Overview and challenges of mercury fractionation and speciation in soils

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Abstract

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

Keywords: mercury; soil; fractionation; speciation; sequential extraction; risk assessment

1. Introduction

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

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

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

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

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

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

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

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

2. Mercury fractionation and speciation methods applied to soil samples

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

2.1 Single extractions

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

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

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

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

The exchangeable fraction includes mercury species adsorbed to the matrix by weak electrostatic bonds that can be released by ion-exchange processes and species coprecipitated with carbonates. Changes in major cationic composition or lowering of pH may cause their release due to ionic exchange and/or dissolution of carbonates. This fraction corresponds to the most mobile and bioaccessible species released into the environment, and is commonly used to access soil-to-plant transfer [55, 56]. Extracting agents (Table 1) include $CaCl_2$, $MgCl_2$, $NaNO_3$ and CH_3COONH_4 (releasing mercury electrostatically bound to organic and inorganic sites by cationic exchange) or weak acids (mercury released by lowering pH). A comparison of extractions using 1.0 mol L^{-1} CH_3COONH_4 and 0.1 mol L^{-1} HCl in the same (air-dried) soil samples revealed that the percentage mercury extracted by the latter solution was higher in all samples (Table 2), indicating that mercury is more sensitive to acidification than to cationic exchange. Mercury extracted by 1.0 mol L^{-1} CH_3COONH_4 usually corresponds to < 10 % of total mercury, while the percentage extracted by 0.1 mol L^{-1} HCl was over 40 % in soil J2 sample (Table 2) [21].

From this analysis, it was concluded that 1.0 mol L^{-1} CH_3COONH_4 and 0.1 mol L^{-1} HCl, used to estimate the exchangeable fraction, did not provide the same information. For risk assessment purposes, the knowledge on the environmental conditions is key to decide the most appropriate extractant. For example, for acidic environments such as the ones surrounding mines, a weak acid provides more protective and factual conclusions. In neutral soils, where pH is unlikely to decrease, a mild extractant, such as 1.0 mol L^{-1} CH_3COONH_4 should provide adequate information on mercury mobility.

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

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

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

2.2 Sequential extraction schemes

In sequential extraction schemes, a sequence of reagents is applied to the same sample in an attempt to sub-divide the total mercury content. The procedure typically contains 3-8 treatments of the solid phase, with the strength of the treatment generally increasing through the steps, from initial mild conditions (e.g. shaking with water, a salt solution or dilute acetic acid) to the use of harsher reagents (e.g. hot mineral acid) [4]. A summary of the most common target phases in sequential extraction schemes and respective mobility in the environment is given in Table 1. Sequential extraction schemes different from those typically used for other elements have been developed to assess mercury speciation and fractionation in soils [4], but, in general, the schemes begin with the extraction of the more labile fractions: water-soluble and/or exchangeable using, respectively, distilled water and salt solutions that remove mercury by ion-exchange (e.g. NH_4Ac, $MgCl_2$, $CaCl_2$). In the next fraction, oxidising reagents, such as NaOH, KOH, HNO_3 or H_2O_2, are applied to extract mercury bound to organic matter. In the last steps, the less reactive species, which are strongly bound to the matrix, are extracted with strong acids, including HNO_3, HF and aqua regia.

