

1 Metal release from contaminated estuarine sediment under pH changes 2 in the marine environment

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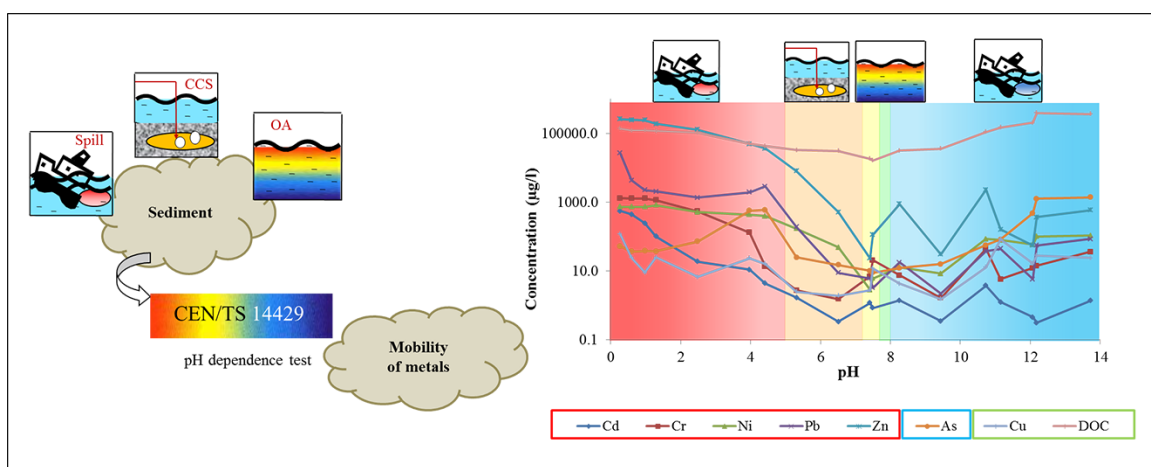
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12

13 Graphical abstract



14

15 Abstract

16 The contaminant release from estuarine sediment due to pH changes is addressed using a
17 modified CEN/TS 14429 pH dependence leaching test. The test is performed in the 0-14
18 pH range using deionised water and seawater as leaching solutions. The experimental

19 conditions mimic different circumstances of the marine environment due to the global
20 acidification, CO₂ leakages from Carbon Capture and Sequestration technologies (CCS)
21 and accidental chemical spills in seawater. Leaching test results using seawater as
22 leaching solution show a better neutralisation capacity, giving slightly lower metal
23 leaching concentrations than when using deionised water. The contaminated sediment
24 shows a low base neutralisation capacity ($BNC_{pH=12}=-0.44$ eq/kg for deionised water and
25 $BNC_{pH=12}=-1.38$ eq/kg for seawater), but a high acid neutralisation capacity when using
26 deionised water ($ANC_{pH=4}=3.58$ eq/kg) and seawater ($ANC_{pH=4}=3.97$ eq/kg).
27 Experimental results are modelled with the Visual MINTEQ geochemical software to
28 predict metal release from sediment using both leaching liquids. Surface adsorption to
29 Fe- and Al-(hydr)oxides was applied for all studied elements. The consideration of the
30 metal-organic matter binding through the NICA-Donnan and Stockholm Humic Model
31 (SHM) models for Pb and Cu respectively, improves the former metal release prediction.
32 Modelled curves can be useful for the environmental impact assessment of seawater
33 acidification due to its match with the experimental values.

34

35 **Keywords:** metal and As; sediment; seawater acidification; pH dependence test;
36 geochemical modelling.

37

38 **Highlights**

- 39 • Metal release under natural ocean acidification, CO₂ leakages and accidental spills
- 40 • Equilibrium conditions at neutral pH using seawater are difficult to reach
- 41 • Salinity slightly decreases metals mobility from pH = 8
- 42 • Modelled metal release concentrations match well with the experimental ones
- 43 • Fe- and Al-(hydr)oxides and humic and fulvic acids improve metal release modelling

44

45 **1. Introduction**

46 Pressures and impacts on marine environments are a subject of environmental concern.

47 In particular, the effects of human activities and climate change can, among other adverse

48 effects, cause seawater pH variations. Global average oceanic surface pH has already

49 declined by 0.1 since the beginning of the industrial revolution; modelled global ocean

50 acidification predicts a pH decrease by another 0.2 to 0.77 units by the next two centuries

51 (Table 1). Carbon capture and storage (CCS) is a very active field of research because of

52 its potential to mitigate global warming (Pacala and Socolow, 2004; IPCC 2014). The

53 projects with the highest total CO₂ storage estimation are offshore (Hosa et al., 2011).

54 The pH value in environmental waters is used as one of the basic performance indicators

55 to measure the possible impact of CO₂ storage and for the design of appropriate

56 monitoring strategies to assess potential impacts of CO₂ seepage. A plethora of

57 investigations exists about CO₂ leakages from CCS at different levels, as shown in Table

58 1 (References of this table are presented in the Supplementary Information). CO₂ leaks

59 can cause short-time drops down to pH=3.0 in specific sea areas around the vents,

60 showing high spatial and temporal variability in pH (Beaubien et al., 2008). In the case

61 of marine chemical spills, pH values below 5 and above 12 have been reported for

62 seawater areas directly surrounding the chemical spill location for a limited period of time

63 (Gouriou et al., 2008; Mamaca et al., 2009).

