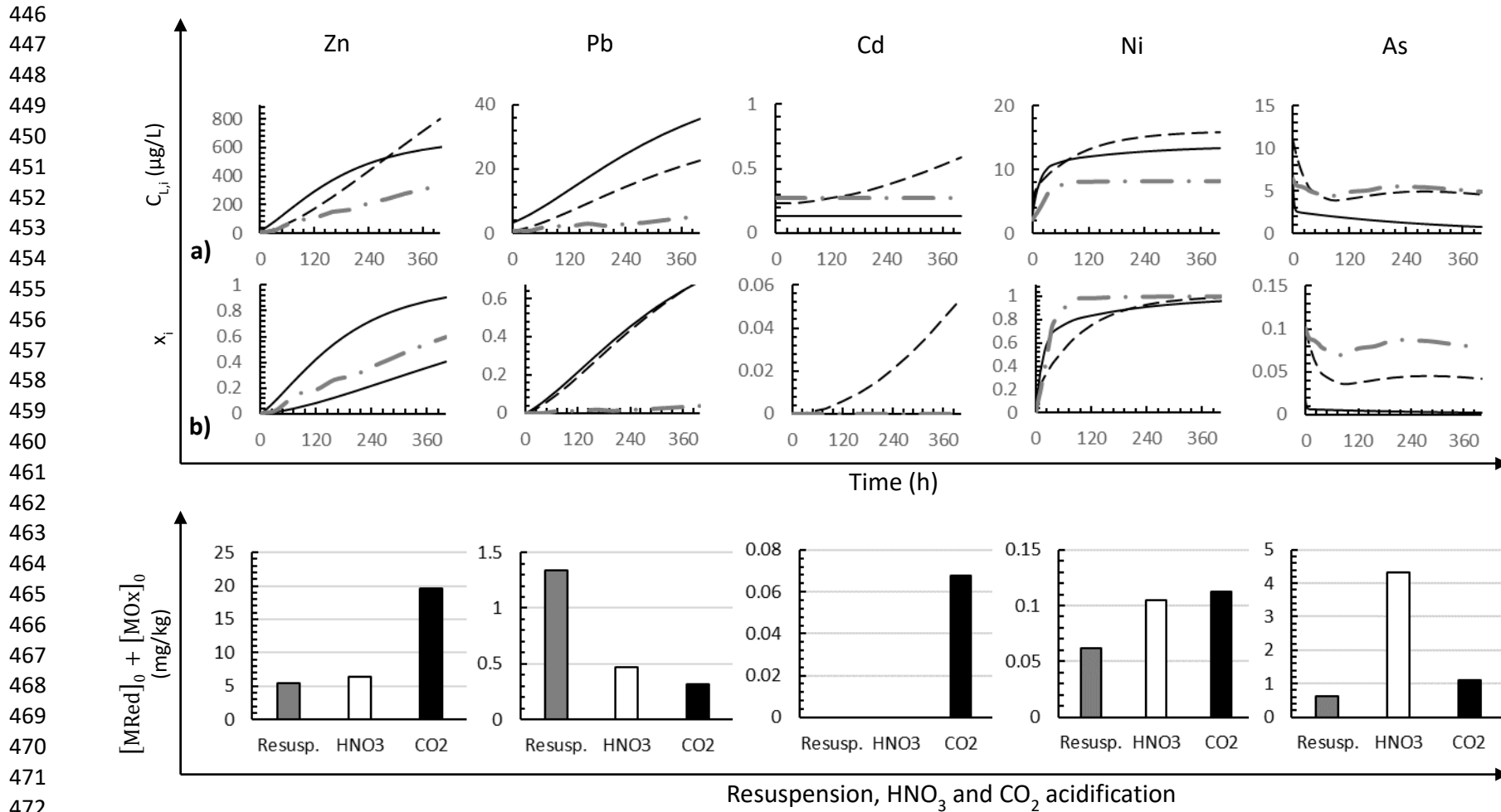
Fig. 8. a) Simulation over time of trace element released concentration ($C_{L,i}$) and release fraction (x_i) from anoxic sediment under resuspension (— ·); acidification at pH = 7.0 with CO_2 (— —) and HNO_3 (——) conditions; b) Maximum concentration that can be leached ($C_{s,0}$) from anoxic sediment under resuspension (— ·); acidification at pH = 7.0 with CO_2 (— —) and HNO_3 (——) conditions.

