

1 **Extraction of available and labile fractions of mercury from**
2 **contaminated soils: the role of operational parameters**

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15 **Abstract**

16 One of the recognized challenges in chemical extraction of mercury from soil is
17 the diversity of procedures that are current available in literature and that differ in
18 terms of the extractant solution used, soil:extractant ratio and duration of extraction.
19 Therefore, this study focused on establishing the role of operational parameters for
20 extraction of the available and labile fractions of mercury from soils, considering
21 different soil:extractant ratios and the kinetics of extraction. The suitability of 1.0 mol
22 L⁻¹ ammonium acetate at pH 7 and 0.1 mol L⁻¹ HCl as extractants for the available
23 fraction and the extraction of the labile fraction using 0.5 mol L⁻¹ hydrochloric acid
24 was investigated. No statistical differences were found between ammonium acetate

25 and 0.1 mol L⁻¹ HCl; therefore both extractants can be used for estimating the
26 available fraction. It was also observed that a soil:extractant ratio of 1.5 g of soil to
27 100 mL of extractant favours mercury extraction. For the available fraction an
28 extraction of 30 minutes seems enough, as no further significant change was
29 observed in the quantity of mercury extracted thereafter. For the labile fraction
30 increase the extraction duration to at least 24 hours is recommended.

31 The data was fitted into kinetic models, and it was observed that the two first-
32 order reactions and the diffusion models help to understand the behaviour of
33 mercury extraction from soil, clearly showing that in all cases the rate of mercury
34 extraction was faster in the first 10 hours and declined after that period. The
35 characteristics of the soil influenced the extraction of mercury, and it was verified that
36 pH and particle size of the soil influenced the mercury extraction process, as results
37 suggested that an acidic soil might have a reduced ability to strongly retain metals
38 and soils with higher porosity showed lower rates of mercury extraction.

39

40 **Keywords:** soil; mercury; fractionation; available fraction; labile fraction;
41 ammonium acetate; hydrochloric acid; extraction kinetics

42 **1 Introduction**

43 Mercury (Hg) is one of the most critical contaminants in the environment (Hissler
44 and Probst, 2006) and can be found in water, air, soils and sediments.
45 Anthropogenic inputs (mining, industry, sludge dumping, etc.) have increased its
46 natural concentration and led to contaminated environments (Hylander and Meili,
47 2003). Soils, in particular, can retain mercury for long periods of time and release it
48 back to the atmospheric, hydrological, and biotic compartments many years after the

49 initial deposition (Oliveira et al., 2007). Mercury can also enter and bioaccumulate in
50 the food chain, causing adverse health effects. These effects are intimately related to
51 the speciation (chemical form) and binding state (precipitated with primary or
52 secondary minerals, complexed by organic ligands, etc.) of the metal in soil, which
53 control its toxicity and mobility (Gleyzes et al., 2002). Hence the importance of
54 understanding mercury association and distribution in the solid fraction
55 (fractionation), which is usually accomplished by applying chemical extraction
56 procedures. These, however, have been widely criticized, with several recognized
57 limitations (Bacon and Davidson, 2008; Issaro et al., 2009). Still, despite the
58 development of alternatives to mercury speciation/fractionation, such as thermo-
59 desorption (Biester and Scholz, 1997; Reis et al., 2012) and X-ray absorption
60 spectroscopy (Kim et al., 2000), the chemical extraction procedures continue to be
61 commonly used and are considered an essential tool in establishing element
62 fractionation in soils (Gleyzes et al., 2002). This is particularly important in the
63 assessment of the most bioavailable and toxic forms of the metal.

64 One of the major problems concerning mercury chemical extractions is the
65 variety of procedures available in literature (Issaro et al., 2009). The 3-step BCR
66 scheme remains amongst the most widely used sequential extraction schemes for
67 elements such as Cd, Cr, Cu, Ni, Pb and Zn (Bacon and Davidson, 2008) and,
68 although it has been applied to mercury fractionation in sediments (Sahuquillo et al.,
69 2003), it has not been validated for this element. On the other hand, Han et al.
70 (2003) developed an extraction procedure, specific for mercury fractionation, that
71 divides mercury species according to their potential mobility in the environment. This
72 scheme has been acknowledge by EPA - method 3200 (EPA, 2005).

73 A common step in all sequential extraction procedures for soil targets the so-
74 called exchangeable fraction, which is the more mobile and available fraction of the
75 metal in soil. A large number of extractants have been used to assess plant available
76 trace elements, including: i) chelating solutions, such as EDTA (Fangueiro et al.,
77 2005); ii) salt solutions such as NH_4Ac , MgCl_2 , or CaCl_2 , due to their capacity to
78 release Hg by ion-exchange (Gismera et al., 2004; Han et al., 2006); and iii) dilute
79 solutions of acid, such as for example HCl (Kashem et al., 2007). Amongst these,
80 the neutral (pH 7.00) 1.0 mol L^{-1} ammonium acetate (NH_4Ac) extraction is one of the
81 most widely applied reagents for leaching the exchangeable fraction (Bondareva et
82 al., 2014; Filgueiras et al., 2002; Hagarová et al., 2003; Hass and Fine, 2010; Jing et
83 al., 2008; Nyale et al., 2014). Additionally, due to its strong complexing power,
84 acetate should prevent the re-adsorption or precipitation of the released metal ions
85 (Filgueiras et al., 2002). Use of 0.1 mol L^{-1} HCl has also been regarded to estimate
86 the available fraction of the metal in soil (Kashem et al., 2007).

87 Another approach is to determine in one step the labile fraction of the metal in
88 soil, by application of a single extraction procedure (Sutherland, 2002). This should
89 include the more available species, such as water-soluble, exchangeable, and
90 carbonate associated. Though this single extraction does not provided exactly the
91 same geochemical information as sequential extraction does, it provides enough
92 information about the more toxic and available species present in the soil, while it
93 has the advantages of being faster, cost-effective, and require less technical skill and
94 reagents (Sutherland and Tack, 2008). Of the numerous reagents that can be used
95 for extraction of the labile fraction, dilute HCl has been the most commonly applied
96 (Andrews and Sutherland, 2004; Snape et al., 2004; Sutherland, 2002; Sutherland
97 and Tack, 2008).

98 Besides the already discussed variety of extractants, other operational
99 conditions change as well, namely the soil:extractant ratio and the duration of
100 extraction. Soil:extractant ratio can vary from 1.0 g of soil per 100 mL of extractant to
101 20 g of soil per 100 mL of extractant, while the duration of extraction has been
102 reported to vary from 30 minutes to 18 hours (Biester and Scholz, 1997; Bloom et al.,
103 2003; Boszke et al., 2006; Neculita et al., 2005; Panyametheekul, 2004; Renneberg
104 and Dudas, 2001). The extraction procedures needed to be optimized in order to
105 better reflect the reactions taking place in the environment and to recover the entire
106 target fraction. The kinetics involved in the extraction of mercury from soil have
107 occasionally been considered (Issaro et al., 2010; Reis et al., 2014), but there is still
108 shortage of information needed to help harmonize extraction procedures. Studying
109 the rate and extent of metal extraction from the matrix is important as on it depends
110 the fate, transport, and bioavailability of metals in soils.

111 Therefore, this study focused on establishing optimal procedural conditions for
112 extraction of the available and labile fractions of mercury from soils, considering
113 different soil:extractant ratios and the kinetics of mercury extraction from soils. The
114 soil's characteristics and the origin of the contamination can influence the
115 fractionation as, usually, metals of anthropogenic origin tend to be in more readily
116 extractable fractions (exchangeable, carbonate bound, Fe and Mn oxide bound,
117 organic matter bound) and therefore are more labile, while metals of geogenic
118 occurrence are typically found in the residual fraction (Ratuzny et al., 2009).
119 Therefore, soil samples from an industrially impacted zone and from a mine area
120 were considered in the study.

121 Overall, this study intends to contribute to the understanding of mercury
122 behaviour in soil, and optimize crucial steps of mercury extraction procedures and of
123 soil toxicity assessment methods.

124

125 **2 Materials and methods**

126 **2.1 Sampling sites and methodology**

127 For this work, soils from two contaminated areas were chosen - Estarreja
128 (North-East Portugal) and Caveira (South-East Portugal). Mercury in Estarreja soils
129 results from the effluents of mercury-cells of a chlor-alkali plant (Reis et al., 2009),
130 while the latter is a mine area, situated in the Iberian Pyrite Belt (Barriga, 1990).

