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1 **Overview and challenges of mercury fractionation and speciation in**
2 **soils**
3

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13 **Abstract**

14 Analytical procedures to assess mercury speciation in soils still lack consensus.
15 This article presents an overview of the mercury fractionation and speciation
16 procedures used in soils. Mercury fractionation is the most common approach
17 despite the operational definition of the fractions. Application of single extraction
18 procedures that target the water-soluble, exchangeable and acid-soluble fractions
19 and the application of EPA method 3200 for mercury sequential extraction are
20 examined in soils with different physicochemical characteristics. A step forward in
21 mercury speciation is thermo-desorption, a useful tool to rapidly obtain needed
22 information about contaminated soils. The advantages and limitations of these
23 procedures are compared; the importance of soils' physicochemical characteristics
24 highlighted. Criteria to be considered when choosing a suitable method are given -
25 assessing total mercury concentration, soil physicochemical characteristics,
26 environmental conditions, and legislation. It is recommended that the interpretation
27 of results is done wisely, to correctly support decisions concerning intervention
28 strategies at contaminated sites.

29
30 **Keywords:** mercury; soil; fractionation; speciation; sequential extraction; risk
31 assessment
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35 **1. Introduction**

36 Healthy soil systems are essential for protection of plants, soil-dwelling
37 organisms, groundwater, and the food chain; for sustainability of agricultural
38 practices and ecosystem services; and for the wellbeing of animals and humans that
39 directly or indirectly benefit from these systems. However, many soil systems have
40 been contaminated, impairing their quality, and ultimately affecting human health and
41 the overall environment. Several efforts have been made to establish limit values for
42 the concentration of potentially toxic elements (PTEs) in soil, e.g. [1-3]. Thresholds
43 are based on the lowest concentrations that have been reported to produce
44 undesired effects. The behaviour of PTEs depends largely on how the elements
45 interact with the matrix, which determines their fate, transport, bioaccessibility, and
46 toxicity. Assessing element speciation in natural and polluted solid systems [4, 5] is
47 crucial to establish ready and accessible element-specific tools and data sets in
48 order to make informed, science-based decisions in risk assessment and
49 remediation strategies.

50 Because of the potential toxicity of mercury (Hg), this element is one of the
51 most critical contaminants in the environment [6], particularly in areas impacted by
52 mining, industry and sludge dumping [7]. Soils play an important role in the mercury
53 cycle, acting both as a sink and source to biota, the atmosphere and hydrological
54 compartments [8]. Chemical, physical and biological processes at the solid-solution
55 interface control its speciation affecting solubility, bioaccessibility, toxicological, and
56 ecological effects [9-11]. Mercury adsorption onto the soil matrix can occur as
57 nonspecific or specific adsorption (Figure 1). In the first case, cation exchange is
58 involved, resulting in outer-sphere complexes. This process is reversible in nature,
59 occurs rather quickly, and both organic and inorganic ligands are involved. In specific
60 adsorption, stable complexes are formed and after some time mercury at the colloid
61 surface diffuses towards the interior of particles, forming inner-sphere complexes
62 and hindering subsequent desorption [12]. In the matrix, Hg^{2+} can be bound directly
63 to the mineral surface or to the organic matter present; the latter can, in turn, be
64 associated to the mineral surface, resulting in organo-mineral complexes (Figure 1).
65 Reactive sites for the sequestration of the metal occur on adsorption sites of organic
66 matter (S-containing functional groups), and mineral surfaces (e.g. clays, oxides and
67 hydroxides of aluminium, iron and manganese, and silicate minerals) [13]. In natural
68 occurring conditions, Hg associates with the matrix and only trace amounts are

69 found in soil solution, the availability to plants and organisms being determined by
70 the activity of Hg^{2+} and Hg^{2+} complexes [14]. Soil solution chemistry is controlled by
71 the properties of the solid fraction, adsorption-desorption equilibrium, and the
72 kinetics of reactions at the solid-solution interface, which include precipitation,
73 dissolution, and uptake-release by plants and organisms [13]. Consequently,
74 knowledge of the chemical forms of mercury present in soil is indispensable to
75 understand the real risk that mercury-contaminated compartments represent to the
76 overall environment.

77 Due to the numerous and diverse species of each element, with unique
78 physical and chemical properties, the fractionation of this element is very difficult and
79 complex. Consequently, research dedicated to mercury speciation/fractionation has
80 gained attention in recent years [15-29].

81 Several protocols can be found in the literature regarding mercury speciation
82 and fractionation, as reviewed by Issaro et al. [29], and three main lines can be
83 identified in mercury speciation/fractionation methodologies: 1) chemical extraction
84 [26, 27, 29-34]; 2) thermo-desorption [23, 26, 35]; and 3) X-ray absorption
85 techniques [36, 37]. X-ray techniques are expensive and require samples with
86 mercury concentration greater than 100 mg kg^{-1} [37], which strongly limits their
87 applicability in environmental samples, therefore they are not further discussed.

88 Although some steps have already been taken towards the establishment of
89 robust and reproducible methodology, the complex chemistry of mercury, in
90 conjunction with the intricacy of soil chemistry and the interaction of the contaminant
91 with the soil matrix, have not yet allowed this objective to be fulfilled. The literature
92 vehemently stresses the need to develop speciation methods specific for mercury,
93 as well as adequate quality control procedures and associated reference materials
94 [38, 39]. Despite several attempts to develop such methods, there is still not a
95 consensual protocol regarding mercury fractionation and/or speciation in soil
96 samples [29].