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

potential mobility - mobile, semi-mobile, and non-mobile - that are extracted consecutively with a solution of 1:1 (v/v) 2% HCl + 10% ethanol, a solution of 1:2 (v/v) HNO_3:DDI water, and a solution of 1:6:7 (v/v/v) HCl:HNO_3:DDI water, respectively. The residual fraction can be determined by quantifying the mercury left in the residue at the end [27, 32]. This sequential extraction procedure was applied to soil samples from industrially impacted and mine areas [27, 64]. Overall, the extractions yielded good recoveries, the semi-mobile phase accounting for 46-97% of the total mercury (Table 3). According to Han et al. [32], this fraction encompasses Hg^0, some (unspecified) mercury complexes and minor fraction of Hg_2Cl_2. However, the presence of the first species is questionable, since, due to its high volatility, Hg^0 is easily lost after the vigorous treatment involved in extraction of mobile and semi-mobile fractions [23]. The application of this extraction scheme allowed inferences to be drawn on the influence of soil properties in mercury fractionation in contaminated areas and has proven to be useful in distinguishing between anthropogenic and geogenic sources [27, 64]. Reis et al. [27] concluded that aluminium, manganese, organic matter and sulfur content were the main soil characteristics associated with mercury mobility in their samples, while Frentiu et al. [64] included also calcium, copper and iron. Soils with higher pH exhibited larger percentages of mobile mercury (Table 3), most likely due to leaching of organic matter from the matrix, resulting in a decrease of adsorption sites in the solid fraction. Some organic matter leached to the soil solution tends to desorb mercury form the solid phase, increasing the concentration of dissolved Hg^{2+} complexes, and, in turn, mercury accessibility. This phenomenon is not observed in natural organic matter ligands, such as humic and fulvic acids, that have a strong bond with mercury; thus, these complexes are not labile or bioavailable.

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

The mobile fraction extracted by the acidic ethanol solution yielded results similar to the ones obtained using 0.5 mol L^{-1} HCl for the same soil samples (Tables

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

2.3 Soil:extractant ratio and time of extraction

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

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

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

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

2.4 Speciation by thermo-desorption

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

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

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

3. Overview and final remarks

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

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

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

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

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

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

After the selection and application of the most suitable method based on the above information, the interpretation of the results must be done wisely, in order to correctly support decisions concerning intervention or remediation strategies at contaminated sites. This is one of the numerous challenges that the scientific community faces in mercury speciation in soils. Interpretation of data needs to be done within the context, considering the operations used to obtain the fractions or species, and the nomenclature. For example, the interpretation of the (potential) 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], Hg^0 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

this: 1) extractions are labor-intensive, costly and time-consuming; 2) mercury speciation seems to be a matter of academic research importance and most laboratories are not cognizant with the importance of speciation. Regulatory acceptance of the importance of metal speciation is another challenge. Legislation regarding mercury determination in environmental samples usually only establishes limits for total mercury, which does not contribute to raise awareness of the significance of mercury speciation. A limited number of countries include assessment of metal fractions in risk assessment and management of contaminated soils, with only Austria and Germany considering the mercury transfer from soil-to-plant and soil-to-groundwater, respectively [80]. In risk assessment, total mercury concentration is assumed as the "worst case scenario", resulting in an overestimation of the real risk, but there are cost-effective and environmental protection advantages in a more detailed analysis of the species/fractions present. Regarding this aspect, for the reasons aforementioned, speciation by thermo-desorption can be a useful tool to rapidly obtain needed information about a 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	Reis et al. [20, 45, 57]
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	
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	Neculita et al. [48]
soil N2	0.1				n.a.	7.9 [b]	1.82	n.a.	n.a.	0.05	Chlor-alkali	
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	Panyametheekul [46]
soil P2	< LOD			0.24	n.a.	5.8 [n.a]	16.7[c]	n.a.	n.a.	0.08	urban/industrial	
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	Frentiu et al. [56]
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	
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 LOI

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])