131 One sample was collected in an agricultural field close to a former effluent stream
132 of the Industrial Complex of Estarreja, where during more than 50 years a large
133 chlor-alkali plant operated using the mercury cell process (Ullrich et al., 2007).
134 Mercury-cell chlor-alkali plants have previously been identified as a major source of
135 mercury to the environment (Lacerda and Salomons, 1998; Ullrich et al., 2007). Due
136 to its persistency, the metal can still be found in Estarreja soils even after the plant
137 completely ceased the use of mercury in 2002 (Ospar Commission, 2006; Reis et al.,
138 2009). The Caveira mine sample was collected at an agricultural field located near
139 the mine pit. The Caveira sulfide mine is situated in the Iberian Pyrite Belt (IPB), a
140 mining district of worldwide significance due to its unusual concentration of large and
141 medium sized mineral deposits, including ores of copper, iron, lead, sulfur and zinc.
142 Antimony, arsenic, cadmium, cobalt, gold, mercury, selenium and silver can also be
143 found in soils from the IPB (Barriga, 1990). Currently, the mine is not being exploited,

144 but the tailings are still present in the surroundings and acid mine drainage
145 constitutes a problem.

146 Sampling was performed using a plastic spatula and samples were placed in
147 plastic bags for transport to the laboratory. The soil sampling depth was 0–15 cm.
148 Once in the laboratory, soil samples were air dried at room temperature to constant
149 weight. Stones were removed and soil clumps were crushed and homogenised
150 during the drying stage. The dried samples were sieved to < 2 mm using a nylon
151 sieve. The air-dry soil, < 2 mm fraction, was used for the chemical extraction
152 procedures.

153

154 **2.2 Soils samples physical-chemical characterization**

155 The soil pH (CaCl_2) was determined using a WTW pH meter-538, according to
156 the ISO 10390:1994 method. Total carbon (TotC) was measured on an elemental
157 analysis instrument (LECO CNH-2000), according to ISO 10694:1995. For the
158 determination of organic carbon content (OrgC), an excess of 4 mol L⁻¹ of
159 hydrochloric acid was added to a crucible containing a weighed quantity of soil. The
160 crucibles were left to stand for 4 hours at room temperature and then were digested
161 for 16 hours at 60-70°C to remove the organic carbon. The residue was then
162 analysed to give the inorganic carbon content, and organic carbon was calculated by
163 the difference.

164 The particle size distribution and clay contents of the soil samples were
165 determined using a Coulter LS230 laser diffraction particle size analyzer. The
166 classification of soils followed the USDA Texture Classes: sand fraction
167 (0.050 < % < 2mm), silt fraction (0.002 < % < 0.050mm), and clay fraction (% < 0.002mm).

168 Classification of samples was achieved by using the *Talwin 42*[®] classification
169 software program.

170

171 **2.3 Procedures for chemical extraction of mercury from soil samples**

172 For the experiments, the effect of leaching duration on metal extraction was
173 evaluated using the following solutions: 1.0 mol L⁻¹ NH₄Ac (pH 7.0), 0.1 mol L⁻¹ HCl,
174 and 0.5 mol L⁻¹ HCl. The first two solutions were used to study the available fraction
175 of mercury in soils (Jing et al., 2008; Kashem et al., 2007) and 0.5 mol L⁻¹ HCl was
176 employed to assess the labile fraction of mercury (Sutherland and Tack, 2008).

177 For the three mentioned solutions, soil:extractant ratios considered were 1.5
178 g:100 mL (1.5:100), 10 g:100 mL (10:100) and 20 g:100 mL (20:100). As soils are
179 very heterogeneous media, samples were thoroughly homogenized prior to
180 weighting. The mixtures (12 g, 80 g, and 160 g of sample in 800 mL of extractant)
181 were shaken at room temperature (23±5 °C), using an end-over-end shaker at a
182 constant rate of 60 rpm, and all extractions were performed in duplicate.

183 Eight mL of the mixture were removed for analysis, using a syringe, at t=30
184 seconds, 15 minutes and 30 minutes, 1, 2, 4, 6, 18 and 24 hours, and then every 24
185 hours until equilibrium had been reached Care was taken in order to ensure that a
186 homogenous aliquot was removed from solution and that the soil:extractant ratio was
187 preserved in the remaining suspension. Removed aliquots were immediately filtered
188 through a 0.45 µm filter of cellulose type membranes (Millipore[®], USA) and stored at
189 4°C until analysis (performed within 24 hours).

190 Possible variations in the pH could affect the extraction process and therefore,
191 the pH of the suspension was controlled during the experiment.

192

193 **2.4 Mercury quantification in soils and extracting solutions**

194 Mercury contents in soils and in extracted solutions were determined by thermal
195 decomposition atomic absorption spectroscopy (AAS) with gold amalgamation
196 (LECO model AMA-254), as described by Costley *et al.* (2000). The system consists
197 of a nickel boat in a quartz combustion tube containing a catalyst in which the
198 sample is initially dried, prior to combustion at 750°C (150 seconds) in an oxygen
199 atmosphere (oxygen flow: 200 mL min⁻¹). The mercury vapor produced is trapped on
200 the surface of a gold amalgamator. After a pre-specified time interval (120–150
201 seconds), the amalgamator is heated to 900°C to quantitatively release the mercury
202 which is transported to a heated cuvette (120°C) prior to analysis by AAS using a
203 silicon diode detector at 253.6 nm. A quantification limit of 0.05 ng of mercury was
204 established.

205

206 **2.5 Quality control and quality assurance of the results**

207 Analytical procedures were conducted using ultra-clean glassware (previously
208 soaked in 5% Derquin for 24 hours; then 25%, HNO₃ for 24 hours), to avoid
209 contamination of sample extracts. Care was taken to avoid cross-
210 contamination of the samples. The extractant solutions were all tested and
211 found to be sufficiently low in mercury (less than 10 ng L⁻¹) before use.

212 Quality control for the determination of total carbon in LECO CNH-2000 was
213 performed through the analysis of certified reference material Synthetic Mix for Soil
214 #3 from EuroVector, for which a recovery of 111-115% was obtained.

215 The accuracy of the Leco AMA-254 instrument was assessed daily by the
216 analysis of certified reference materials BCR CRM 142R (Light sandy soil; certified
217 Hg concentration: 0.067 mg kg⁻¹) and RTC CRM 021 (Sandy loam; certified Hg
218 concentration: 4.7 mg kg⁻¹). Mercury concentrations obtained were always within the
219 certified interval of confidence and recoveries were within the range 82–109% (n=16
220 for CRM 142R; n=12 for CRM 021). Because certified reference materials are not
221 available for mercury fractionation, it is not possible to check the accuracy of the
222 chemical extractions.

223

224 2.6 Chemical extraction data fitting

225 In order to perform the extraction data fitting, the results were expressed as
226 mercury extracted per unit of soil (mg kg⁻¹) between extraction initiation time (t₀) and
227 t_i, and as a function of the volume of extractant solution (V) and sample mass (m).

228

229 **Equation 1**
$$Hg_{t_0 < t < t_i} = [Hg_{t_i} - Hg_{t_0}] \times \frac{V}{m}$$

230

231 The removal rate per unit time (mg kg⁻¹ h⁻¹), between extraction initiation time (t₀)
232 and t_i was determined as:

233

234 **Equation 2**
$$Removed\ Hg_{t_0 < t < t_i} = \frac{Hg_{t_i} - Hg_{t_0}}{t_i - t_0}$$

235

236 The data obtained for mercury extracted per unit of soil was modeled by
237 nonlinear regression analysis, using GraphPad Prism 5 (trial version) that uses the
238 least-squares fitting method and the method of Marquardt and Levenberg for

239 adjusting the variables; this method blends the method of linear descent and the
240 method of Gauss–Newton.

241 The most common models used to fit data from metal extraction from soil, the two
242 first-order reactions model and the diffusion model, were used to fit the extraction
243 rate data. Each of the kinetic models was tested for data fitting. In order to assess
244 the goodness of the fit to the experimental data the coefficient of determination (R^2)
245 and the standard deviation of residues ($S_{x/y}$) were determined. A relatively high R^2
246 and low value of $S_{x/y}$ were used as criteria for best fit. For each case, the fitting was
247 tested using the mean of the whole set of chemical extraction data.