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69 **Table 1.** Estimated and measured pH changes on the marine environment due to the climate change,
 70 leakages of CO₂ and chemical spills.

	Cause	Place	pH change effect
Climate change	Current global ocean acidification (OA). (Caldeira and Wickett, 2003). Modelled OA under several scenarios for proposed future CO ₂ emissions. (Jeffree et al., 2009; Orr et al., 2005).	Global average oceanic surface pH.	pH has already declined by 0.1 units. pH decline by another 0.2 to 0.4 units by 2100 and by a maximum of 0.77 units at around the year 2300.
Leakages of CO₂ from natural storage and for CCS by injection into porous rock formations deep below the sea	Natural and industrial analogue sites from CO ₂ storage reservoirs. (Beaubien et al., 2008; Gilfillan et al., 2009; Koornneef et al., 2012; Lewicki et al., 2007; Noble et al., 2012; Shitashima et al., 2008, 2013; Ziogou et al., 2013). (e.g.: Sleipner and Snøhvit offshore sites; Okinawa hydrothermal area).	Naturally occurring CO ₂ reservoirs and natural gas storage sites analogues for the potential release of CO ₂ from geologic storage sites.	Studies focused on: migration behaviour and fluxes of CO ₂ , transfer of gas to the atmosphere, seismic activity, reservoir characterisation, storage capacity and CO ₂ dissolution in formation brine. pH of shallow waters: 5.48; pH of brine: 3.5; pH in the sediment pore water: 4-6.2.
	Laboratory experiments mimicking leakage from a sub-seabed CO ₂ storage site and simulating “worst” case local scenarios of leakages. (Briffa et al., 2012; Cahill and Jakobsen, 2013; Carey et al., 2009; de Orte et al., 2014; Ellis et al., 2011; Jacquemet et al., 2009; Murray et al., 2013; Payán et al., 2012a, b; Widdicombe et al., 2013,2011).	Acidified seawater/ saline brine/ groundwater/ porewater at short-term (minutes to several days) contact with caprock formation/ sediment / environment.	In field scale injection experiments, pH is used as geochemical indicator of a leak. Various laboratories, start pH values (3.86, 4.4, 5.0, 6.5) depending on the simulated system, as the worst expected local scenario.
	Simulation models for a number of hypothetical leakage scenarios. (Amin et al., 2014; Bolourinejad et al., 2014; Zheng et al., 2009).	Model of the pH evolution, CO ₂ plume, groundwater quality.	ΔpH=0.1-1.0 in seawater; Brine pH drop to 4.3; Initial cap rock formation water at pH=7.67 drops to pH= 3.0 at short time and stabilises at pH=5.8 at long time (Sleipner offshore field).
Accidental chemical spills	Acid chemical spill of 1700 t of sulphuric acid. (Mamaca et al., 2009).	Port of Río Grande, Brazil (low tide).	Chemical monitoring of pH (not reported data).
	Hydrodynamic and physicochemical simulation of an acid spill during the ECE incident (10,000 t of H ₃ PO ₄ acid). (Gouriou et al., 2008).	Phosphoric acid spill in the English channel, west coast of France.	pH < 5 can be found in the area directly surrounding the spill location and only for a limited period of time.
	Alkaline chemical spill of 490 t of caustic soda from a barge. (Mamaca et al., 2009).	Bay of Newark, NJ, USA.	pH alongside the barge reached 12 very quickly and lowered to 9 three hours later.
	Accidental mining spill in Aznalcóllar. (Blasco et al., 2002; Gómez-Parra et al., 2000; Morillo et al., 2005; Riba et al., 2004,2002).	Spill affecting Guadalquivir estuary Gulf of Cádiz, Atlantic Ocean, Spain.	Spill of acid-polluted water at pH=4.5; estuarine sediment acidification down to pH= 6.5.
	Submarine acidic groundwater discharges to estuarine environments (Simpson et al., 2004)	Estuarine bays adjacent to industrial	Column leaching test experiments with acidified (HCl) groundwater solutions to pH 3, 4, 5.

		land. Sydney Harbour, Australia	
	In situ sediment solidification /stabilization (Renholds, 1998)	Several in-situ treatment projects	High pH values (pH=10) of sediments and surrounding area that results in a prevention of chemical release

71

72 Chemical additions or subtractions from the oceans can cause natural or human-induced
73 seawater pH changes (Table 1). Broad pH changes could take place in local and short-
74 term conditions, but in places where the pH may not rebound quickly to background
75 conditions, or constituent concentrations of sediments in contact rebounded to values
76 higher than the original background (Trautz et al., 2013). The major factors controlling
77 the released concentrations for each metal are related to the solid matrix (sediments,
78 marshes and caprock formations) characteristics, the fluid (seawater pH) characteristics
79 and the solid-liquid contact characteristics (e.g. dilution, mixing degree and time
80 following mixing) (Simpson et al., 2014). Changes in the pH of the seawater may increase
81 metal mobility and availability from solid matrices in contact with seawater, that can
82 result in irreversible, cumulative and interactive negative effects on specific sea areas
83 around the vents and spill, with potential lethal and sublethal effects and metal
84 bioaccumulation in the marine ecosystem (Ardelan et al., 2009; Briffa et al., 2012; Carrol
85 et al., 2014; de Orte et al., 2014; Roberts et al., 2013).