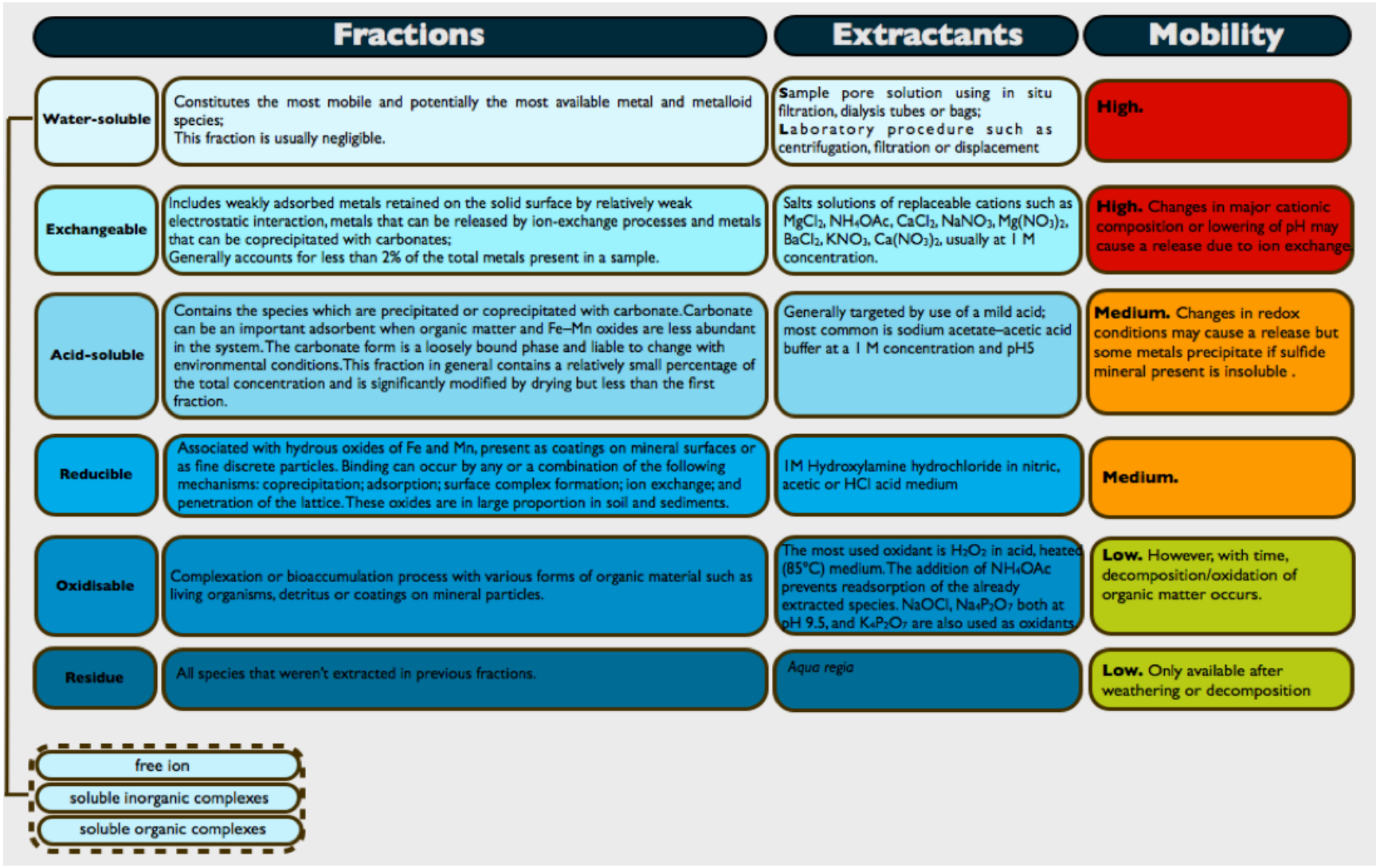

Table 3. Application of EPA method 3200 to mercury-contaminated samples. Sample characterisation of selected samples.

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	Reis et al. [20, 45, 57]
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	
soil R8	3.86	65.86	1.36	silt loam	5.5 [a]	2.48	1.86	72	< 0.05	Chlor-alkali	
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	Frentiu et al. [56]
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	
soil F4	11.7	57.1	28.6	n.a	8.5 [b]	0.15	2.64	0.50	n.a	Chlor-alkali	
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.