248

249 **2.6.1 Two first-order reactions model**

250 This model has been regarded as the most appropriate model to explain the
251 kinetics involved in metal fractionation in soil (and sediment) (Fangueiro et al., 2005;
252 Issaro et al., 2010). It advocates that extraction of the metal from soil takes place in
253 multiple steps (first-order reactions) which reaction rates are independent from each
254 other. This implies that metals are bound to distinct sites available in soil, resulting in
255 a readily extractable (C_1) and a less extractable (C_2) metal fraction. In addition, the
256 total non extractable metal fraction (C_3) can be estimated through the difference
257 between total mercury and C_1+C_2 . The two first-order reactions model is described
258 as:

259

260 **Equation 3**
$$C = C_1(1 - e^{k_1t}) + C_2(1 - e^{k_2t})$$

261

262 where C_1 and C_2 (mg kg^{-1}) are mercury concentration extracted in the first and
263 second stages, respectively, and k_1 and k_2 are the associated apparent rate
264 constants.

265

266 2.6.2 Diffusion model

267 The diffusion model assumes that the desorption of metals from the soil matrix is
268 initially fast but the rate is limited by the diffusion from the mineral lattice or the intra-
269 particle diffusion from pores of inner soil surfaces (Gismera et al., 2004). According
270 to Gismera *et al.* (2004), the metal desorption rate of a solid fraction due to diffusion-
271 controlled kinetics may be described as:

272

273 **Equation 4**
$$\frac{\partial C}{\partial t} = \frac{kDS(C_{eq} - C)}{V\delta}$$

274

275 Where C is the removed metal concentration; C_{eq} is the metal concentration at the
276 equilibrium; t is the time; D is the diffusion coefficient; S is the surface area of the
277 solid particle, V is the solution volume; δ is the thickness of the diffusion layer around
278 the particle; and k is a constant of proportionality. Including the parameters D , S , δ
279 and V in the constant k and rearranging and solving Equation 4, a first-order
280 equation is obtained:

281

282 **Equation 5**
$$C = C_{eq} \times (1 - e^{-kt})$$

283

284 **3 Results and discussion**

285 **3.1 Soil samples physical-chemical characteristics**

286 The Estarreja sample has a total mercury content of 70.0 mg kg⁻¹, and is
287 classified as loamy sand soil (sand 78%; silt 19%; clay 3%), with a pH of 6.0 and
288 total and organic carbon contents of 2.2% and 1.9%, respectively.

289 The Caveira sample has lower total mercury content and pH - 6.3 mg kg⁻¹ and
290 3.3, respectively. Total carbon content is 4.1%, while organic carbon constitutes
291 3.5%, and the soil is classified as silt loam (sand 27%; silt 58%; clay 15%).

292

293 **3.2 Mercury extracted from soil**

294 The amounts of mercury extracted per unit time are depicted in Figure 1, while
295 Table 1 presents the mercury extracted from the solid matrix per kg of soil, and the
296 percentage of extracted mercury (percentage of mercury extracted in comparison
297 with total mercury). In general, all the extraction curves are similar in shape, with a
298 fast extraction rate in the first 10 hours that becomes slower after that period. This
299 type of extraction rate data, with two distinct stages, has been observed in other
300 studies concerning metal extraction from soils (Bermond et al., 2005; Issaro et al.,
301 2010; Reis et al., 2014; Varrault and Bermond, 2011). Studying extraction processes
302 in heterogeneous systems such as soils is therefore challenging, due to the
303 complexity of the matrix and the numerous components that it is constituted of.
304 These components interact with each other resulting in a multitude of sites for metal
305 sorption with different reactivity. In this context, the present study demonstrated that
306 mercury extraction from soil is associated with kinetically different compartments:
307 one, for short extraction periods ($t \leq 10$ hours), corresponding to faster extraction
308 rate of mercury species that are weakly sorbed to the soil matrix, i.e. associated with

309 more exposed, reactive sites; and a second where the slower extraction of the metal
310 indicates its release from sites of relatively higher bonding energy that need more
311 time to dissociate, diffusion from the intricate mineral lattice or from pores of inner
312 soil surfaces that need more time to dissociate. It must be clarified though that these
313 compartments are only operationally defined and not related to soil compartments,
314 such as iron oxides or organic matter, for example. In terms of risks to the living
315 organisms present in the environment, the first stage (i.e. the metal that is extracted
316 in the first hours) has more impact because it is easily mobilized to the soil solution,
317 becoming readily available for plant uptake, contaminating crops or the aquatic
318 compartment.

319 The interpretation of the obtained results is next presented in order to highlight
320 the differences between extractants and the influence of soil:extractant ratio,
321 duration of extraction and soil sample physical-chemical characteristics.

322 **3.2.1 Differences between extractant solutions**

323 For the three extractant solutions studied, the percentage of mercury removed
324 from soil samples was higher when 0.5 mol L⁻¹ HCl was applied, followed by 0.1 mol
325 L⁻¹ HCl and 1.0 mol L⁻¹ NH₄Ac (Table 1). To evaluate the statistical difference among
326 the three extraction procedures, Friedman's test, followed by post-hoc test for
327 pairwise comparison, was performed. The results presented in Table 1 show that
328 more mercury is extracted when using 0.1 mol L⁻¹ HCl, when compared to 1.0 mol L⁻¹
329 NH₄Ac, and that the difference between extractant solutions is larger in Caveira
330 soil. As both these extractant solutions are used to estimate the available fraction of
331 metals in soil, the Friedman's test was used and showed that there is a significant
332 difference between the 0.1 mol L⁻¹ HCl and 1.0 mol L⁻¹ NH₄Ac procedures only in the

333 10:100 and 1.5:100 ratios for the Estarreja sample. In other cases, the test did not
334 show statistical differences between extraction procedures.

335 The 0.5 mol L⁻¹ HCl has frequently been used in single extractions of the labile
336 fraction of a metal in solid fraction (Sutherland and Tack, 2008), providing
337 information of environmental importance. As more mercury was extracted using this
338 solution when compared to the other two considered in this study (between 5 and
339 13% in Estarreja sample, and 21 to 33% in Caveira sample), this means that the
340 available fraction is only a small part of the labile fraction of mercury in the studied
341 soils. Friedman's test revealed that results when applying 0.5 mol L⁻¹ HCl are
342 statistically different from the ones obtained for the other two solutions (used to
343 estimate the available fraction; Table 2).

344

345 **3.2.2 Influence of soil:extractant solution ratio**

346 The effect of soil:extractant ratio is an important factor in metal removal from soils
347 but rarely considered in this kind of studies. The soil (g):extractant solution (mL)
348 effect was tested by comparing the ratios 1.5:100, 10:100, and 20:100. The data
349 here presented shows that mercury extraction from soil was favoured by lower
350 soil:extractant ratio, as the percentage of mercury removed from soil generally
351 follows the trend 1.5:100 > 10:100 > 20:100 (Table 1 and Figure 1); exceptions were
352 observed for the extraction with 1.0 mol L⁻¹ NH₄Ac in Estarreja soil and 0.5 mol L⁻¹
353 HCl in Caveira soil. The Friedman's test did not reveal statistical differences among
354 the three considered ratios ($p=0.280$; $\alpha=0.05$). Therefore, soil:extractant solution
355 ratio does not seem to have a major effect in mercury extraction from these soils
356 samples, as it had been previously observed for the water-soluble fraction extraction
357 (Reis et al., 2014). It is usually considered that it is best to use the lowest solid-to-

358 liquid ratio possible to more efficiently leach the mercury species (Issaro et al.,
359 2010), but in practice other implications must be considered. While in this study no
360 problems of reproducibility were experienced when using 1.5 g of sample to 100 mL
361 of extractant solution (therefore this ratio seems feasible), in fractionation studies the
362 choice of the ratio must assure the accurate weigh of small sample masses, that is
363 repeatable among replicates, i.e., representativeness of the sample. For example, 3-
364 step BCR scheme applied by Sahuquillo et al. (2003) for mercury speciation in
365 sediments considered a solid:liquid ratio of 1:40 and an RSD lower than 10% was
366 obtained in most of the samples. Quantification of mercury in solution must also be
367 guaranteed. A higher concentration of metal in solution will result from the use of a
368 higher soil:extractant, which has the advantage of overcoming any potential
369 problems with detection limits of the instruments used for metal quantification. On
370 the other hand, higher soil:extractant ratios can lead to extractant saturation and can
371 also hinder the filtration process due to filter clogging. In the current work, when
372 using the 20:100 ratio, more than one filter was needed, meaning that the soil was in
373 contact with the solution for a longer time and increasing the procedures financial
374 costs.