97 This work aims to overview the analytical procedures for mercury fractionation
98 and speciation in soils, through application of single and sequential extraction
99 schemes, and speciation by thermo-desorption, as well as to test leaching capacity
100 of weak, mild and strong extractants, time of extraction, soil:extractant ratio, and
101 intrinsic factors controlling the behaviour of mercury in soil. Difficulties and

102 challenges associated with these methodologies and the feasibility of their
103 implementation in routine analysis are examined.

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106 **2. Mercury fractionation and speciation methods applied to soil samples**

107 Speciation is defined as the “measurement of the amount of one or more
108 individual chemical species in a sample” [40]. Fractionation should be understood as
109 the process of classification of “an analyte or a group of analytes from a certain
110 sample according to physical (e.g. size, solubility) or chemical (e.g. bonding,
111 reactivity) properties [40, 41].

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114 **2.1 Single extractions**

115 Extraction procedures are divided between selective extractions (otherwise
116 called single extractions) and sequential extractions. The first are used to target only
117 one fraction of interest and are currently used for estimating the most potentially
118 mobile and/or toxic fractions.

119 A one-step extraction is generally fast, cost-effective, and requires low technical
120 skill. Several extractants have been used to assess mercury associated with the
121 different soil phases. Single extractions mainly aim at determination of the
122 organometallic fraction [42-45], by acid or alkaline extraction combined with solvent
123 extraction, distillation, or solid-phase microextraction. While the organometallic
124 fraction has been the main focus of interest in mercury speciation, due to its
125 extremely toxicity, it usually represents less than 3% of total mercury in soils [46-48].
126 Elemental Hg (Hg^0) has too been determined by single extraction, using a
127 combination of strong acids such as H_2SO_4 and HNO_3 and heat [49]. Procedures
128 vary in temperature and time of heating, therefore data interpretation and
129 comparison is equivocal. At the same time, the treatment may also remove other
130 volatile species, such as $HgCl_2$, overestimating Hg^0 .

131 Other sought fractions include: the ones indicative of transfer from soil to other
132 environmental compartments (water and organisms); the more bioaccessible
133 fractions; and the carbonate-bound fraction. These fractions are usually determined
134 by the application of mild extractants that mostly work by cation exchange,
135 complexation and through weak acid dissolution.

136 Determination of the water-soluble fraction [22, 45] has been used to estimate
137 the potential risk of groundwater contamination, biological uptake and toxicity for
138 aquatic organisms when leaching, runoff, or erosion occur [50]. This fraction
139 comprises the most mobile and potentially bioaccessible mercury forms that are
140 usually present in soil solution and pore water. Mercury concentrations are usually
141 low (Table 2) [16, 25, 35, 51-54], implying that the estimation of this fraction is only
142 worthwhile when soils are highly contaminated or the *in-situ* environmental
143 conditions are favourable to leaching.

144 The exchangeable fraction includes mercury species adsorbed to the matrix by
145 weak electrostatic bonds that can be released by ion-exchange processes and
146 species coprecipitated with carbonates. Changes in major cationic composition or
147 lowering of pH may cause their release due to ionic exchange and/or dissolution of
148 carbonates. This fraction corresponds to the most mobile and bioaccessible species
149 released into the environment, and is commonly used to assess soil-to-plant transfer
150 [55, 56]. Extracting agents (Table 1) include CaCl_2 , MgCl_2 , NaNO_3 and $\text{CH}_3\text{COONH}_4$
151 (releasing mercury electrostatically bound to organic and inorganic sites by cationic
152 exchange) or weak acids (mercury released by lowering pH). A comparison of
153 extractions using $1.0 \text{ mol L}^{-1} \text{CH}_3\text{COONH}_4$ and $0.1 \text{ mol L}^{-1} \text{HCl}$ in the same (air-dried)
154 soil samples revealed that the percentage mercury extracted by the latter solution
155 was higher in all samples (Table 2), indicating that mercury is more sensitive to
156 acidification than to cationic exchange. Mercury extracted by 1.0 mol L^{-1}
157 $\text{CH}_3\text{COONH}_4$ usually corresponds to $< 10 \%$ of total mercury, while the percentage
158 extracted by $0.1 \text{ mol L}^{-1} \text{HCl}$ was over 40% in soil J2 sample (Table 2) [21].

159 From this analysis, it was concluded that $1.0 \text{ mol L}^{-1} \text{CH}_3\text{COONH}_4$ and 0.1 mol
160 $\text{L}^{-1} \text{HCl}$, used to estimate the exchangeable fraction, did not provide the same
161 information. For risk assessment purposes, the knowledge on the environmental
162 conditions is key to decide the most appropriate extractant. For example, for acidic
163 environments such as the ones surrounding mines, a weak acid provides more
164 protective and factual conclusions. In neutral soils, where pH is unlikely to decrease,
165 a mild extractant, such as $1.0 \text{ mol L}^{-1} \text{CH}_3\text{COONH}_4$ should provide adequate
166 information on mercury mobility.

167 The diffusive gradients in thin film technique (DGT) has been successfully used
168 to indirectly estimate the labile mercury fraction in soil solution, i.e., the fraction that
169 correlates with the metal bioavailability, for example, the potential uptake by plants or

170 other soil organisms [57]. DGT is used for in situ extraction, therefore minimizing the
171 possibility of contamination and species conversion during storage and pretreatment.
172 For mercury speciation, DGT units consist of a plastic piston covered by a layer of
173 polyacrylamide gel containing Spheron-Thiol resin (with –SH groups) and an
174 agarose diffusive gel [58, 59].

175 The use of stronger acids simulates the effect of, for example, acid rain, acid
176 mine drainage, continuous acidic effluent discharges, or accidental acid spills onto
177 soils. Extraction with 0.5 mol L⁻¹ HCl (room-temperature) has been presented as a
178 good estimator for metal release upon acidification [60, 61]. Increase in acidity
179 enhances extractability of mercury, although the percentage of released mercury is
180 lower in soils with high organic matter content (Table 2). This confirms previous
181 observations that highly organic soils retain metals, even in harsh conditions [27].