477 Fig. 8a shows the modelled curves for the trace element release over time under

478 resuspension and acidification (pH = 7.0) conditions. The 'release fraction' (x_i) is

479 shown in Fig. 8b in order to address in detail, and without the influence of the initial

480 dissolved concentrations, the trace element mobilisation under each studied scenario.

481 Moreover, the slope of these modelled curves indicates the release rate of each element.

482 Hence, at short times, the most rapid release of Zn, Pb and Ni occurs in the assay

483 acidified by HNO_3 (Fig. 8b).

484

485 In Fig. 8c the maximum concentrations that can be leached from the sediment ($C_{s,0} =$

486 $[MRed]_0 + [MOx]_0$) are shown. In the cases of Zn, Pb, Cd and Ni, this maximum

487 concentration is achieved at long times whereas in the case of As, it occurs at $t = 0$. The

488 concentrations of As in the liquid phase at longer times are always lower than the initial

489 one due to the adsorption process. The higher maximum dissolved concentrations of Zn,

490 Cd and Ni that can be leached from the sediment are shown under CO_2-acidified

491 conditions. However, the metal Pb releases the most under resuspension scenario. This

492 fact highlights how anthropogenic activities or natural events might provoke higher

493 risks than slight acidification conditions.

494

495 The oxyanion As is the only element which is adsorbed or precipitated after an initial

496 release. Although the dissolved concentration of As at $t = 0$ is higher in HNO_3-

497 acidified assays than in the other two cases, it is the lowest at long times (Fig. 8b).

498 Higher initial dissolved concentrations of As, make the trace element more available to

499 precipitate or adsorb when nitric acid is added to the sediment-seawater mixture.

500

501

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 $\pm$ 7.00 mV) and oxic (27.0 $\pm$ 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

29

527 higher than under resuspension conditions showing that even a slight acidification can
528 endanger the aquatic environment through an important mobilisation of contaminants.
529 However, resuspension conditions might mobilise some contaminants, like Pb, more
530 than slight acidification levels.

531

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

536

542

543

544 **REFERENCES**
545 Almagro-Pastor, V.; Conradi, M.; DelValls, T.Á.; Riba, I. 2015. Alterations in the
546 macrobenthic fauna from Guadarranque River (Southern Spain) associated with
547 sediment–seawater acidification deriving from CO_2 leakage. Marine Pollution Bulletin
548 96, 65–75. DOI: 10.1016/j.marpolbul.2015.05.044.

549

550 Atkinson, C.; Jolley, D.F.; Simpson, S.L. 2007. Effect of overlying water pH, dissolved
551 oxygen, salinity and sediment disturbances on metal release and sequestration from
552 metal contaminated marine sediments. Chemosphere 69 (9), 1428-1437. DOI:
553 10.1016/j.chemosphere.2007.04.068.

554

555 Benson, S.M.; Cole, D.R. 2008. CO_2 sequestration in deep sedimentary formations.
556 Elements 4, 325-331. DOI: 10.2113/gselements.4.5.325.

557 BOE, 2008. Resolución de 28 de noviembre de 2007 (Resolution of 28 November
558 2007). Boletín Oficial del Estado (BOE), 8 febrero 2008, vol. 34, pp. 7099-7102.
559 Spanish Ministry of Industry, Tourism and Trade, Madrid, Spain.

560

561 Burdige, D.J. 1993. The biogeochemistry of manganese and iron reduction in marine
562 sediments. Earth-Science Reviews 35, 249–284. DOI: 10.1016/0012-8252(93)90040-E.

563

564 Cai, Y., Mi, Y., Yu, J., Zhang, H. 2016. Arsenic speciation and kinetic release
565 simulation of stream sediment contaminated by gold mining, Journal of Soils and
566 Sediments. 16:1121–1129. DOI: 10.1007/s11368-015-1334-9

567

568 Calmano, W.; Hong, J.; Förstner, U. 1993. Binding and mobilization of heavy metals in
569 contaminated sediments affected by pH and redox potential. Water Science and
570 Technology 28 (8-9) 223-235. DOI: 10.15480/882.450.

571

572 Cappuyns, V., Swennen, R. 2005. Kinetics of element release during combined
573 oxidation and pHstat leaching of anoxic river sediments. Applied Geochemistry 20,
574 1169–1179. DOI: 10.1016/j.apgeochem.2005.02.004.