375

376 **3.2.3 Effect of time on mercury extraction from soils**

377 Desorption and sorption of a metal in soil are time dependent phenomena, but
378 the mercury extraction kinetics from soil has rarely been studied. The results
379 presented in Figure 2 show similar curve shapes for mercury extracted from both soil
380 samples by using the three extractants and the three considered soil:extractant
381 ratios.

382 As already mentioned, the mercury extraction profile is made up of two different
383 stages: a fast extraction stage ($t < 10$ hours) and a relatively slower one ($t > 10$
384 hours). It is important to note that mercury extraction from soil is almost immediate,
385 as between 60 to 90 % of the total metal extracted occurs in the first 30 seconds.

386 When using $1.0 \text{ mol L}^{-1} \text{ NH}_4\text{Ac}$ for mercury extraction, equilibrium was reached at
387 ca. 24 hours (which corresponds to the maximum quantity of mercury extractable by
388 this solution). For the extraction with 0.1 mol L^{-1} and $0.5 \text{ mol L}^{-1} \text{ HCl}$, the reaction did
389 not reach equilibrium in either sample, even after 150 hours (Figure 2). For the
390 Caveira soil, the extraction with $0.5 \text{ mol L}^{-1} \text{ HCl}$ was extended to 216 hours (9 days)
391 and still the equilibrium was not reached. This suggests that, in acidic conditions,
392 mercury present in soil can be continuously released from the solid matrix into other
393 environmental compartments, such as water bodies. It also means that the duration
394 suggested in extraction procedures, usually 30 minutes to 1 hour (Han et al., 2006;
395 Kashem et al., 2007; Sutherland and Tack, 2008), may only estimate a portion of the
396 target fraction. The comparison of the percentage extracted at the end of the
397 experiment with the percentage extracted at 30 minutes revealed that for the
398 extractions with $1.0 \text{ mol L}^{-1} \text{ NH}_4\text{Ac}$ and $0.1 \text{ mol L}^{-1} \text{ HCl}$ this difference is 0.45% in
399 Estarreja and 1.5% in Caveira. Therefore, it can be suggested that for the study of
400 the available fraction of mercury in soils using the two considered solutions, it would
401 be possible to use an extraction time of 30 minutes, without neglecting important
402 information. When using $0.5 \text{ mol L}^{-1} \text{ HCl}$ to estimate the labile fraction in soil, the
403 difference in percentage of mercury extracted at 1 hour reached 5.7 % and 7.8%,
404 respectively in Estarreja and Caveira soil samples, which suggests that it is
405 advisable to increase the extraction to longer than one hour in soils that have
406 physicochemical properties that result in metal retention.

407

408 **3.2.4 Fitting of kinetics data of mercury extraction from soil**

409 To test for the fitting of the kinetic results, the mercury extracted per kg of soil
410 was plotted against time (Figure 2). The experimental data were fitted into the two
411 first-order reactions model (Equation 3), as this model considers the observed
412 biphasic extraction behaviour and, therefore, seemed appropriate for the dataset.
413 Because a diffusion mechanism may also be involved in mercury extraction, the
414 diffusion model (Equation 5) was tested as well. The kinetic parameters are
415 presented in Tables 3 and 4. As can be seen, the R^2 values obtained with the
416 diffusion model are generally slightly lower than the ones obtained with the two first-
417 order reactions model. Nevertheless, in most cases the two models fitted the
418 experimental data and the good agreement between the experimental and fitted
419 curves is visible in Figure 2. The standard deviation of residues obtained was in most
420 cases high and data of the extraction with $1.0 \text{ mol L}^{-1} \text{ NH}_4\text{Ac}$ rarely fitted to either of
421 the adopted models. The phenomenon of re-adsorption that can be observed during
422 the extraction process is particularly noted for this extractant solution, causing a
423 more “irregular” dataset, hampering its fit. Re-adsorption problems are one of the
424 disadvantages recognized to chemical extraction procedures (Bacon and Davidson,
425 2008).

426 Concerning the two first-order reactions model, the kinetic constant k_1 is always
427 larger than k_2 , corroborating the two different kinetic stages and the faster removal
428 rate during the first hours. For mercury extraction with HCl (both concentrations) k_1
429 and k_2 from Estarreja soil are superior to k_1 and k_2 from Caveira soil, which can be
430 related to the soils physicochemical characteristics. Estarreja and Caveira soils have
431 different textures, as the latter are richer in clay particles resulting in a soil with

432 higher porosity. In turn, the high porosity of this soil suggests that mercury extraction
433 could be controlled by intra-particle diffusion. This desorption mechanism had
434 already been observed in the study of the water-soluble fraction and a thorough
435 explanation can be found in Reis *et al.* (2014). Additionally, the smaller particle size
436 of the Caveira soil increases its mercury retention capacity but metal extraction is
437 also dependent on soil-extractant equilibrium (extractant solution may become
438 saturated) and on the strength of the bound between the metal and the solid
439 particles. In short, all these processes can contribute to the observed results.

440 In general, the C_2 fraction estimated by the two first-order reactions model was
441 larger than the C_1 fraction and both increased with decreasing soil:extractant ratio
442 (exception for Caveira soil, 0.5 mol L⁻¹ HCl). This confirms previous observation that
443 more mercury is extracted when low soil:extractant ratios are applied. It also means
444 that, even though the extraction is faster in the first 10 hours, a smaller quantity is
445 extracted in that period, when compared to the second stage.

446 The C_{eq} values estimated by the diffusion model increase in the order 1.0 mol L⁻¹
447 NH₄Ac < 0.1 mol L⁻¹ HCl < 0.5 mol L⁻¹ HCl, and decrease as soil:extractant ratio
448 increases. Also, C_{eq} in Estarreja is higher than C_{eq} in Caveira soil sample. The
449 kinetic constant, k , is larger in 0.5 mol L⁻¹ HCl than in 0.1 mol L⁻¹ HCl, confirming that
450 extraction reaction occurs faster in the presence of more concentrated acid. Between
451 the two studied samples, there is no meaningful difference in the constant k ,
452 although in Caveira soil the process is slightly slower. The explanation for the slower
453 mercury extraction in Caveira soil can be due to the sample texture and was already
454 discussed.

455 The relative error between the experimental and the estimated values of C_1 , and
456 C_2 , both from the two first-order reactions model and C_{eq} from the diffusion model

457 were calculated. The experimental value of C_1 was defined as the amount of
458 mercury desorbed per unit of soil at $t=10$ hours; the experimental value of C_2 was
459 calculated by the difference between the amount of mercury extracted at equilibrium
460 and C_1 . C_{eq} , in the diffusion model, was defined as the amount of mercury desorbed
461 per unit of soil at $t=$ equilibrium. The relative error associated with C_1 and C_2 is not
462 satisfactory as it ranges from 6% to approximately 60% and, in a few cases, is as
463 high as 95%. Both under and overestimation of the experimental value occurred. The
464 error associated with C_{eq} is considerably lower, meaning that this constant better
465 estimates the real concentration reached at equilibrium.

466 In summary, both the two first-order reactions and the diffusion models help to
467 understand the mechanisms involved in mercury extraction, meaning that mercury
468 extraction from the studied soils occurs in two concurrently stages and that
469 extraction is limited by diffusion of less labile mercury complexes.

470

471 **3.2.5 Effect of soil physicochemical characteristics on mercury extraction**

472 Mercury availability can be dependent on contamination source (anthropogenic or
473 geogenic) and it is generally recognized that metals are more labile in
474 anthropogenic-contaminated soils (Ratuzny et al., 2009). The results of this work,
475 are however different, as a higher percentage of mercury was extracted in Caveira
476 soil (although at an apparent slower rate), a mine soil where mercury is of geogenic
477 origin, when compared to the percentage extracted in the Estarreja soil, where
478 contamination results from the effluents of a chlor-alkali plant. Caveira soil has
479 physicochemical characteristics that would apparently retain mercury more
480 efficiently, like higher content of organic matter, sulfur and clay. The observed
481 behaviour can be explained by the soil pH, since this parameter can have a strong

482 influence on mercury extraction from soil. The pH was adjusted to 7 in the 1.0 mol L⁻¹
483 NH₄Ac solution, and was controlled during the extraction, during which time pH
484 changes were not relevant. For Estarreja soil, pH varied between 6.6 and 7.0 and for
485 Caveira between 5.2 to 5.8 (pH was slightly higher in the 1.5 g:100 mL ratio).
486 However, Caveira soil is considerable more acid than Estarreja soil (3.3 versus 6.0),
487 therefore, and due to soil's buffering capacity, it is expected that the solutions will
488 also have lower pH. The increased tendency for a soil to release metals with
489 decreasing pH has been well documented, due to H⁺ removing and replacing the
490 metal cations (Gabriel and Williamson, 2004). Also, Sutherland and Tack (2008)
491 showed that metal extraction with diluted HCl was greater in soil richer in finer
492 particles, as is the case with the Caveira sample.