182

183

184 **2.2 Sequential extraction schemes**

185 In sequential extraction schemes, a sequence of reagents is applied to the
186 same sample in an attempt to sub-divide the total mercury content. The procedure
187 typically contains 3-8 treatments of the solid phase, with the strength of the treatment
188 generally increasing through the steps, from initial mild conditions (e.g. shaking with
189 water, a salt solution or dilute acetic acid) to the use of harsher reagents (e.g. hot
190 mineral acid) [4]. A summary of the most common target phases in sequential
191 extraction schemes and respective mobility in the environment is given in Table 1.
192 Sequential extraction schemes different from those typically used for other elements
193 have been developed to assess mercury speciation and fractionation in soils [4], but,
194 in general, the schemes begin with the extraction of the more labile fractions: water-
195 soluble and/or exchangeable using, respectively, distilled water and salt solutions
196 that remove mercury by ion-exchange (e.g. NH₄Ac, MgCl₂, CaCl₂). In the next
197 fraction, oxidising reagents, such as NaOH, KOH, HNO₃ or H₂O₂, are applied to
198 extract mercury bound to organic matter. In the last steps, the less reactive species,
199 which are strongly bound to the matrix, are extracted with strong acids, including
200 HNO₃, HF and aqua regia.

201 The method proposed by Rahman et al. [62] was adopted as the official method
202 for mercury fractionation in soil samples (EPA method 3200 [63]) and subjected to
203 inter-laboratory validation [62]. This method classifies fractions according to their

204 potential mobility - mobile, semi-mobile, and non-mobile - that are extracted
205 consecutively with a solution of 1:1 (v/v) 2% HCl + 10% ethanol, a solution of 1:2
206 (v/v) HNO₃:DDI water, and a solution of 1:6:7 (v/v/v) HCl:HNO₃:DDI water,
207 respectively. The residual fraction can be determined by quantifying the mercury left
208 in the residue at the end [27, 32]. This sequential extraction procedure was applied
209 to soil samples from industrially impacted and mine areas [27, 64]. Overall, the
210 extractions yielded good recoveries, the semi-mobile phase accounting for 46-97%
211 of the total mercury (Table 3). According to Han et al. [32], this fraction encompasses
212 Hg⁰, some (unspecified) mercury complexes and minor fraction of Hg₂Cl₂. However,
213 the presence of the first species is questionable, since, due to its high volatility, Hg⁰
214 is easily lost after the vigorous treatment involved in extraction of mobile and semi-
215 mobile fractions [23]. The application of this extraction scheme allowed inferences to
216 be drawn on the influence of soil properties in mercury fractionation in contaminated
217 areas and has proven to be useful in distinguishing between anthropogenic and
218 geogenic sources [27, 64]. Reis et al. [27] concluded that aluminium, manganese,
219 organic matter and sulfur content were the main soil characteristics associated with
220 mercury mobility in their samples, while Frentiu et al. [64] included also calcium,
221 copper and iron. Soils with higher pH exhibited larger percentages of mobile mercury
222 (Table 3), most likely due to leaching of organic matter from the matrix, resulting in a
223 decrease of adsorption sites in the solid fraction. Some organic matter leached to the
224 soil solution tends to desorb mercury from the solid phase, increasing the
225 concentration of dissolved Hg²⁺ complexes, and, in turn, mercury accessibility. This
226 phenomenon is not observed in natural organic matter ligands, such as humic and
227 fulvic acids, that have a strong bond with mercury; thus, these complexes are not
228 labile or bioavailable.

229 Sequential extraction exhibits a few drawbacks, namely that it is time-
230 consuming and that its complexity limits the procedural robustness. It also requires
231 an elevated technical skill to ensure the quality of the results. Cross-contamination of
232 samples and mercury losses, for example, can easily occur, if the operator is not
233 sensitized to these problems. Additionally, problems common to all sequential
234 extraction schemes can occur, such as lack of extractant selectivity, re-adsorption,
235 and incomplete extraction [19, 27, 65].

236 The mobile fraction extracted by the acidic ethanol solution yielded results
237 similar to the ones obtained using 0.5 mol L⁻¹ HCl for the same soil samples (Tables

238 2 and 3). This confirms that the first step extracts the water-soluble and
239 exchangeable mercury species, as well as fractions that could be mobilized at a
240 particularly acidic pH (pH < 3, i.e. harsher conditions than normally found in the
241 environment), such as the metal adsorbed to amorphous iron oxides, to organic
242 matter and, to a lesser extent, to clay.

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2.3 Soil:extractant ratio and time of extraction

246 The soil:extractant ratio and time of extraction are operational parameters that
247 differ among procedures. Low soil:extractant ratios (for example, 1.0 g:100 mL or 1.5
248 g:100 mL) favour mercury extractions [24, 28, 55], although the analyst should
249 assure sample homogeneity and representativeness and guarantee that detection
250 limits for mercury quantification are achieved. This can be difficult in the water-
251 soluble fraction, even in highly contaminated samples, since it generally represents a
252 very low percentage of total mercury in soil [25].