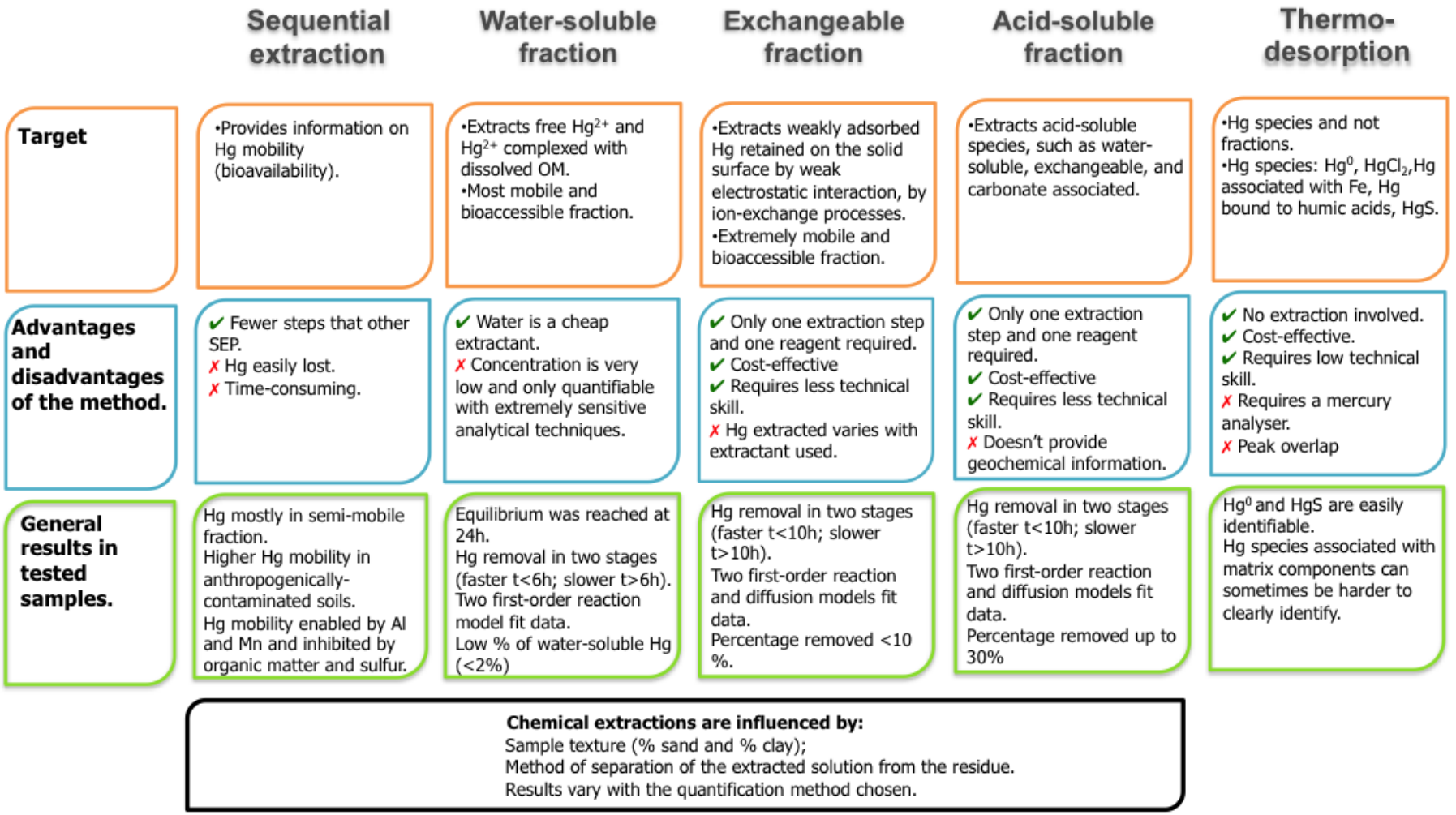

FIGURE CAPTION

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 ± standard deviation, n=3). The thermogram shows 3 clearly distinguishable peaks: the first, released at 120-210 ºC 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.