575

576 Cappuyns, V.; Swennen, R. 2006. Comparison of metal release from recent and aged
577 Fe-rich sediments. Geoderma 137 (1-2), 242–251. DOI:
578 10.1016/j.geoderma.2006.08.013.

579

580 Cappuyns, V., Swennen, R., Niclaes, M. 2007. Application of the BCR sequential
581 extraction scheme to dredged pond sediments contaminated by Pb–Zn mining: A
582 combined geochemical and mineralogical approach. Journal of Geochemical
583 Exploration 93, 78–90. DOI: 10.1016/j.gexplo.2006.10.001

584

585 Cappuyns, V.; Alian, V.; Vassilieva, E.; Swennen, R. 2014. pH dependent leaching
586 behavior of Zn, Cd, Pb, Cu and As from mining wastes and slags: kinetics and
587 mineralogical control. Waste and Biomass Valorization 5, 355–368. DOI
588 10.1007/s12649-013-9274-3.

589

590 CEN/TS 14997, 2006. European Committee for Standardization (CEN). Technical
591 specification (TS) 14997:2006. Characterization of waste - leaching behaviour tests -
592 influence of pH on leaching with continuous pH-control. CEN Management Centre,
593 Brussels, Belgium.

594

595 Choppala, G., Bush, R., Moon, E., Ward, N., Wang, Z., Bolan, N., Sullivan, L., 2017.
596 Oxidative transformation of iron monosulfides and pyrite in estuarine sediments:
597 Implications for trace metals mobilisation. Journal of Environmental Management 186,
598 158-166. DOI: 10.1016/j.watres.2013.05.052

599

600 De Orte, M.R.; Sarmiento, A.M.; DelValls, T.Á.; Riba, I. 2014. Simulation of the
601 potential effects of CO_2 leakage from carbon capture and storage activities on the
602 mobilization and speciation of metals. Marine Pollution Bulletin 86 (1-2), 59-67. DOI:
603 10.1016/j.marpolbul.2014.07.042.

604

605 Dooley, J.J.; Dahowski, R.T.; Davidson, C.L.; Wise, M.A.; Gupta, N.; Kim, S.H.;
606 Malone, E.L. 2006. Carbon dioxide capture and geologic storage: a core element of a
607 global energy technology strategy to address climate change. A technology report from
608 the second phase of the Global energy technology strategy program. United States of
609 America. [Consulted in July 2016]. Available in:
610 http://www.globalchange.umd.edu/data/gtsp/workshops/2006/ccs_report.pdf.

611

612 Eggleton, J.; Thomas, K.V. 2004. A review of factors affecting the release and
613 bioavailability of contaminants during sediment disturbance events. Environment
614 International 30(7), 973-80. DOI: 10.1016/j.envint.2004.03.001.

615

616 EN 14997, 2015. European Committee for Standardization (CEN). Standard
617 14997:2015. Characterization of waste - Leaching behaviour test - Influence of pH on
618 leaching with continuous pH control. CEN Management Centre, Brussels, Belgium.

619

620 Fonti, V., Dell'Anno, A., Beolchini, F. 2013. Influence of biogeochemical interactions
621 on metal bioleaching performance in contaminated marine sediment. Water Research
622 47, 5139-5152. DOI: 10.1016/j.watres.2013.05.052

623

624 Frohne, T., Rinklebe, J., Diaz-Bone, R.A., Du Laing, G. 2011. Controlled variation of

625 redox conditions in a floodplain soil: impact on metal mobilization and biomethylation

626 of arsenic and antimony. Geoderma 160, 414-424. DOI:

627 10.1016/j.geoderma.2010.10.012

628

629 Gammer, D. 2016. Reducing the cost of CCS. Developments in capture plant

630 technology. Energy Technologies Institute (RTI). pp. 18. Loughborough, UK.

631 [Consulted in July 2016]. Available in: http://www.eti.co.uk/wp-

632 content/uploads/2016/05/Capture-Plant-Insight-MP2.pdf.

633

634 Ho, H.H.; Swennen, R.; Cappuyns, V. ; Vassilieva, E.; Van Gerven T.; Tran, T.V. 2012.

635 Potential release of selected trace elements (As, Cd, Cu, Mn, Pb and Zn) from

636 sediments in Cam River-mouth (Vietnam) under influence of pH and oxidation. Science

637 of the Total Environment 435–436, 487–498. DOI: 10.1016/j.scitotenv.2012.07.048.