86

87 In the context of ocean pH changes, information about the metal release from shallow
88 sediment is essential for risk assessment and pre-incident planning and can be used as
89 a geochemical indicator of leaks. Therefore, the evaluation of the pH dependence of metal
90 leaching is an important tool in the assessment of the expected long-term leaching
91 behaviour of marine sediments in scenarios of ocean acidification as well as in extreme
92 and/or accidental CO₂ leakages and chemical spills scenarios (Roberts et al., 2013).

93

94 Laboratory leaching tests, such as acidification using inorganic acids, in conjunction with
95 routine sediment characterisations, can be used as cost-effective methods to predict
96 constituent release, whose concentrations would rapidly rise at a field site due to the pH
97 changes and important negative effects are expected at local scale. pH_{stat} leaching test
98 based on CEN/TS 14429 has been widely used in different solid matrices of
99 environmental interest as a powerful laboratory tool for the characterisation of

100 environmental samples (Table SII-Supplementary information). The test complements
101 and enhances the information derived from the use of common single extractions, and
102 from other tests addressed to estimate the maximum leachability of inorganic pollutants.
103 Although the pH_{stat} test may not be representative of in situ conditions, it can be
104 environmental relevant when field tests are not possible or difficult to carry out, and
105 useful to simulate worst case scenarios where acidified/alkalinised seawater is in contact
106 with recent sediment from a potential CCS site or located in the area directly surrounding
107 spill location, under total mixed conditions (Varadharajan et al., 2013; XXXXXXXX).

108

109 This paper addresses the effect of pH on the leaching of As, Cd, Cr, Cu, Ni, Pb, Zn and
110 Dissolved Organic Carbon (DOC) from contaminated estuarine sediment. The modified
111 pH dependence leaching test with initial acid/base addition (CEN/TS 14429), covering
112 the whole pH range (0-14), is done using deionised and seawater as leaching liquids. The
113 use of different solutions allows to mimic different ocean acidification/alkalinisation
114 conditions due to the current and modelled ocean acidification, CO_2 leakages from CCS
115 technologies and accidental chemical spills.

116

117 Experimental research and geochemical modelling using Visual MINTEQ software were
118 conducted to predict and explain the pH dependent leaching behaviour of contaminants;
119 the proposed model considers surface complexation reactions on Fe- and Al-(hydr)oxides
120 and bindings to dissolved organic matter through Gaussian, NICA-Donnan and
121 Stockholm Humic Model (SHM). This model approach expands the previous developed
122 model (Payán et al., 2012a,b) providing more accurate information to assess the risk
123 related to metals release from marine sediments exposed to changes in pH.

124

125 **2. Materials and experimental method**

126 **2.1. Sediment sample collection and characterisation**

127 All sampling and laboratory material was pre-cleaned, acid washed (10% HNO₃) and
128 rinsed with Milli-Q water (Direct-Q 5 UV, Merck Millipore). The estuarine surface
129 sediment samples were collected in November 2011 from the estuary of Suances
130 (Northern Spain) a narrow and shallow mesotidal estuary, with 5.5 km long and a 150 m
131 mean width (surface area of 389 ha, 76% of which is occupied by intertidal flats). Land
132 reclamation has reduced the original estuarine area by 30%, while 50% of the estuary is
133 bordered by dikes (over 13000 m) (Bárcena et al., 2011). The estuary of Suances should
134 be classified as highest priority site with regard to its pollution with very high levels of
135 Pb and Zn and high toxicity in the whole estuary and the specific site selected in this
136 work, nearest to the sea, is representative of the whole estuary (Álvarez-Guerra et al.,
137 2008). The estuary, is part of an area that has been classified as a potential receiving site
138 of Carbon Capture and Sequestration (CCS) techniques, by the Spanish Government
139 (BOE, 2008).

140

141 A detailed description of the methodology used to determine the crystalline sediment
142 phases, the total metal content and the organic carbon of the sediment is presented in the
143 Supplementary Information.

144

145 The amounts of Fe- and Al-(hydr)oxides were estimated in duplicate by the sodium
146 dithionite-sodium citrate with NaHCO₃ buffer system method (Mehra and Jackson,
147 1960). Selective chemical extractions were performed in duplicate on the sediment to
148 determine the amounts of humic acids (HA) and fulvic acids (FA). The humic and fulvic
149 fractions were determined with a batch method derived from the currently recommended

150 procedure of the International Humic Substances Society (IHSS) (Swift, 1996; Thurman
151 and Malcolm, 1981).

152

153 **2.2. Leaching tests**

154 The pH dependence leaching test with initial acid/base addition, as described in the
155 standard CEN/TS 14429, was performed in duplicate with some modifications. Two set
156 of experiments with deionised water and seawater where performed, with predetermined
157 amounts of acid (HNO₃) or base (NaOH) added to subsamples at L/S=10 l/kg at 10 rpm
158 for 48 h in three stages at 0, 30 and 120 minutes (t_0 , $t_{0+30\text{min}}$, $t_{0+2\text{h}}$). The pH of the leachate
159 was measured after each stage and the equilibrium at the end of the experiment verified.
160 It was considered that the equilibrium was achieved if the difference between pH_{44h} and
161 pH_{48h} was smaller than 0.3. Moreover this test allows to obtain the acid and base
162 neutralisation curve which is useful to know the quantity of acidification needed to reach
163 a determined pH value. Whole pH range (0-14) to mimic potential environmental risks
164 situations, as ocean acidification by natural or anthropogenic CO₂ leakages and potential
165 chemical spills, have been used. This approach using wider range of pH than standard, has
166 been apply previously by different authors (Table SI1 Supplementary Information).