493 Nonetheless, for environmental relevance, it is more important to consider
494 absolute mercury concentration that is, in fact, released to other compartments. The
495 total Hg concentration in the two soil samples is very different and hence a small
496 fraction of a large amount represents considerably more than a large fraction of a
497 small amount. Indeed, when considering absolute concentrations, mercury found in
498 extracts from Caveira is in lower concentration (Table 1).

499

500 **3.2.6 Comparison with the Kingston method (mobile fraction)**

501 The Kingston method had been previously applied to the same samples (Reis et al.,
502 2010). The first fraction (mobile fraction) includes the most mobile/bioaccessible
503 species (Han et al., 2003) and, hence, should be comparable to the results
504 presented in this study. The comparison presented in Figure 3 shows that the mobile
505 fraction yields similar results to the ones obtained using 0.5 mol L⁻¹ HCl. For the
506 mobile fraction, 1.5 g of soil are extracted with 2.5 mL of extractant solution, while

507 the labile fraction was extracted with 1.5 g:100 mL, which again shows that
508 soil:extractant ratio does not have a major influence on the extraction procedure. In
509 both cases mercury extracted is superior to the amount extracted by any of the
510 reagents used for the exchangeable fraction. In terms of the laboratory work involved
511 in both extractions (mobile in the Kingston method vs. 0.5 mol L⁻¹ HCl labile), the
512 latter is less labor intensive, and therefore less prone to procedural errors. Although
513 this was not tested, 0.5 mol L⁻¹ HCl could be an alternative reagent in extraction of
514 the mobile fraction in Kingston method and it would be interesting, in a future
515 assessment, to consider and study this hypothesis.

516

517 **4 Conclusion**

518 In this work some parameters have been studied in order to determine the
519 optimal experimental conditions for the extraction of available and labile fractions of
520 mercury from soil. The experiment considered the effects of the extractant used,
521 soil:extractant ratio, time of extraction and extraction kinetics, and soil
522 physicochemical properties.

523 From a general point of view, it was determined that:

- 524 a) Soil physicochemical characteristics have a strong influence on mercury
525 fractionation. In the analysed samples, soil pH and texture controlled the
526 rate and mechanism of extraction;
- 527 b) Extraction time needs to be increased, particularly in labile fraction
528 extraction (at least 24 hours). The majority of procedures recommend a 30
529 minute period for extraction that will left-out important information;

- 530 c) It is recommendable to use the lowest soil:extractant ratio that offers
531 efficient extraction, because this gives the best chance that mercury
532 concentrations will be above quantification limits, and also improves the
533 representativeness of the soil sample.
- 534 d) The work showed that it is feasible to use both 1.0 mol L⁻¹ NH₄Ac (pH 7)
535 and 0.1 mol L⁻¹ HCl to estimate the mercury available fraction, as both
536 solutions yielded equivalent results. However, some problems of mercury
537 re-adsorption were observed with 1.0 mol L⁻¹ NH₄Ac, and therefore 0.1 mol
538 L⁻¹ HCl seems more advantageous.

539

540 The outcomes of this study contribute to a better estimation of the labile fractions
541 of mercury in soil and therefore for a more accurate risk assessment of contaminated
542 sites. Future research should be focused on validation of the procedures here
543 presented, such as organization of an interlaboratory trial.

544

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553

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Table 1. Mercury extracted from soils by 1.0 mol L⁻¹ NH₄Ac, 0.1 and 0.5 mol L⁻¹ HCl solutions at three soil:extractant ratios. Amounts are expressed as mg of mercury extracted per kg soil for t ≤ 10 hours, t > 10 hours and total extracted (in equilibrium). Percentage of total mercury extracted was determined in comparison to total mercury in soil.

| | Hg removed (mg kg ⁻¹) t<10h | C ₁ | Relative error | Hg removed (mg kg ⁻¹) t>10h | C ₂ | Relative error | total Hg removed (mg kg ⁻¹) | total Hg removed (%) | C _{eq} | Relative error | | |
|--|---|---|-------------------|--|----------------|-------------------|--|-------------------------|-----------------|-------------------|--------|------|
| Estarreja (total Hg 70 mg kg ⁻¹) | 20:100 | 0.086 | 0.06 | 43 | -0.023 | n.e. | - | 0.063 | 0.09 | 0.069 | -8.4 | |
| | 1.0 mol L ⁻¹ NH ₄ Ac 10:100 | 0.01 | 0.0089 | 13 | 0.0059 | 0.0049 | 20.4 | 0.016 | 0.023 | 0.013 | 23 | |
| | 1.5:100 | 0.032 | 0.029 | 12 | 0.0044 | n.e. | - | 0.037 | 0.053 | 0.029 | 27 | |
| | 20:100 | 0.051 | 0.035 | 47 | 0.048 | 0.062 | -22.4 | 0.1 | 0.14 | 0.083 | 20 | |
| | 0.1 mol L ⁻¹ HCl 10:100 | 0.089 | 0.064 | 39 | 0.28 | 2.4 | -88.3 | 0.37 | 0.53 | 0.41 | -9.8 | |
| | 1.5:100 | 0.22 | 0.46 | -52 | 1 | n.e. | - | 1.3 | 1.8 | 1.1 | 15 | |
| | 20:100 | 1.4 | 0.93 | 51 | 2.4 | 3.9 | -39.5 | 3.8 | 5.4 | 3.5 | 7.4 | |
| | 0.5 mol L ⁻¹ HCl 10:100 | 1.7 | 1.1 | 57 | 4.4 | 5.4 | -19.4 | 6.1 | 8.7 | 5.9 | 3.1 | |
| | 1.5:100 | 2.6 | 1.4 | 84 | 6.8 | 8.1 | -15.6 | 9.4 | 13 | 8.9 | 5.8 | |
| | Caveira (total Hg 6.3 mg kg ⁻¹) | 20:100 | 0.0074 | 0.016 | -54 | 0.0022 | 0.009 | -76 | 0.0096 | 0.15 | 0.0091 | 5.3 |
| | | 1.0 mol L ⁻¹ NH ₄ Ac 10:100 | 0.012 | 0.016 | -24 | -0.0027 | 0.0083 | -132 | 0.0095 | 0.15 | 0.011 | -13 |
| | | 1.5:100 | 0.047 | 0.028 | 67 | 0.16 | 0.19 | -18 | 0.2 | 3.2 | 0.21 | -3.3 |
| 20:100 | | 0.018 | 0.15 | -88 | 0.1 | n.e. | - | 0.12 | 1.9 | 0.14 | -14 | |
| 0.1 mol L ⁻¹ HCl 10:100 | | 0.01 | 0.13 | -92 | 0.09 | n.e. | - | 0.1 | 1.6 | 0.13 | -23 | |
| 1.5:100 | | 0.0072 | 0.48 | -98 | 0.25 | 0.000026 | 972054 | 0.26 | 4.1 | 0.49 | -47 | |
| | 20:100 | 0.66 | 0.62 | 6.3 | 1.4 | 2.5 | -44 | 2.1 | 33 | 1.9 | 7.9 | |
| | 0.5 mol L ⁻¹ HCl 10:100 | 0.47 | 0.24 | 95 | 1.6 | 2.2 | -26 | 2.1 | 33 | 2.2 | -5 | |
| | 1.5:100 | 0.49 | 0.51 | -4.5 | 1.1 | 1.7 | -35 | 1.6 | 25 | 1.5 | 6.7 | |

Table 2. Friedman's test (p-value; $\alpha = 0.05$) for extraction procedure comparison.