638

639 Hwang, K.-Y.; Kim, H.-S.; Hwang, I. 2011. Effect of Resuspension on the Release of

640 Heavy Metals and Water Chemistry in Anoxic and Oxic Sediments. Clean – Soil, Air,

641 Water 39 (10), 908–915. DOI: 10.1002/clen.201000417.

642

643 IEA, International Energy Agency. 2013. Technology roadmap: carbon capture and

644 storage. OECD/IEA. Paris, France. [Consulted in May 2016]. Available in:

645 http://www.iea.org/publications/freepublications/publication/TechnologyRoadmapCarb

646 onCaptureandStorage.pdf.

647

648 IPIECA, International Petroleum Industry Environmental Conservation Association.

649 2003. Carbon dioxide capture and geological storage: contributing to climate change

650 solutions. Summary brochure in an IPIECA Workshop, Brussels, Belgium, 21–22

651 October 2003. [Consulted in May 2016]. Available in:

652 http://www.ipieca.org/publication/carbon-dioxide-capture-and-geological-storage-

653 contributing-climate-change-solutions.

654

655 Kalnejais, L.H.; Martin, W.R.; Bothner, M.H. 2015. Porewater dynamics of silver, lead

656 and copper in coastal sediments and implications for benthic metal fluxes. Science of

657 the Total Environment 517, 178–194. DOI: 10.1016/j.scitotenv.2015.02.011.

658 Kharaka, Y.K.; Thordsen J.J.; Kakouros, E.; Ambats, G.; Herkelrath, W.N.; Beers,

659 S.R.; Birkholzer, J.T.; Apps, J.A.; Spycher, N.F.; Zheng, L.; Trautz, R.C.; Rauch, H.W.;

660 Gullickson, K.S. 2010. Changes in the chemistry of shallow groundwater related to the

661 2008 injection of CO_2 at the ZERT field site, Bozeman, Montana. Environmental Earth

662 Sciences 60(23), 273-284. DOI: 10.1007/s12665-009-0401-1.

663

664 Kristensen, E. 2000. Organic matter diagenesis at the oxic/anoxic interface in

665 coastal marine sediments, with emphasis on the role of burrowing animals.

666 Hydrobiologia 426 (1), 1-24. DOI: 10.1023/A:1003980226194.

667

668 Lions, J.; Devau, N.; de Lary, L.; Dupraz, S. ; Parmentier, M. ; Gombert, P.; Dictor, M.-

669 C. 2014. Potential impacts of leakage from CO_2 geological storage on geochemical

670 processes controlling fresh groundwater quality: a review. International Journal of

671 Greenhouse Gas Control 22, 165–175. DOI: 10.1016/j.ijggc.2013.12.019.

672

673 Martín-Torre, M.C., Payán, M.C., Verbinnen, B., Coz, A., Ruiz, G., Vandecasteele, C.,

674 Viguri, J.R. 2015a. Metal release from contaminated estuarine sediment under pH

675 changes in the marine environment. Archives of Environmental Contamination

676 and Toxicology 68(3), 577–587. DOI: 10.1007/s00244-015-0133-z.

677

678 Martín-Torre, M.C., Ruiz, G., Galán, B., Viguri, J.R. 2015b. Generalised mathematical

679 model to estimate Zn, Pb, Cd, Ni, Cu, Cr and As release from contaminated estuarine

680 sediment using pH-static leaching tests. Chemical Engineering Science 138, 780-790.

681 DOI: 10.1016/j.ces.2015.08.053.

682

683 Martín-Torre, M.C.; Ruiz, G., Galán, B., Viguri, J.R. 2016. CO_2 seawater acidification

684 by CCS-simulated leakage: Kinetic modelling of Zn, Pb, Cd, Ni, Cr, Cu and As from

685 contaminated estuarine sediment using pH-static leaching tests. International Journal of

686 Greenhouse Gas Control 54, 185-199. DOI: 10.1016/j.ijggc.2016.09.004.

687

688 Millero, F.J.; Woosley, R.; DiTrolio, B.; Waters, J. 2009. Effect of ocean acidification

689 on the speciation of metals in seawater. Oceanography 22(4), 72–85. DOI:

690 10.5670/oceanog.2009.98.

691

692 Popenda, A. 2014. Effect of redox potential on heavy metals and As behavior in
693 dredged sediments. Desalination and Water Treatment 52 (19-21), 3918-3927. DOI:
694 10.1080/19443994.2014.887449.