167

168 Each leachate sample obtained at the end of the experiment, was filtered through a 0.45
169 µm pore size nitrocellulose filtration membrane and divided in two subsamples: one for
170 measuring the pH using a pH meter equipped with a suitable electrode for samples with
171 suspended solids and for determining DOC by the high temperature combustion method;
172 the other subsample was acidified to determine Cl⁻ by titration and As, Cd, Cr, Cu, Ni,
173 Pb, Zn concentrations by an Agilent 7500CE ICP-MS equipment using He collision
174 mode. All analyses were carried out in duplicate. A detailed description of the pH

175 dependence leaching test performed, as well as of the analysis of the leachates is presented
176 as Supplementary Information.

177

178 **2.3. Modelling of metal leaching data using Visual MINTEQ software**

179 Geochemical modelling was carried out using the software Visual MINTEQ (ver. 3.0)
180 (Gustafsson, 2012). The model input files were composed of the maximum concentration
181 obtained in the modified CEN/TS 14429 of the elements of interest (As, Cd, Cr, Cu, Ni,
182 Pb, Zn) and of the inorganic carbon (CO_3^{2-}) as well as of the major components (Al^{3+} ,
183 Ba^{2+} , Ca^{2+} , Mg^{2+} , Si^{2+} and Fe^{3+}) and metal binding ligands (PO_4^{3-} , SO_4^{2-} and SO_3^{2-}) of the
184 sediment under study. Possible solid phases of the major components and the considered
185 elements of the sediment were selected based on experimental analysis of previous studies
186 (Payán et al. 2012a,b).

187

188 Surface complexation and bindings to organic matter were considered using sequentially
189 the available models in the software. Adsorption on Fe- and Al-(hydr)oxides was taken
190 into consideration whereas the Gaussian, NICA-Donnan and Stockholm Humic Model
191 (SHM) were used to assess metal binding to organic matter.

192

193 The ionic strength and the concentration of the major ions (Na^+ , Cl^- , SO_4^{2-} and Mg^{2+}) of
194 seawater were also considered to model the metal behaviour when seawater was the
195 leaching liquid. Visual MINTEQ was successfully used to model metals behaviour in
196 saline waters (Cidu et al., 2013; Gabrijel et al., 2009) and marine waters (Åstrom et al.,
197 2012; Ndungu, 2012).

198

199 **3. Results and Discussion**

200 **3.1. Sediment sample characterisation**

201 Quartz, aluminium oxide, calcite and dolomite are the principal crystalline phases in the
202 studied sediment whereas Pb and Zn are the trace elements that are present in the highest
203 concentrations. The selective chemical extractions performed on the sediment show that
204 it contains 15.14 ± 0.44 mg/g of Fe (hydr)oxides, 1.67 ± 0.02 mg/g of Al-(hydr)oxides,
205 120.9 ± 37.2 mg/kg of humic acids and 790.5 ± 23.2 mg/kg of fulvic acids. Detailed
206 description of the sediment characterisation results is presented in the Supplementary
207 Information.

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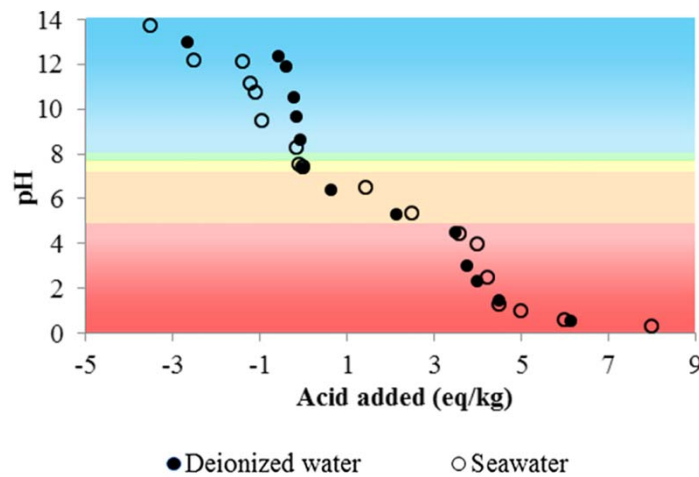
209 Although the sampled sediment is considered superficial because the maximum depth is
210 about 10 centimetres it is supposed to be a reduced sediment due to the black and not grey
211 colour and the negative redox potential, presenting values as low as -130 mV. In many
212 sediments, redox zonation is not clear, and oxic (oxyhydroxides) and anoxic (sulphide)
213 phases coexist at that depths (Burdige, 1993; Williamson et al., 1999; Simpson et al.,
214 2000).