| | | 20g:100mL | 10g:100mL | 1.5g:100mL |
|------------------|--|-----------|-----------|------------|
| Estarreja | 1 mol L ⁻¹ NH ₄ Ac - 0.1 mol L ⁻¹ HCl | p=0.102 | p=0.014 | p=0.015 |
| | 1 mol L ⁻¹ NH ₄ Ac - 0.5 mol L ⁻¹ HCl | p=0.0001 | p=0.0005 | p=0.0003 |
| | 0.1 mol L ⁻¹ HCl - 0.5 mol L ⁻¹ HCl | p=0.004 | p=0.014 | p=0.014 |
| Caveira | 1 mol L ⁻¹ NH ₄ Ac - 0.1 mol L ⁻¹ HCl | p=0.855 | p=0.465 | p=0.068 |
| | 1 mol L ⁻¹ NH ₄ Ac - 0.5 mol L ⁻¹ HCl | p=0.002 | p=0.0001 | p=0.0003 |
| | 0.1 mol L ⁻¹ HCl - 0.5 mol L ⁻¹ HCl | p=0.003 | p=0.003 | p=0.018 |

Table 3. Kinetic models' parameters for the Estareja soil.

| Sample | Kinetic model | | 1 mol L ⁻¹ NH ₄ Ac | | 0.1 mol L ⁻¹ HCl | | 0.5 mol L ⁻¹ HCl | | | | |
|------------------------|---------------------------------|--|---|---|---|---|---|---|---|---|--|
| | 20:100 | 10:100 | 15:100 | 20:100 | 10:100 | 15:100 | 20:100 | 10:100 | 15:100 | | |
| Estareja | two-first order | | 6.0x10 ⁻² ±5.7x10 ⁻² | 8.9x10 ⁻³ ±1.0x10 ⁻³ | 2.9x10 ⁻² ±3.0x10 ⁻³ | 3.5x10 ⁻² ±6.0x10 ⁻³ | 6.4x10 ⁻² ±1.2x10 ⁻² | 0.93±0.12 | 1.1±0.1 | 1.4±0.1 | |
| | C ₁ | | 0.17±0.32 | 83±58 | 2.3±0.7 | 2.8±1.5 | 1.4±1.1 | 1.3±0.1 | 2.0±0.7 | 1.9±0.4 | |
| | k ₁ | | ~ -3.3x10 ⁻⁶ | 4.9x10 ⁻³ ±1.6x10 ⁻³ | ~ -6.1x10 ⁻⁵ | 6.2x10 ⁻² ±7.0x10 ⁻³ | 2.4±1.8 | 3.9±0.7 | 5.4±0.2 | 8.1±0.1 | |
| | C ₂ | | ~ -7.9x10 ⁻¹² | 0.18±0.17 | ~ 6.1x10 ⁻⁵ | 2.7x10 ⁻² ±1.0x10 ⁻² | 8.4x10 ⁻³ ±3.0x10 ⁻³ | 9.5x10 ⁻³ ±3.4x10 ⁻³ | 1.3x10 ⁻² ±1.0x10 ⁻³ | 1.5x10 ⁻² ±1.0x10 ⁻³ | |
| | k ₂ | | | | | | | | | | |
| | 95% Confidence Intervals | | | | | | | | | | |
| | C ₁ | | -0.071 - 0.19 | 0.0058 - 0.012 | 2.3x10 ⁻² - 3.5x10 ⁻² | 2.310 ⁻² - 4.7x10 ⁻² | 3.7x10 ⁻² - 9.2x10 ⁻² | 0.67 - 1.2 | 0.86 - 1.3 | 1.3 - 1.6 | |
| | k ₁ | | -0.56 - 0.89 | -48.2 - 215.0 | 0.69 - 3.9 | -0.39 - 5.9 | -0.89 - 3.7 | 9.4x10 ⁻² - 2.6 | 0.44 - 3.6 | 1.0 - 2.8 | |
| | C ₂ | | (Very wide) | 0.0011 - 0.0086 | (Very wide) | 4.7x10 ⁻² - 7.7x10 ⁻² | -15 - 20 | 2.4 - 5.5 | 4.9 - 5.7 | 7.9 - 8.4 | |
| | k ₂ | | (Very wide) | -0.21 - 0.56 | (Very wide) | 4.3x10 ⁻³ - 4.8x10 ⁻² | 5.7x10 ⁻³ - 7.4x10 ⁻³ | 2.0x10 ⁻³ - 1.7x10 ⁻² | 1.0x10 ⁻² - 1.6x10 ⁻² | 1.3x10 ⁻² - 1.6x10 ⁻² | |
| | Goodness of Fit | | | | | | | | | | |
| | R ² | | 0.388 | 0.8424 | 0.9051 | 0.9483 | 0.9718 | 0.9853 | 0.9947 | 0.9987 | |
| Sy/x | | 4.1x10 ⁻² | 2.1x10 ⁻³ | 4.0x10 ⁻³ | 8.0x10 ⁻³ | 2.2x10 ⁻² | 0.17 | 0.18 | 0.13 | | |
| Ceq | | 6.9x10 ⁻² ±2.0x10 ⁻² | 1.3x10 ⁻² ±1.0x10 ⁻³ | 2.9x10 ⁻² ±1.0x10 ⁻³ | 8.3x10 ⁻² ±6.0x10 ⁻³ | 0.41±0.08 | 3.5±0.3 | 5.9±0.3 | 8.9±0.0 | | |
| k | | 0.17±0.17 | 4.1±1.6 | 2.3±0.6 | 0.14±0.05 | 1.1x10 ⁻² ±4.0x10 ⁻³ | 3.2x10 ⁻² ±8.0x10 ⁻³ | 2.4x10 ⁻² ±4.0x10 ⁻³ | 2.5x10 ⁻² ±3.0x10 ⁻³ | | |
| diffusion | | | | | | | | | | | |
| Ceq | | 0.025 - 0.11 | 1.1x10 ⁻² - 1.4x10 ⁻² | 2.6x10 ⁻² - 3.2x10 ⁻² | 7.1x10 ⁻² - 9.7x10 ⁻² | 0.24 - 0.57 | 2.9 - 4.2 | 5.9 - 6.4 | 8.2 - 9.6 | | |
| k | | -0.22 - 0.54 | 0.57 - 7.6 | 1.1 - 3.6 | 0.049 - 0.23 | 2.3x10 ⁻³ - 0.021 | 1.5x10 ⁻³ - 5.0x10 ⁻² | 1.5x10 ⁻² - 3.2x10 ⁻² | 1.8x10 ⁻² - 3.2x10 ⁻² | | |
| Goodness of Fit | | | | | | | | | | | |
| R ² | | 0.4089 | 0.7349 | 0.9050 | 0.7900 | 0.9017 | 0.8866 | 0.9474 | 0.9673 | | |
| Sy/x | | 0.0366 | 2.4x10 ⁻³ | 3.6x10 ⁻³ | 1.5x10 ⁻² | 3.9x10 ⁻² | 0.44 | 0.53 | 0.64 | | |
| a | | 0.057±0.154 | 10.9±20.3 | 2.3±2.9 | 9.2x10 ⁻² ±3.0x10 ⁻³ | 7.5x10 ⁻³ ±2.5x10 ⁻³ | 0.37±0.12 | 0.37±0.08 | 0.51±0.07 | | |
| b | | 82±69 | 918±177 | 317±54 | 74±8 | 6.4±1.8 | 1.2±0.2 | 0.65±0.06 | 0.41±0.03 | | |
| Elovich | | | | | | | | | | | |
| a | | -0.2814 - 0.3954 | -34 - 56 | -4.2 - 8.9 | 3.4x10 ⁻³ - 0.18 | 2.5x10 ⁻³ - 1.2x10 ⁻² | 0.12 - 0.82 | 0.21 - 0.53 | 0.36 - 0.67 | | |
| b | | -70.69 - 234.5 | 529 - 1308 | 197 - 439 | 56 - 91 | 2.6 - 10 | 0.82 - 1.5 | 0.53 - 0.78 | 0.35 - 0.47 | | |
| Goodness of Fit | | | | | | | | | | | |
| R ² | | 0.2857 | 0.8524 | 0.8658 | 0.9321 | 0.9157 | 0.9443 | 0.9742 | 0.9876 | | |
| Sy/x | | 0.0402 | 1.7x10 ⁻³ | 4.3x10 ⁻³ | 8.5x10 ⁻³ | 3.6x10 ⁻² | 0.31 | 0.37 | 0.4 | | |

Table 4. Kinetic models' parameters for the Caveira soil.