695

696 Pourabadehei, M.; Mulligan, C.N. 2016. Resuspension of sediment, a new approach for
697 remediation of contaminated sediment. Environmental Pollution 213, 63-75. DOI:
698 10.1016/j.envpol.2016.01.082.

699

700 PTECO$_2$, Plataforma Tecnológica Española del CO$_2$. 2014. Captura de CO$_2$: tecnologías
701 para una captación a gran escala. Plataforma Tecnológica Española del CO$_2$.

702

703 Riba López, I.; Kalman, J., Vale, C.; Blasco, J. 2010. Influence of sediment
704 acidification on the bioaccumulation of metals in Ruditapes philippinarum.
705 Environmental Science and Pollution Research 17, 1519-1528. DOI: 10.1007/s11356-
706 010-0338-7.

707

708 Roberts, D.A.; Birchenough, S.N.R.; Lewis, C.; Sanders, M.B.; Bolam, T.; Sheahan, D.
709 2013. Ocean acidification increases the toxicity of contaminated sediments. Global
710 Change Biol 19, 340–51. DOI:10.1111/gcb.12048.

711

712 Rodríguez-Romero, A., Basallote, M. D., De Orte, M. R., Delvalls, T. Á., Riba, I.,
713 Blasco, J. 2014. Simulation of CO$_2$ leakages during injection and storage in sub-seabed
714 geological formations: Metal mobilization and biota effects. Environment International
715 68, 105−117. DOI: 10.1016/j.envint.2014.03.008.

716

717 Schulz-Zunkel, C.; Rinklebe, J.; Bork, H.-R- 2015. Trace element release patterns from
718 three floodplain soils under simulated oxidized–reduced cycles. Ecological Engineering
719 83, 485-495. DOI: 10.1016/j.ecoleng.2015.05.028.

720

721 Sheppard, M.C.; Socolow, R. H. 2007. Sustaining fossil fuel use in a carbon-constrained
722 world by rapid commercialization of carbon capture and sequestration. American
723 Institute of Chemical Engineers (AIChE) Journal 53 (12), 3022-3028. DOI
724 10.1002/aic.11356.

725

726 Simpson, S.L.; Apte, S.C.; Bately, G.E. 1998. Effect of short-term resuspension events
727 on trace metal speciation in polluted anoxic sediments. Environmental Science &
728 Technology 32 (5), 620–625.DOI: 10.1021/es970568g.
729

730 Tack, F.M.; Lapauw, F.; Verloo, M.G. 1997. Determination and fractionation of sulphur
731 in a contaminated dredged sediment. Talanta 44, 2185–2192.
732

733 Wang, Z.; Wang, Y.; Zhao, P.; Chen, L.; Yan, C.; Yan, Y.; Chi, Q. 2015. Metal release
734 from contaminated coastal sediments under changing pH conditions: Implications for
735 metal mobilization in acidified oceans. Marine Pollution Bulletin 101 (2), 707–715.
736 DOI: 10.1016/j.marpolbul.2015.10.026.
737

738 Williamson, R.B.; Wilcock, R.J.; Wise, B.E.; Pickmere, S.E. 1999. Effect of burrowing
739 by the crab Helice Crassa on chemistry of intertidal muddy sediments. Environmental
740 Toxicology and Chemistry 18(9), 2078–2086. DOI: 10.1002/etc.5620180928.
741

742 Xu, W.; Li, X.; Wai, O.W.H.; Huang, W.; Yan, W. 2015. Remobilization of trace
743 metals from contaminated marine sediment in a simulated dynamic environment.
744 Environmental Science and Pollution Research 22, 19905–19911. DOI:
745 10.1007/s11356-015-5228-6.
746

747 Ye, S.; Laws, E.A.; Gambrell, R. 2013. Trace element remobilization following the
748 resuspension of sediments under controlled redox conditions: City Park Lake, Baton
749 Rouge, LA. Applied Geochemistry 28, 91–99. DOI: 10.1016/j.apgeochem.2012.09.008.
750

751 Zheng, L., Apps, J. A., Zhang, Y., Xu, T., Birkholzer, J. T. 2009. On mobilization of
752 lead and arsenic in groundwater in response to CO_2 leakage from deep geological
753 storage. Chemical Geology 268, 281–297. DOI: 10.1016/j.chemgeo.2009.09.007.
754