215

216 **3.2. pH dependence leaching test results with deionised water and seawater**

217 The pH curve obtained from the pH titration helps to predict changes in the pH of a sample
218 when affected by acidic or basic stresses (Rigol et al., 2009). Figure 1 shows the changes
219 in pH after the addition of acid (positive scale) or base (negative scale) in a deionised and
220 seawater environment. The experimental results show that the sediment has a low
221 neutralisation capacity to base addition ($BNC_{pH=12} = -0.44$ eq/kg when using deionised
222 water and $BNC_{pH=12} = -1.38$ eq/kg for seawater), but a relatively high acid neutralisation
223 capacity ($ANC_{pH=4} = 3.58$ eq/kg for deionised water and $ANC_{pH=4} = 3.97$ eq/kg for
224 seawater), due to its high carbonate content. The buffering capacity of the seawater also

225 influences the test because a higher amount of acid or base is needed to achieve the same
 226 pH value when seawater is used. This buffering capacity is the result of the consumption
 227 of H^+ and CO_2 by reaction with CO_3^{2-} , counteracting much of the H^+ and CO_2 increase
 228 (Egleston et al., 2010).



229

230 **Fig. 1** pH vs. eq/kg of added acid in the pH dependence leaching test when using deionised water and
 231 seawater. The bands represent different local potential situations under: alkaline chemical spills (pH>8) in
 232 colour blue; natural seawater (pH: 8-7.9) in colour green; ocean acidification (pH: 7.9-7.2) in yellow;
 233 leakages from a CO_2 storage site (pH: 7.2-5) in orange and under acid chemical spills (pH<5) in red

234

235 Some difficulties were found to achieve samples which reach the test equilibrium
 236 conditions (defined as $pH_{48h}-pH_{44h}=\Delta pH_{eq}<0.3$), especially working with seawater
 237 around the neutral pH. It shows that a 48 h experiment might not be sufficient for a
 238 thorough assessment of metal leaching; thus longer time tests (96 h) were performed to
 239 check the equilibrium at different periods of time. For the studied sediment, the
 240 performance of longer time tests did not help to reduce the number of samples necessary
 241 to achieve the equilibrium condition ($\Delta pH_{eq}<0.3$); moreover, the use of longer times
 242 decreased the final pH in the basic zone and increased it in the acidic zone, slowly
 243 neutralizing the initial pH value due to the buffer capacity of the seawater used as leaching

244 agent. Details related to the pH difference to reach the equilibrium, number of samples
245 performed and pH evolution with time, are included in the Supplementary Information.

246

247 This shows that the natural environment tends to reduce the external modifications
248 although some hard stresses, like CO₂ leakages due to CCS technologies and chemical
249 spills, could not be totally absorbed. Furthermore, and because of the minor differences
250 found in the experimental results, it is concluded that 48 hours of experiment is enough
251 to evaluate the contaminant release from this polluted sediment in several pH
252 environments in contact with deionised water and seawater.

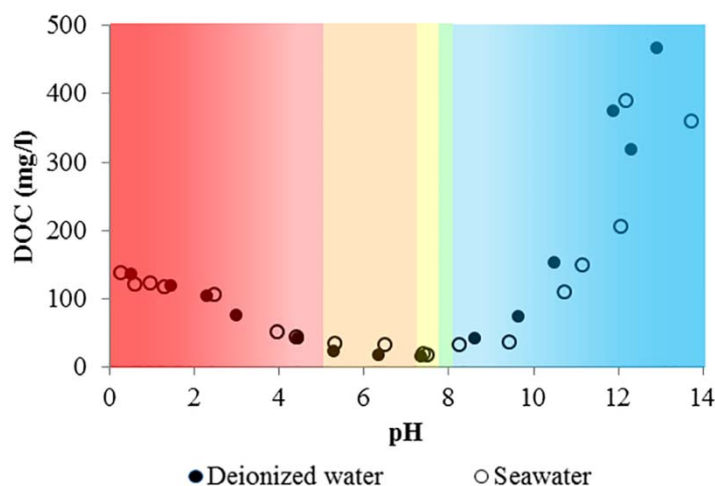
253

254 **3.3. Metal and DOC release for pH dependence leaching test with deionised water** 255 **and seawater**

256 The release of cations from solid matrices is to a large extent determined by the release
257 of Dissolved Organic Carbon (DOC) (Dalgren et al., 2011). Figure 2 shows the DOC
258 (mg/l) release during the pH dependence leaching test.

259

260 For both leaching solutions, DOC releases at acidic conditions probable due to the
261 solubility of FA at low pH values (Cappuyens and Swennen, 2008), reaching minimal
262 concentration at neutral pH value (15 mg/l). From this pH value, DOC increases
263 exponentially with pH due to the higher negative charges on both organic matter and soil
264 inorganic solid surfaces so that these repel each other (You et al., 1999). This exponential
265 increase of DOC at basic pH values is smaller when using seawater as liquid solution.
266 This might be due to the weaker electrical repulsion force experienced by the organic
267 molecules (mainly humic and fulvic acids) interaction with the sediment surface (Münch
268 et al., 2002).



269

270 **Fig. 2** DOC (mg/l) experimental release with pH for deionised water and seawater

271

272 The influence of pH on metal leaching from the studied sediment is emphasised by the
 273 large changes in the release concentration results (Fig. 3). Metal leaching for deionised
 274 water and seawater presents similar results and tendencies, showing a slightly higher
 275 release in the case of deionised water, especially in the basic range.