| Sample | Kinetic model | 1 mol L ⁻¹ NH ₄ Ac | | | 0.1 mol L ⁻¹ HCl | | | 0.5 mol L ⁻¹ HCl | | | |
|---------------------|--------------------------|---|---|---|--|---|--|---|--|---|---|
| | | 20:100 | 10:100 | 1.5:100 | 20:100 | 10:100 | 1.5:100 | 20:100 | 10:100 | 1.5:100 | |
| Caveira | two-first order | C ₁ | 1.6x10 ⁻² ±1.0x10 ⁻³ | 1.6x10 ⁻² ±1.0x10 ⁻³ | 2.8x10 ⁻² ±8.0x10 ⁻³ | 0.15±0.15 | 0.13±0.23 | 0.48±0.63 | 0.62±0.09 | 0.24±0.11 | 0.51±0.09 |
| | | k ₁ | 149±54 | 113±26 | 72±149 | 1.7x10 ⁻² ±1.0x10 ⁻² | 1.3x10 ⁻² ±2.0x10 ⁻² | 6.3x10 ⁻³ ±9.9x10 ⁻³ | 0.15±0.03 | 0.14±0.08 | 0.10±0.02 |
| | | C ₂ | 9.9x10 ⁻³ ±1.4x10 ⁻³ | 8.3x10 ⁻³ ±8.6x10 ⁻⁴ | 0.19±0.1 | ~8.2x10 ⁻⁹ | ~1.1x10 ⁻⁹ | 2.6x10 ⁻⁵ ±0.8 | 2.5±0.7 | 2.2±0.1 | 1.7±0.3 |
| | | k ₂ | 0.21±0.1 | 6.2x10 ⁻² ±2.0x10 ⁻² | 1.3x10 ⁻² ±6.0x10 ⁻³ | ~7.1x10 ⁻¹¹ | ~6.8x10 ⁻¹⁰ | 2.2x10 ⁻¹⁰ ±53 | 4.9x10 ⁻² ±2.5x10 ⁻³ | 1.3x10 ⁻² ±2.0x10 ⁻² | 6.1x10 ⁻³ ±2.5x10 ⁻³ |
| | | 95% Confidence Intervals | | | | | | | | | |
| | diffusion | C ₁ | 1.3x10 ⁻² - 1.9x10 ⁻² | 1.4x10 ⁻² - 1.7x10 ⁻² | 1.1x10 ⁻² - 4.7x10 ⁻² | -0.19 - 0.48 | -0.37 - 0.63 | -0.90 - 1.9 | 0.41 - 0.83 | 4.8x10 ⁻³ - 0.47 | 0.30 - 0.71 |
| | | k ₁ | 31 - 267 | 56 - 170 | -253 - 397 | -0.011 - 0.044 | -0.024 - 0.049 | -0.015 - 0.028 | 0.068 - 0.23 | -0.039 - 0.32 | 5.1x10 ⁻² - 0.15 |
| | | C ₂ | -1.3x10 ⁻² - -6.8x10 ⁻³ | -1.0x10 ⁻² - -6.4x10 ⁻³ | 0.11 - 0.29 | (Very wide) | (Very wide) | -1.9x10 ⁻⁷ - -1.9x10 ⁻⁷ | 0.91 - 4.1 | 2.0 - 2.4 | 1.0 - 2.3 |
| | | k ₂ | 3.0x10 ⁻² - 0.38 | 1.9x10 ⁻² - 0.10 | -2.4x10 ⁻⁴ - 2.6x10 ⁻² | (Very wide) | (Very wide) | -114 - 114 | -5.4x10 ⁻⁴ - 1.0x10 ⁻² | 8.6x10 ⁻³ - 1.7x10 ⁻² | 6.6x10 ⁻⁴ - 1.2x10 ⁻² |
| | Elovich | Goodness of Fit | | | | | | | | | |
| | | R ² | 0.8673 | 0.9322 | 0.8351 | 0.9927 | 0.9791 | 0.8967 | 0.9962 | 0.9982 | 0.998 |
| | | Syx | 1.8x10 ⁻³ | 1.3x10 ⁻³ | 1.9x10 ⁻² | 4.8x10 ⁻³ | 6.7x10 ⁻³ | 3.9x10 ⁻² | 4.9x10 ⁻² | 3.9x10 ⁻² | 2.9x10 ⁻² |
| | | Ceq | 9.1x10 ⁻³ ±1.1x10 ⁻³ | 1.1x10 ⁻² ±1.0x10 ⁻³ | 0.21±0.03 | 0.14±0.01 | 0.13±0.01 | 0.49±0.32 | 1.9±0.1 | 2.2±0.1 | 1.5±0.1 |
| | | k | ~2.7x10 ³ | 227±250 | 2.1x10 ⁻² ±7.0x10 ⁻² | 1.7x10 ⁻² ±2.0x10 ⁻² | 1.3x10 ⁻² ±3.0x10 ⁻³ | 5.9x10 ⁻³ ±5.4x10 ⁻³ | 2.5x10 ⁻² ±3.0x10 ⁻² | 1.8x10 ⁻² ±1.0x10 ⁻³ | 2.4x10 ⁻² ±3.0x10 ⁻³ |
| | n.e. non-estimated. | 95% Confidence Intervals | | | | | | | | | |
| Ceq | | 6.8x10 ⁻³ - 1.1x10 ⁻² | 9.3x10 ⁻³ - 1.3x10 ⁻² | 0.14 - 0.26 | 0.13 - 0.16 | 0.10 - 0.16 | -0.19 - 1.2 | 1.7 - 2.1 | 2.1 - 2.4 | 1.4 - 1.6 | |
| k | | (Very wide) | -309 - 764 | 6.0x10 ⁻³ - 3.7x10 ⁻² | 1.3x10 ⁻² - 2.0x10 ⁻² | 6.9x10 ⁻³ - 1.8x10 ⁻² | -5.7x10 ⁻⁵ - 1.8x10 ⁻² | 1.7x10 ⁻² - 3.3x10 ⁻² | 1.5x10 ⁻² - 2.0x10 ⁻² | 1.8x10 ⁻² - 2.9x10 ⁻² | |
| Goodness of Fit | | | | | | | | | | | |
| R ² | | 0.2492 | 0.4163 | 0.8649 | 0.9932 | 0.9791 | 0.8967 | 0.9684 | 0.9952 | 0.9826 | |
| n.e. non-estimated. | Syx | 4.0x10 ⁻³ | 3.5x10 ⁻³ | 2.6x10 ⁻² | 4.3x10 ⁻³ | 6.2x10 ⁻³ | 3.7x10 ⁻² | 0.13 | 5.9x10 ⁻² | 7.9x10 ⁻² | |
| | a | 6.6x10 ⁻³ ±2.7x10 ⁻³ | 6.6x10 ⁻³ ±2.7x10 ⁻³ | 2.9x10 ⁻³ ±9.7x10 ⁻⁴ | 2.8x10 ⁻³ ±3.7x10 ⁻⁴ | 1.8x10 ⁻³ ±1.1x10 ⁻³ | 2.9x10 ⁻³ ±9.7x10 ⁻⁴ | 8.8x10 ⁻³ ±1.1x10 ⁻² | 5.6x10 ⁻³ ±3.0x10 ⁻³ | 6.1x10 ⁻² ±4.0x10 ⁻² | |
| | b | n.e. | n.e. | 13±4 | 14±2 | 13±3 | 2.3±2.6 | 1.7±0.1 | 1.1±0.1 | 1.9±0.1 | |
| | 95% Confidence Intervals | | | | | | | | | | |
| | a | 7.6x10 ⁻⁴ - 1.2x10 ⁻² | 7.6x10 ⁻⁴ - 1.2x10 ⁻² | 4.6 - 22 | 1.9x10 ⁻³ - 3.6x10 ⁻³ | 1.1x10 ⁻³ - 2.4x10 ⁻³ | 7.9x10 ⁻⁴ - 4.9x10 ⁻³ | 6.5x10 ⁻² - 0.11 | 4.9x10 ⁻² - 6.3x10 ⁻² | 5.2x10 ⁻² - 7.0x10 ⁻² | |
| n.e. non-estimated. | Goodness of Fit | | | | | | | | | | |
| | R ² | 0.2306 | 0.3895 | 0.8602 | 0.9858 | 0.9729 | 0.8941 | 0.9908 | 0.9975 | 0.9967 | |
| | Syx | 4.1x10 ⁻³ | 3.5x10 ⁻³ | 2.6x10 ⁻² | 6.2x10 ⁻³ | 7.1x10 ⁻³ | 3.7x10 ⁻² | 7.2x10 ⁻² | 4.3x10 ⁻² | 3.5x10 ⁻² | |

FIGURE CAPTION

Figure 1. Mercury extracted from soil samples for the three soil:extractant solution ratios (mg kg^{-1} of soil) as function of the time (hours) for Caveira (left) and Estarreja (right) samples. Extractants are, from top to bottom, 1 mol L^{-1} NH_4Ac pH 7, 0.1 and 0.5 mol L^{-1} HCl.