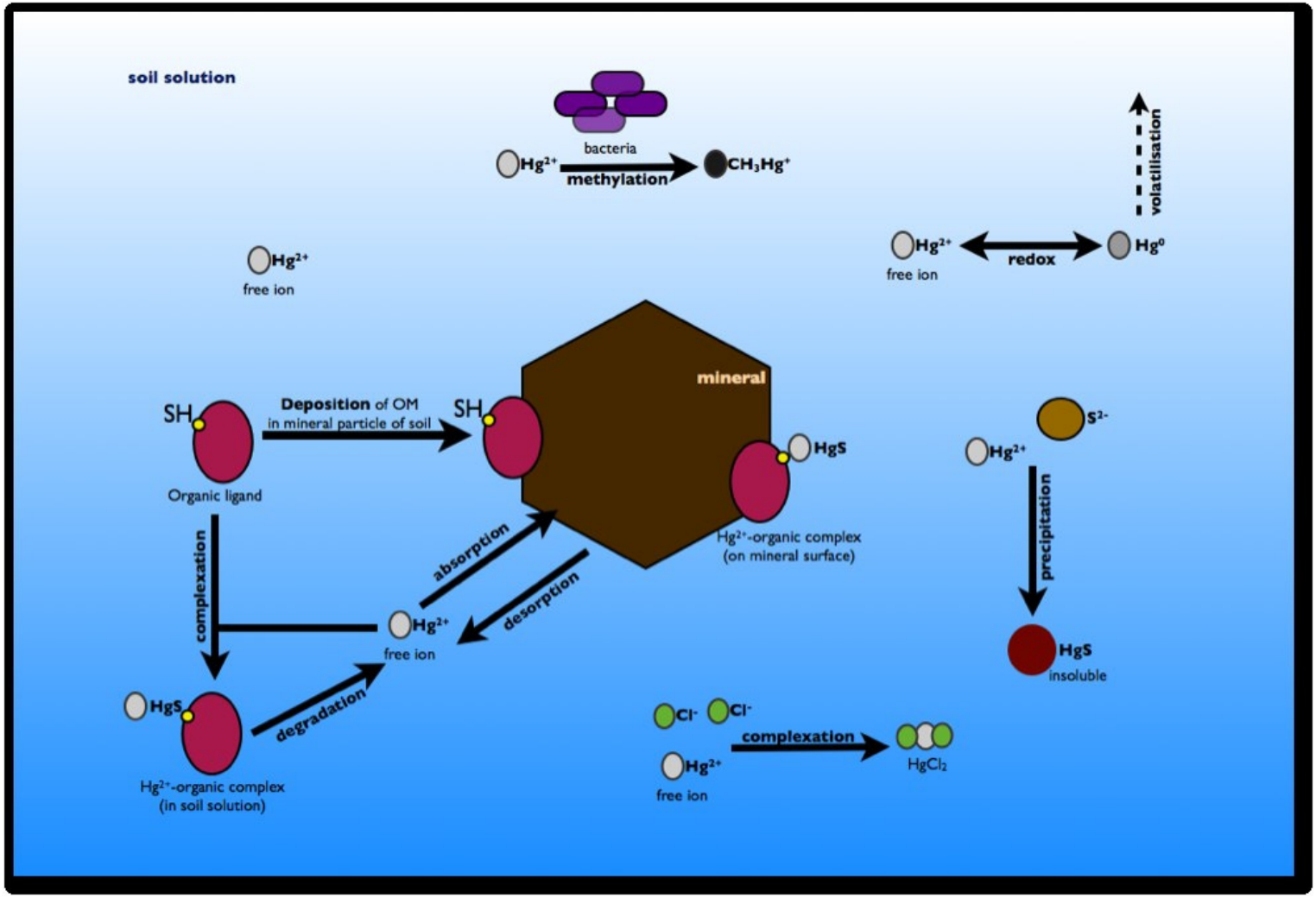
soil solution
bacteria
Hg^{2+}
methylation
CH_3Hg^+
volatilisation
Hg^{2+}
free ion
redox
Hg^0
Hg^{2+}
free ion
mineral
SH
Deposition of OM
in mineral particle of soil
SH
HgS
Organic ligand
Hg^{2+}-organic complex
(on mineral surface)
S^{2-}
Hg^{2+}
precipitation
complexation
absorption
desorption
Hg^{2+}
free ion
HgS
insoluble
HgS
degradation
Cl^-
Cl^-
complexation
$HgCl_2$
Hg^{2+}
free ion
Hg^{2+}-organic complex
(in soil solution)

Figure 2.