253 A study of the extraction kinetics [24, 25] with distilled water, 1.0 mol L⁻¹
254 ammonium acetate, 0.1 mol L⁻¹ hydrochloric acid and 0.5 mol L⁻¹ hydrochloric acid,
255 using an end-over-end shaker at a constant rate of 60 rpm, revealed the existence of
256 two extraction stages. In the first step (6 hours for water and 10 hours for the
257 remaining solutions), mercury was released at a faster rate than afterward, most
258 likely because the latter mercury species are intricately associated with the matrix. It
259 was also observed that equilibrium in the water-soluble fraction was achieved at 24
260 hours. For the other extractants, mercury continued to be released at slow rates
261 even after a week. This suggests that small quantities of mercury can be
262 continuously released into the environment. Although soils rarely fall into the ultra
263 acid category (pH < 3.5) [66], occurrences such as acid rain, mine spoil, weathering
264 of minerals, plant root activity or high rainfall can lower the soil pH, making it more
265 susceptible to the leaching of labile mercury species. No procedure was found in
266 literature that recommended such long extraction times. In most cases, time of
267 extraction varies between 30 minutes and 1 hour [35, 51, 52]. It is estimated that in
268 one hour less than 50 % of the potentially extractable mercury is released from the
269 soil matrix. Hence longer extraction periods should be considered when assessing
270 the exchangeable and acid-soluble fractions, to avoid underestimation of the real
271 risk. The kinetic studies also permitted to assess the influence of the soil texture on

272 the rate of mercury released into the environment. Prevalence of small particles
273 slows the process, as a diffusion mechanism is involved. Overall, mercury retention
274 in soil is controlled by soil chemical composition (sulfur and organic matter), but the
275 rate of desorption is controlled by soil physical properties (particle size).

276 Another aspect to consider when performing extraction studies is the shaking /
277 stirring rate and the need to adjust it to particle size. The shaking or stirring rate
278 should guarantee that all sample is in contact with the extractant solution and avoid
279 the soil particles settling. Thus, samples with large particles need a higher shaking
280 speed. Notwithstanding soil's buffering capacity, the pH should be controlled during
281 the experiment. A decrease in pH may cause the soil to release mercury, due to H⁺
282 removing and replacing metal cations [67]. This must be taken into account when
283 interpreting the extraction results.

284

285 **2.4 Speciation by thermo-desorption**

286 In order to pursue a simpler, cheaper and faster identification of Hg species in
287 the soil matrix, speciation by thermo-desorption (TD) arose as an alternative to
288 chemical extraction. The premise behind mercury speciation by TD is the release of
289 different species at specific temperatures. Two methodologies have been purposed
290 to perform TD speciation. The extensive work by Biester et al. [10, 35, 68-71]
291 demonstrated the adaptation of an atomic absorption spectrometer, by means of an
292 in-house apparatus consisting of an electronically controlled heating unit and a
293 mercury detection unit [69]. An alternative method for mercury speciation by thermo-
294 desorption consists of the use of direct mercury analysers, such as the LECO® AMA-
295 254 [23, 26] or Lumex® RA-915+ PYRO-915 [72, 73], by simply adjusting combustion
296 temperature and the heating programme. Thermo-desorption methods present some
297 advantages over conventional chemical extraction methods and x-ray absorption
298 methods. Direct mercury analysers appear to be even more advantageous, as they
299 already use thermal-decomposition for total mercury quantification, are easy to use
300 by the non-expert analyst and, since the equipment is automated and commercially
301 available, operational conditions are standardized and results obtained by different
302 laboratories can be compared.

303 The following advantages of speciation by thermo-desorption should be
304 underlined [26]: only a small quantity (<1 g) of sample is required; free of cross-
305 contamination; applicability to a vast range of mercury concentrations; little to no

306 sample treatment preventing the loss of volatile mercury-compounds; good
307 repeatability; negligible losses of mercury; lack of residues. Results are depicted as
308 mercury thermo-desorption curves (or thermograms), which represent signal or
309 mercury release (mg kg^{-1}) plotted against temperature ($^{\circ}\text{C}$). The mercury species are
310 identified on the basis of the release temperature range and the samples'
311 thermograms compared with reference ones of pure mercury compounds for
312 identification. Species that can be identified include Hg^0 , HgCl_2 , Hg associated with
313 iron oxides, Hg bound to humic acids and HgS. Although in certain samples the
314 separation of mercury species may be masked by peak overlapping [35, 71], the
315 differentiation of the mineral and organic fraction can be achieved (see example in
316 Figure 2). Although speciation by thermo-desorption does not give direct information
317 about mercury mobility, this method is clearly a step forward to identify mercury
318 species and to assess the potential risk associated with mercury contamination at a
319 given site. Thermo-desorption is a particularly useful tool for a preliminary screening
320 of the samples, with its results being helpful to decide on further sample analysis,
321 including the application of extraction methods. It is also the best technique to
322 identify and quantify Hg^0 , since it prevents mercury losses and does not require any
323 sample preparation.

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326 **3. Overview and final remarks**

327 Table 4 provides an overview of methods to assess mercury speciation in soils
328 and their advantages and limitations. Despite the recognized problems associated
329 with chemical extraction procedures, they provide valuable information for mercury
330 geochemistry interpretation in soils, allowing information to be inferred on reactivity
331 and bioaccessibility, or response to changes in environmental conditions such as
332 rainfall events or pH changes. Even though there has been significant improvement
333 in sequential extraction schemes and selective extractions in the last years [22, 66]
334 there are still no unequivocal methods of distinguishing between different forms of
335 mercury in soils. Furthermore, no speciation/fractionation protocol has been shown
336 to satisfactorily perform under all conditions, for all soils due to variability of their
337 physical and chemical characteristics, such as pH, organic matter, iron, manganese,
338 and sulfur contents and texture.