Figure 2. Kinetics of the extraction of mercury from soil samples, using 1 mol L^{-1} NH_4Ac pH 7, 0.1 and 0.5 mol L^{-1} HCl (top to bottom), and curves obtained with the two first-order reactions and diffusion models for Caveira (left) and Estarreja (right) samples.

Figure 3. Comparison of mercury extracted (mg kg^{-1}) in the exchangeable and labile fractions with mercury extracted in mobile fraction of the Kingston method (Reis et al., 2010).

Figure 1

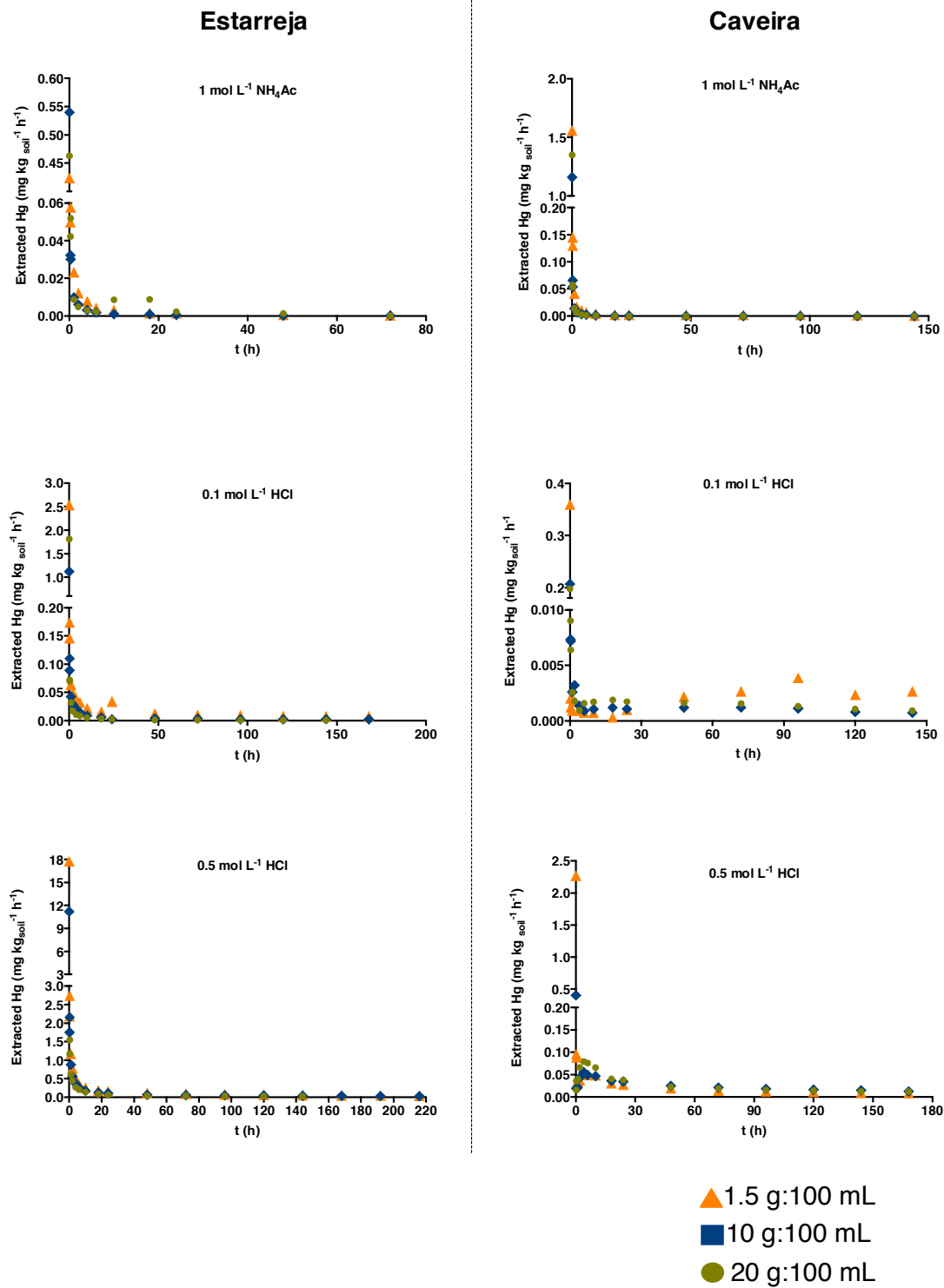


Figure 2

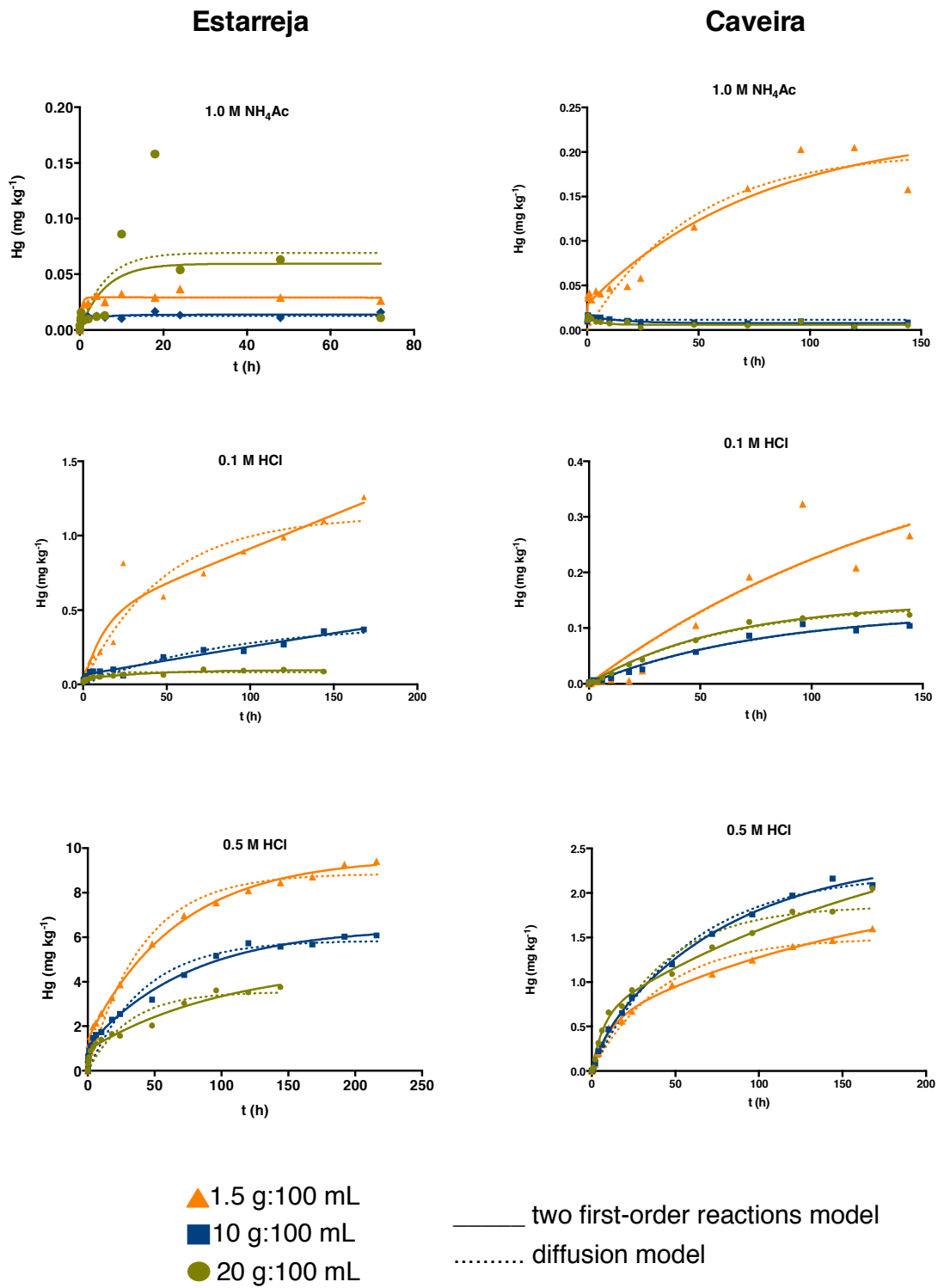


Figure 3