276

277 The pollutant As (Fig. 3) behaves like an oxyanion, showing not only a minimum but also
 278 a maximum concentration and a high release at basic pH due to the negatively charged
 279 surfaces above the point of zero charge, when the sorption of anions is less favourable
 280 (Rigol et al., 2009). The maximum leaching for Cr, Ni, Pb and Zn is observed in the pH
 281 range 0-4, which is consistent with the observation that at acidic pH the solid surfaces are
 282 positively charged and metal sorption is not favoured. Metal release decreases until
 283 minimum values at pH between 6 and 10 and increases again in the alkaline pH range,
 284 probably as a consequence of the dissolution of organo-metallic complexes (Almås et al.,
 285 2000; Güngör and Bekbolet, 2010; Impellitteri et al., 2002).

286

287 Cu shows a more similar behaviour to DOC than the other elements. Cu sorption is weak
288 at low pH, increases with increasing pH, presenting the maximum sorption, and as a
289 consequence the minimum release, at pH 5-9. Cu sorption decreases at basic pH values
290 probably because of inorganic and organic complexation of Cu in solution (Impellitteri et
291 al., 2002; Rigol et al., 2009; Strobel et al., 2001). Also Pb seems to have a high degree of
292 complexation with DOC; both metals have a relative to Ni, Zn and Cd higher affinity for
293 specific binding to humic substances (Ahmad et al., 2012; Buffle, 1988; Milne et al.,
294 2003). Hence it is shown that the release of Cu and Pb at high pH values using seawater
295 is lower than when using deionised water as leaching liquid according to the lower
296 quantity of DOC in the seawater experiments.

297

298 **3.4. Geochemical modelling of the metal release for pH dependence leaching tests** 299 **with deionised water and seawater**

300 During the assay, the oxidation of different compounds, S^{2-} included, happens. The
301 reasons for this process are the absence of an inert atmosphere, the contact of some air
302 with the sediment-sample inside the bottle (headspace) and the intrusion of air when the
303 recipient is opened to add the needed acid or base and to measure the pH.

304

305 As a consequence of this oxidation, an increase in the redox potential, achieving positive
306 values, and a colour change in the sediment (being brown-yellow) are appreciated. These
307 two reasons allow us to think that oxidation of sulphide during the leaching tests can
308 cause these changes.

309

310 Additionally, in order to verify that these changes are produced because of the presence
311 of oxygen, additional experiments were carried out in the laboratory (see Supplementary
312 information).

313

314 Although it is known that metals bind stronger with sulphide phases than with carbonate,
315 Fe- or Mn-(hydr)oxides or particulate organic carbon (Simpson et al., 2004), these
316 compounds are kinetically stable only over periods of some hours (Simpson et al., 1998).
317 Hence, the longer duration of the assay under study (48 h) allows all the sulphides to be
318 oxidised. During the oxidation process the S^{2-} becomes to sulphates while dissolved metal
319 concentrations increases due to their release (Simpson et al., 2000).

320

321 As the geochemical model is done in equilibrium conditions ($t=48$ hours), all the S is
322 expected to be oxidised. As mentioned in the methodology section S is taken into account
323 as SO_4^{2-} and SO_3^{2-} in the geochemical modelling to represent the complete oxidation of
324 all sulphide compounds.

325

326 The previous decision is also supported because in contaminated sediments, high
327 proportions of Zn and Pb may not be present as metal sulphides, even when elevated
328 sulphide concentrations are present (Simpson et al., 2000). Zn and Pb can also be
329 incorporated as trace elements in Fe-monosulphides and pyrite (Brennan and Lindsay,
330 1996). However, Pb, Zn and Cd are generally only pyritized to a few percent, as a
331 consequence of the precipitation of metal-sulphide phases prior to FeS formation and
332 subsequent pyrite formation (Morse and Luther, 1999).

333

334 Although it was reported that under conditions in which there is an abundance of SO_4^{2-}
335 compared to Fe the control by pyrite (FeS_2) would have no effect (Brennan and Lindsay,
336 1996), the influence of this phase was tried in the geochemical software. Other metal
337 sulphides such as chalcopyrite (CuFeS_2), galena (PbS), mackinawite ($(\text{Fe,Ni})_{1+x}\text{S}$) or
338 chalcocite (Cu_2S) were introduced in the geochemical software to verify their influence
339 and assess the assumption that all the S was oxidised in the experimental assay. Another
340 phases like tennantite (Cu_3AsS_3), enargite (Cu_3AsS_4) (Wildeman) or pyrrhotite ($\text{Fe}_{1-x}\text{S}_x$)
341 (Balistrieri et al., 2007; Chapman et al., 1998; Zhuang et al., 1994) could not be
342 considered because we did not find the formation constants to add them to the database
343 of the software. Predicted curves did not change, or even were worse, so it could be
344 concluded that the shown predicted curves are the most reliable under complete oxidation
345 conditions. Even if experimentally it would not happen, its consideration allow to obtain
346 the most conservative values and avoid the environment to be damaged due to the higher
347 predicted release of the elements under study as a consequence of the consideration of the
348 complete oxidation.

349

350 For modelling purposes, the sum of Fe- and Al-(hydr)oxides, due to the absence of a
351 database for adsorption on aluminum(hydr)oxides, was considered as solid adsorbent.
352 Among the different models available in the software, the Generalised Two Layer Model
353 (GTLM), named HFO, provided by Dzombak and Morel (1990) and the Fh 3-site
354 (Gustafsson et al., 2011) are those which best fit with the experimental values. The match
355 between experimental and modelled results are better using the HFO model in the case of
356 Cr, Cu and Zn and the Fh 3-site model for Cd, Ni and Pb.