339 Literature review shows that the quantity of mercury extracted from soil can be
340 extremely variable, depending on the nature of both the soil and the leaching
341 solution [74]. Therefore, it is difficult for a researcher to identify the suitable method
342 according to their particular situation, but the choice of mercury speciation method to
343 use for a specific sample ought to consider a number of criteria:

344 1) Determining the total mercury concentration of the site is important to decide
345 if the contamination level entails further speciation studies;

346 2) Knowledge of the contaminated area, including source of contamination and
347 the environmental conditions of the area. The source of contamination can provide a
348 good indication of likely mercury mobility. It is generally recognized that, in
349 anthropogenically-contaminated soils, mercury is more likely to be present in more
350 labile species [75]. Considering the distance to the source of contamination is
351 important in the sampling stage, as the sampling grid must be denser nearer the
352 source. The environmental conditions (e.g. pH; precipitation) prevalent at the site
353 and that affect mercury speciation and release from soil must also be taken into
354 consideration. Soils prone to acidification, changes in redox potential, or flooding will
355 retain less mercury in the solid matrix and facilitate its mobility to other environmental
356 compartments or biological uptake.

357 3) Soil physicochemical characteristics such as pH, organic matter, iron,
358 manganese, and sulfur contents, texture (percentage of finer particles, in particular),
359 redox and humidity conditions are parameters that “control” mercury’s retention or
360 release on/from the solid matrix; hence, a thorough characterisation of the soil is a
361 requirement and this data must be taken into account in results’ analysis;

362 4) Soil use (agriculture, recreational, mining, construction, landscape
363 development, etc.) and according legislation and/or local regulatory agency
364 recommendations are important aspects to consider.

365 After the selection and application of the most suitable method based on the
366 above information, the interpretation of the results must be done wisely, in order to
367 correctly support decisions concerning intervention or remediation strategies at
368 contaminated sites. This is one of the numerous challenges that the scientific
369 community faces in mercury speciation in soils. Interpretation of data needs to be
370 done within the context, considering the operations used to obtain the fractions or
371 species, and the nomenclature. For example, the interpretation of the (potential)
372 bioavailable and mobile fractions needs to take into account that, in the environment

373 or organism, other factors (environmental, physical, chemical) will determine the
374 actual bioavailability or mobility of mercury [4].

375 It also important to consider soil heterogeneity, sample pretreatment and storage
376 [76]. Samples collected should be as representative as possible of the contaminated
377 locale and every precaution should be taken to ensure samples remain unaltered. In
378 mercury speciation assessments, particular attention must be given to potential
379 losses of mercury. It is common practice that, for comparison among samples, with
380 other studies and with certified reference materials, dried (hence stable) samples are
381 used. However, it has been observed that, while drying and sieving soils prior to
382 analysis increases the sample homogeneity [23, 77], Hg⁰ loss can happen, with this
383 species no longer present in samples after a short 10-day storage period [23].
384 Moreover, the results obtained by Baeyens et al. for speciation of Fe, Mn and Pb in
385 sediments indicate that drying samples prior to extraction can change the speciation,
386 causing a shift from less available/mobile metal fractions to more available/mobile
387 fractions. Although this study did not consider mercury speciation, the results
388 achieved suggest that, if possible, speciation/fractionation should be carried out on
389 wet samples (in the case of samples taken from reduced redox conditions, several
390 steps should even be carried out in oxygen free conditions), even if that means that
391 higher relative standard deviations will, most likely, be obtained.

392 The lack of certified reference materials is, probably, the major limitation. So
393 far, only a few reference materials were certified for methylmercury quantification in
394 fish and sediment [78, 79], with none yet available for other key species and
395 matrices. These are required to validate the analytical methodologies, data, and
396 ensure consistency between laboratories and the comparability of results. The
397 effects of changes in operational conditions that can easily diverge among
398 laboratories, such as the type of shaker or temperature, have yet to be studied.
399 Interlaboratory exercises are a way of addressing these issues, since they will test
400 the robustness of the procedures; the tested soil samples can, eventually, be
401 certificate as reference materials. The ILAE-Hg-02 intercalibration exercise [74]
402 proposed the extraction of bioaccessible and organometallic fractions, in addition to
403 measurement of total mercury, due to their environmental relevance. However, the
404 results of this interlaboratory exercise revealed that there is some reluctance in
405 performing chemical extractions, as proven by the low number of participants who
406 returned speciation results. When questioned, the participants gave two reasons for

407 this: 1) extractions are labor-intensive, costly and time-consuming; 2) mercury
408 speciation seems to be a matter of academic research importance and most
409 laboratories are not cognizant with the importance of speciation. Regulatory
410 acceptance of the importance of metal speciation is another challenge. Legislation
411 regarding mercury determination in environmental samples usually only establishes
412 limits for total mercury, which does not contribute to raise awareness of the
413 significance of mercury speciation. A limited number of countries include assessment
414 of metal fractions in risk assessment and management of contaminated soils, with
415 only Austria and Germany considering the mercury transfer from soil-to-plant and
416 soil-to-groundwater, respectively [80]. In risk assessment, total mercury
417 concentration is assumed as the “worst case scenario”, resulting in an
418 overestimation of the real risk, but there are cost-effective and environmental
419 protection advantages in a more detailed analysis of the species/fractions present.
420 Regarding this aspect, for the reasons aforementioned, speciation by thermo-
421 desorption can be a useful tool to rapidly obtain needed information about a
422 contaminated soil.

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Table 1. Leachability of mercury by the use of different extractants in single extractions. Sample characterisation of selected samples.

Sample	Extractant (%)				Soil physicochemical characterisation					Hg source	References	
	water	1M NH4Ac	0.1M HCl	0.5M HCl	Texture	pH	Org C (%)	Fe (%)	Mn (mg/kg)			S (%)
soil R1	1.2				sandy loam	4.0 ^a	1.63	4.85	1790	< 0.05	Mine	
soil R2	0.5				sandy loam	5.3 ^a	3.83	6.56	402	0.42	Mine	
soil R3	1.2				sandy loam	4.6 ^a	2.00	6.68	2439	0.07	Mine	
soil R4		0.2	1.8	13	silt loam	3.6 ^a	4.09	5.47	559	0.36	Mine	
soil R5					silt loam	4.2 ^a	5.08	5.22	459	0.24	Mine	
soil R6					sandy loam	4.2 ^a	2.50	2.20	425	0.08	Mine	
soil R7					silt loam	4.6 ^a	3.18	4.20	225	< 0.05	Mine	
soil R8		0.037	4.1	25	silt loam	5.5 ^a	2.48	1.86	72	< 0.05	Chlor-alkali	Reis et al. [20, 45, 57]
soil R9					silt loam	4.8 ^a	1.66	1.59	201	< 0.05	Chlor-alkali	
soil R10	1.8				loamy sand	5.0 ^a	2.16	1.81	203	< 0.05	Chlor-alkali	
soil R11					loamy sand	5.5 ^a	2.43	1.87	172	< 0.05	Chlor-alkali	
soil R12					silt loam	5.5 ^a	2.08	0.93	185	< 0.05	Chlor-alkali	
soil R13					sandy loam	5.0 ^a	1.87	1.14	146	0.11	Chlor-alkali	
soil R14					loamy sand	6.0 ^a	1.90	2.06	184	< 0.05	Chlor-alkali	
soil R15	0.57				silt loam	5.1 ^a	1.92	1.38	133	< 0.05	Chlor-alkali	
soil N1	0.9				n.a.	7.9 ^b	0.24	n.a.	n.a.	0.06	Chlor-alkali	
soil N2	0.1				n.a.	7.9 ^b	1.82	n.a.	n.a.	0.05	Chlor-alkali	Neculita et al. [48]
soil N3	0.5				n.a.	9.1 ^b	0.00	n.a.	n.a.	0.03	Chlor-alkali	
soil P1	< LOD			0	n.a.	4.2 ^{n.a.}	42.8 ^c	n.a.	n.a.	0.16	urban/industrial	
soil P2	< LOD			0.24	n.a.	5.8 ^{n.a.}	16.7 ^c	n.a.	n.a.	0.08	urban/industrial	Panyametheekul [46]
soil P3	< LOD			0.31	n.a.	7.2 ^{n.a.}	11.1 ^c	n.a.	n.a.	0.08	urban/industrial	
soil P4	< LOD			0	n.a.	7.3 ^{n.a.}	12.3 ^c	n.a.	n.a.	0.07	urban/industrial	
soil F1	1.1				n.a.	8.0 ^b	2.78	2.75	0.69	NA	Chlor-alkali	
soil F2	2.8				n.a.	9.3 ^b	0.55	3.15	0.61	NA	Chlor-alkali	
soil F3	7.9				n.a.	7.7 ^b	0.68	2.79	0.59	NA	Chlor-alkali	Frentiu et al. [56]
soil F4	0.6				n.a.	8.5 ^b	0.15	2.64	0.50	NA	Chlor-alkali	
soil F5	0.011				n.a.	8.4 ^b	2.41	2.45	0.41	NA	Chlor-alkali	
soil L1	0.28				paddy soil	7.8 ^{n.a.}	6.80	n.a.	400	n.a.	Mine	Li et al. [49]
soil L2	0.46				paddy soil	7.9 ^{n.a.}	6.00	n.a.	320	n.a.	Mine	
soil J1		6.0	42		silty loam / paddy	6.0 ^b	1.16	n.a.	n.a.	n.a.	Added for experiment	Jing et al. [25]
soil J2		3.9	8.5		yellowish red / paddy	5.1 ^b	2.97	n.a.	n.a.	n.a.	Added for experiment	
soil S1	0.0	0.5			sandy loam	n.a.	0.43	n.a.	n.a.	n.a.	Mine	Sánchez et al. [51]

a) CaCl2

b) water

c) 1.0l

n.a. data not available

Table 2. Operationally-defined phases targeted in most SEP, common extractants and respective mobility (adapted from Filgueiras et al. [56])

Fractions		Extractants	Mobility
Water-soluble	Constitutes the most mobile and potentially the most available metal and metalloid species; This fraction is usually negligible.	Sample pore solution using in situ filtration, dialysis tubes or bags; Laboratory procedure such as centrifugation, filtration or displacement	High.
Exchangeable	Includes weakly adsorbed metals retained on the solid surface by relatively weak electrostatic interaction, metals that can be released by ion-exchange processes and metals that can be coprecipitated with carbonates; Generally accounts for less than 2% of the total metals present in a sample.	Salts solutions of replaceable cations such as MgCl ₂ , NH ₄ OAc, CaCl ₂ , NaNO ₃ , Mg(NO ₃) ₂ , BaCl ₂ , KNO ₃ , Ca(NO ₃) ₂ , usually at 1 M concentration.	High. Changes in major cationic composition or lowering of pH may cause a release due to ion exchange
Acid-soluble	Contains the species which are precipitated or coprecipitated with carbonate. Carbonate can be an important adsorbent when organic matter and Fe-Mn oxides are less abundant in the system. The carbonate form is a loosely bound phase and liable to change with environmental conditions. This fraction in general contains a relatively small percentage of the total concentration and is significantly modified by drying but less than the first fraction.	Generally targeted by use of a mild acid; most common is sodium acetate-acetic acid buffer at a 1 M concentration and pH5	Medium. Changes in redox conditions may cause a release but some metals precipitate if sulfide mineral present is insoluble .
Reducible	Associated with hydrous oxides of Fe and Mn, present as coatings on mineral surfaces or as fine discrete particles. Binding can occur by any or a combination of the following mechanisms: coprecipitation; adsorption; surface complex formation; ion exchange; and penetration of the lattice. These oxides are in large proportion in soil and sediments.	1M Hydroxylamine hydrochloride in nitric, acetic or HCl acid medium	Medium.
Oxidisable	Complexation or bioaccumulation process with various forms of organic material such as living organisms, detritus or coatings on mineral particles.	The most used oxidant is H ₂ O ₂ in acid, heated (85°C) medium. The addition of NH ₄ OAc prevents readsorption of the already extracted species. NaOCl, Na ₄ P ₂ O ₇ both at pH 9.5, and K ₄ P ₂ O ₇ are also used as oxidants	Low. However, with time, decomposition/oxidation of organic matter occurs.
Residue	All species that weren't extracted in previous fractions.	<i>Aqua regia</i>	Low. Only available after weathering or decomposition