357

358 The effect of pH and salinity, especially at basic pH values, on the organic matter
359 motivated to accomplish a modelling strategy which considered DOC models for all the
360 elements studied; however, the influence of DOC on the release of metals was expected
361 to be higher in the case of Cu and Pb (Sundaray et al., 2011; Yap et al., 2002).

362

363 Figure 3 shows the metal leaching and geochemical modelling results for the pH
364 dependence leaching test in the whole pH range using deionised water and seawater as
365 leaching solutions.

366

367 Arsenic is the only element whose modelled release without and with adsorption (HFO
368 model) is shown (Fig. 3). When adsorption is not considered, As precipitates as
369 $\text{BaHAsO}_4\text{H}_2\text{O}$ at pH: 6-12 using deionised water and at pH: 7-11 when seawater is the
370 leaching liquid; the best match between modelled and experimental curves is at $\text{pH} \geq 11$.
371 However, the model overestimates the release at acidic conditions. Considering that it
372 could be due to the adsorption to Fe- and Al-(hydr)oxides, results including the HFO are
373 also shown (Fig. 3). The match at $\text{pH} \geq 11$ is also good so adsorption is not the controlling
374 factor at high pH values (Mamindy-Pajany et al., 2009). Moreover, these modelled curves
375 have the same pattern that the experimental release, including the maximum at $\text{pH}=4$, but
376 underestimate it in three orders of magnitude. Experimentally there is not as much
377 adsorption as the model predicts, probably due to a higher competition between As and
378 ubiquitous anions such as SO_4^{2-} , CO_3^{2-} and Cl^- (Cornelis et al., 2012) than the one
379 considered by the model.

380

381 An increase in acidity does not have an important effect on the mobility of Cd, a typically
382 mobile element, whereas for Ni, Pb and Cr, typically fixed elements, an increase in acidity

383 causes a considerable increase in extractability as has been reported previously by
384 Sauquillo et al., 2003. The main solid phases in Cd model are $\text{Cd}(\text{OH})_2$ and $\text{Cd}_4(\text{OH})_6\text{SO}_4$
385 at basic pH values. The adsorption is an important phenomenon which improves the
386 prediction of its release, especially at basic pH values and using the Fh 3-site model.
387 Nevertheless, the model overestimates the release even in three orders of magnitude at
388 $\text{pH} < 8$. The influence of the organic matter was evaluated using the three available models
389 in the software but predicted curves did not match better with the experimental one.
390 Variation of Cd speciation in sediments has been reported as more significant than other
391 elements. In fact, total Cd concentration was observed in exchangeable fraction, in easily
392 reducible fraction and noticeable portion of Cd was found in residual fraction bound in
393 lithogenic minerals (Cuong and Obbard, 2006; Nemati et al., 2011). Thus, the
394 overestimation could be explained by the influence of clay, silt fractions and oxidic and
395 layer silicate surfaces in Cd sorption (Harichandan et al., 2013; Naidu et al., 1997), not
396 included in the database of the software.

397

398 The adsorption of Cr on the Fe- and Al-(hydr)oxides occurs in almost the whole pH range
399 using the HFO model. The main solid phase is Cr_2O_3 , present at pH values higher than 9
400 for both leaching liquids. Some experimental values in the pH range of 5-10 are below
401 the detection limit so modelled results might be considered an approximation. Under this
402 model scenario a good description of Cr leaching in the full pH range is obtained.

403

404 For Cu, the modelled release pattern shows a minimum release at neutral pH values due
405 to the use of the adsorption (HFO) and the SHM model which considers the dissolution
406 and precipitation of humic and fulvic acids. The modelled curve using seawater (dotted
407 line in Fig. 3) is not complete because the software is not able to present a result at some

408 pH values due to the complexity of the model and the reach of the maximum number of
409 iterations.