free ion

soluble inorganic complexes

soluble organic complexes

Table 3. Application of EPA method 3200 to mercury-contaminated samples. Sample characterisation of selected samples.

Sample	EPA method 3200			Soil physicochemical characterisation						Hg source	References
	M (%)	SM (%)	NM (%)	Texture	pH	Org C (%)	Fe (%)	Mn (mg/kg)	S (%)		
soil R1	0.20	46.29	15.57	sandy loam	4.0 ^a	1.63	4.85	1790	< 0.05	Mine	
soil R2	1.97	67.52	8.34	sandy loam	5.3 ^a	3.83	6.56	402	0.42	Mine	
soil R3	0.32	62.26	34.84	sandy loam	4.6 ^a	2.00	6.68	2439	0.07	Mine	
soil R4	6.22	88.11	1.46	silt loam	3.6 ^a	4.09	5.47	559	0.36	Mine	
soil R5	0.20	73.67	12.50	silt loam	4.2 ^a	5.08	5.22	459	0.24	Mine	
soil R6	0.39	73.47	1.18	sandy loam	4.2 ^a	2.50	2.20	425	0.08	Mine	
soil R7	0.72	81.82	15.45	silt loam	4.6 ^a	3.18	4.20	225	< 0.05	Mine	Reis et al.
soil R8	3.86	65.86	1.36	silt loam	5.5 ^a	2.48	1.86	72	< 0.05	Chlor-alkali	[20, 45, 57]
soil R9	1.18	97.92	3.77	silt loam	4.8 ^a	1.66	1.59	201	< 0.05	Chlor-alkali	
soil R10	1.38	86.89	1.67	loamy sand	5.0 ^a	2.16	1.81	203	< 0.05	Chlor-alkali	
soil R11	1.46	80.42	1.22	loamy sand	5.5 ^a	2.43	1.87	172	< 0.05	Chlor-alkali	
soil R12	1.06	91.18	0.44	silt loam	5.5 ^a	2.08	0.93	185	< 0.05	Chlor-alkali	
soil R13	1.00	86.00	0.26	sandy loam	5.0 ^a	1.87	1.14	146	0.11	Chlor-alkali	
soil R14	1.32	94.60	2.02	loamy sand	6.0 ^a	1.90	2.06	184	< 0.05	Chlor-alkali	
soil F1	4.72	54.2	31.9	n.a	8.0 ^b	2.78	2.75	0.69	n.a	Chlor-alkali	
soil F2	1.13	82.9	8.72	n.a	9.3 ^b	0.55	3.15	0.61	n.a	Chlor-alkali	
soil F3	12.9	82.1	11.4	n.a	7.7 ^b	0.68	2.79	0.59	n.a	Chlor-alkali	Frentiu et al.
soil F4	11.7	57.1	28.6	n.a	8.5 ^b	0.15	2.64	0.50	n.a	Chlor-alkali	[56]
soil F5	4.39	87.8	11.3	n.a	8.4 ^b	2.41	2.45	0.41	n.a	Chlor-alkali	

a) CaCl₂

b) Water

n.a. Data not available

Table 4. Overview of the work presented. Procedures are compared for their target species, advantages and disadvantages. General results obtained are also presented.

	Sequential extraction	Water-soluble fraction	Exchangeable fraction	Acid-soluble fraction	Thermo-desorption
Target	<ul style="list-style-type: none"> •Provides information on Hg mobility (bioavailability). 	<ul style="list-style-type: none"> •Extracts free Hg²⁺ and Hg²⁺ complexed with dissolved OM. •Most mobile and bioaccessible fraction. 	<ul style="list-style-type: none"> •Extracts weakly adsorbed Hg retained on the solid surface by weak electrostatic interaction, by ion-exchange processes. •Extremely mobile and bioaccessible fraction. 	<ul style="list-style-type: none"> •Extracts acid-soluble species, such as water-soluble, exchangeable, and carbonate associated. 	<ul style="list-style-type: none"> •Hg species and not fractions. •Hg species: Hg⁰, HgCl₂, Hg associated with Fe, Hg bound to humic acids, HgS.
Advantages and disadvantages of the method.	<ul style="list-style-type: none"> ✓ Fewer steps than other SEP. ✗ Hg easily lost. ✗ Time-consuming. 	<ul style="list-style-type: none"> ✓ Water is a cheap extractant. ✗ Concentration is very low and only quantifiable with extremely sensitive analytical techniques. 	<ul style="list-style-type: none"> ✓ Only one extraction step and one reagent required. ✓ Cost-effective ✓ Requires less technical skill. ✗ Hg extracted varies with extractant used. 	<ul style="list-style-type: none"> ✓ Only one extraction step and one reagent required. ✓ Cost-effective ✓ Requires less technical skill. ✗ Doesn't provide geochemical information. 	<ul style="list-style-type: none"> ✓ No extraction involved. ✓ Cost-effective. ✓ Requires low technical skill. ✗ Requires a mercury analyser. ✗ Peak overlap
General results in tested samples.	<p>Hg mostly in semi-mobile fraction. Higher Hg mobility in anthropogenically-contaminated soils. Hg mobility enabled by Al and Mn and inhibited by organic matter and sulfur.</p>	<p>Equilibrium was reached at 24h. Hg removal in two stages (faster t<6h; slower t>6h). Two first-order reaction model fit data. Low % of water-soluble Hg (<2%)</p>	<p>Hg removal in two stages (faster t<10h; slower t>10h). Two first-order reaction and diffusion models fit data. Percentage removed <10 %.</p>	<p>Hg removal in two stages (faster t<10h; slower t>10h). Two first-order reaction and diffusion models fit data. Percentage removed up to 30%</p>	<p>Hg⁰ and HgS are easily identifiable. Hg species associated with matrix components can sometimes be harder to clearly identify.</p>
<p>Chemical extractions are influenced by: Sample texture (% sand and % clay); Method of separation of the extracted solution from the residue. Results vary with the quantification method chosen.</p>					

FIGURE CAPTION

Figure 1. Mercury pathways in the soil matrix and soil solution. OM: organic matter; SH: thiol groups.

Figure 2. Example of a thermo-desorption speciation analysis for mine mercury-contaminated soil (mean \pm standard deviation, $n=3$). The thermogram shows 3 clearly distinguishable peaks: the first, released at 120-210 °C is consistent with HgCl_2 and HgFe standards; the second peak suggests the presence of organic Hg^{2+} complexes; the last species that can be identified is cinnabar (retrieved from Reis et al. [23]).

Figure 1.

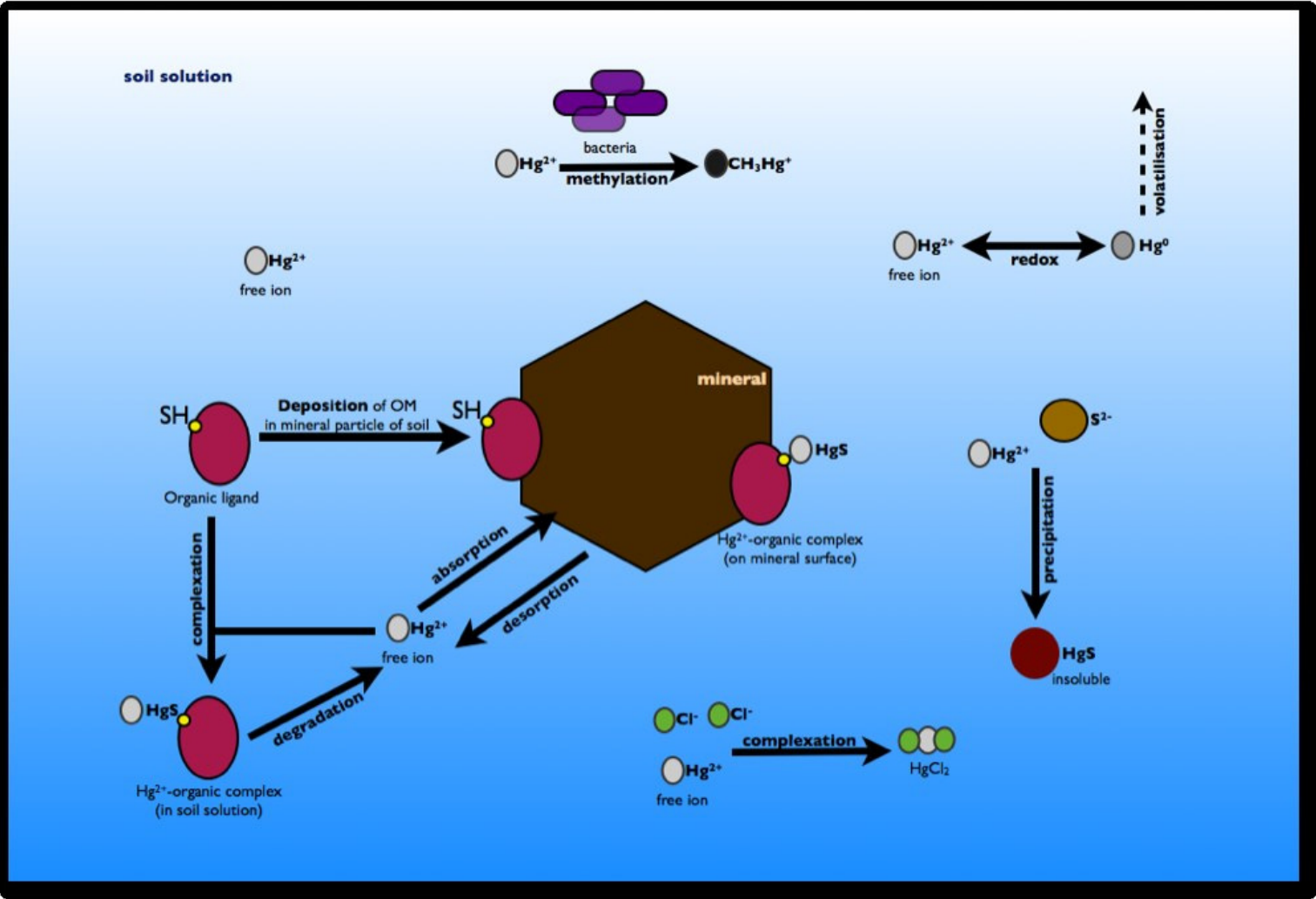


Figure 2.