410

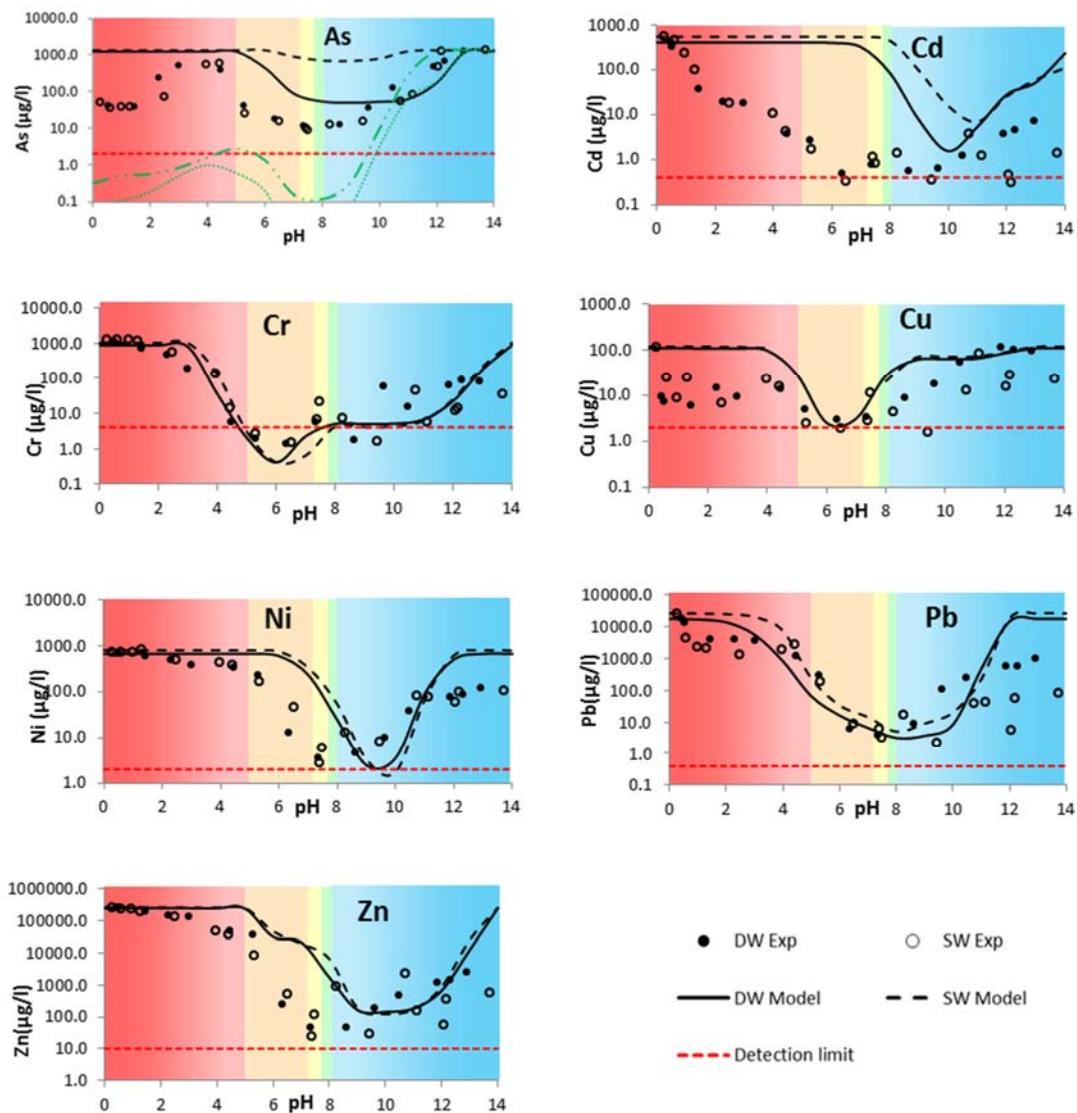
411 The modelled results for Ni using Fh 3-site model show that Ni(OH)₂ is the controlling
412 phase for Ni at basic pH values (pH ≥ 10) as concluded by Dijkstra et al. (2004) and Payán
413 et al. (2012a). The software indicates that the maximum concentration of Ni adsorbed on
414 Fe- and Al-(hydr)oxides occurs in the pH range 7-10 for the two surface adsorption
415 models used.

416

417 According to the modelled curves, Pb may precipitate as chloropyromorphite(c)
418 (Pb₅(PO₄)₃Cl) at pH 5-10. In addition to including the Fh 3-site model, the modelling of
419 this element takes into account the metal-DOC binding by the NICA-Donnan model,
420 which uses the experimental humic and fulvic acids. This model scenario provides a good
421 description of Pb under sediment resuspension conditions and ocean acidification due to
422 the climate change and leakages of CO₂, but overestimates Pb leaching at high pH values.

423

424 Modelled by HFO, Zn precipitates as smithsonite at neutral pH values (6-8) and as zincite
425 at pH values higher than 10. As shown by Zhang et al. (2008), the consideration of the
426 surface adsorption does not have an important influence on Zn release although the curves
427 improve taking it into consideration.



428

429 **Fig. 3** Experimental (Exp) and modelled results of metal leaching as a function of pH for the pH dependence
 430 leaching test using deionised water (DW) and seawater (SW) as leaching solutions. In the case of As, black
 431 curves represent results without adsorption to Fe- and Al-(hydr)oxides whereas the green ones including it
 432 (.....DW; -.-.- SW)

433

434 **4. Conclusions**

435 Contaminated sediment samples from the potential CO₂ store site of Suances (Spain) are
 436 subject to modified pH dependence leaching test using deionised water and seawater as
 437 leaching solutions in the whole pH range.

438 Experimental results confirm that DOC release depends on pH as well as the type of water
439 used. Metal leaching for deionised water and seawater presents similar concentrations
440 and tendencies, although it is slightly higher when using deionised water especially at
441 high pH values.

442

443 The pH-dependent leaching behaviour predicted by Visual MINTEQ agreed well with
444 the analytical values being a useful model to determine metal species in solution over a
445 large pH range in seawater. These results would be helpful to the pre-incident planning
446 of the environmental impact assessment in the sea area directly surrounding the CO₂
447 leakages and under different scenarios of acidification and/or alkalinisation of seawater.
448 The organic complexation of humic and fulvic acids and the adsorption to Fe- and Al-
449 (hydr)oxides are the main mechanisms that can explain the leaching behaviour; however,
450 results of As and Cd make us consider further studies of sediment mineralogy, clay
451 contents and crystallinity to include them in geochemical software. Due to the difficulties
452 found to achieve the equilibrium condition, the evaluation of metal release under the
453 influence of pH with continuous control is proposed as future work.

454

455 In order to verify and know exact quantities of the oxidation process, a sequential
456 extraction in combination with the kinetic evaluation of metal release under the influence
457 of pH with continuous control, is proposed as future work to assess the change of
458 speciation.

459

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