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Thermodynamic and kinetic study of the single extraction of mercury from soil using sodium-thiosulfate

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ABSTRACT

The use of sodium-thiosulfate (Na-thiosulfate) as a reagent for the extraction of mercury (Hg) from soil was investigated. High organic matter content in soil plays a major role in retaining metals. It has previously been reported that using the cold vapour atomic absorption method, powerful reagents such as EDTA, DTPA and cysteine could not release Hg from soil samples. The optimal conditions for using Na-thiosulfate to extract soil-Hg are presented here. Our results show that 50 ± 5% of total Hg was extracted from soil samples using 0.01 mol L^{-1} of the reagent without pH adjustment. Increasing the reagent concentration above this level showed no significant change in Hg extraction. From this extraction three fractions of Hg were obtained, the labile, slowly labile and un-extractable. We further applied the use of a kinetic extraction approach that has never been applied for Hg. We observed a correlation between the first two fractions and the quantity of organic matter content in soils. The labile fraction could be released by using any concentration of the reagent. However, the slowly labile fraction was dependent on time and increased concentrations of Na-thiosulfate. Furthermore, our results suggest that the labile and slowly labile fractions involve two different sites of reduced sulphur groups contained in soil organic matter and Hg levels present in the soil samples did not appear high enough to saturate all these high affinity sulphur sites. The capacity of Na-thiosulfate to reduce (Hg(II)) to (Hg(0)), was determined to be negligible. Our results further suggest the implication of iron (Fe(II)) for reducing Hg(II) to Hg(0). Here we have demonstrated that Na-thiosulfate is an effective reagent in the extraction of Hg from soil, with the particular characteristic of its ability to remove strongly bound Hg from sulphur groups contained in soil organic matter.

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1. Introduction

Mercury (Hg) is a highly toxic and hazardous trace metal that can freely cycle in the environment as part of both natural and anthropogenic activities. The atmospheric depositional fluxes of Hg have increased approximately three times since the industrial revolution [1]. Recent estimations of global anthropogenic Hg emission are considered to be much higher than those coming from natural sources and ranges from 6.6 to 9.4×10^6 kg $year^{-1}$ [2]. Accumulation over time of large inputs of Hg into the environment, especially after the beginning of industrial age, has resulted in the widespread occurrence of Hg in the entire food chain. For this purpose, this metal has been consciously studied since the tragedy of Minamata, Japan, in the 1950s where entire communities were contaminated by the consumption of accumulated methylmercury in fish [3]. Once Hg enters the environment it can occur in different chemical forms depending on physicochemical characteristics and elemental components of the medium. Furthermore, according to the biogeochemical behaviour of Hg, it can be transformed from one chemical form to another and mobilized over different environmental compartments comprising the atmosphere, hydrosphere, lithosphere, and biosphere [4–6]. Therefore, this metal is considered as a global pollutant because it can be transported thousands of kilometres through the atmosphere, evaporated out of oceans, adsorbed or released by soil and sediment, and accumulated in plants and animals as well as in humans.

In this work, we are particularly interested in soil as it is considered a sink for punctual polluted sources and deposited atmospheric Hg [7]. The Hg present in soil is subject to a wide range of chemical an biological transformation processes such as Hg(0) oxidation and Hg(II) reduction or methylation as determined by soil properties (e.g. pH, temperature, moisture, mineral content and organic matter content). The relation of Hg mobility versus its retention in soil has been well documented and the behaviour of Hg in soil is mainly controlled by adsorption and desorption processes relating to the complexation of this metal with potential ligands presented in the medium [8–10]. It has also been reported that soil organic matter (SOM) is the most important component governing

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Hg retention and release [9]. Sulphur containing functional groups in SOM are specifically reported to be the principal ligands binding Hg [11–13].

It should be noted that the study of soil-Hg speciation, aimed at determining the species of Hg, is difficult to achieve when using chemical reagent [14]. This is why, instead of “speciation”, many authors use the term “fractionation” to provide information on Hg fractions according to their extractability behaviours [15]. To study Hg fractionation, sequential extraction procedures using a series of reagents, with operational interpretation according to different soil compartments, are widely referred to [16,17]. However, these suffer from a lack of selectivity of the extraction reagents, co-precipitation, re-precipitation and re-adsorption of the previously released metal. A single extraction study, using a single reagent, is rare despite of its simpler performing experience when compared with those of sequential extraction. A single extraction may also suffer from the same criticisms (selectivity, re-adsorption, re-distribution). Consequently, The great number of procedures used by different authors also results in a large spectrum of non-comparable data. In all cases, it is crucial to note that although the “key” to speciation/fractionation determination is the appropriate choice of reagent used in the extraction step, neither specific extractants, nor standard protocols, exist for the isolation of particular soil-Hg forms [18]. Aside from both methods mentioned above, the kinetics extraction has been considered as a more correct approach to the distribution of metal species in a natural environment. Applying the kinetic models to the experimental results could allow the study of metal fractions with different labilities [19]. The feasibility of this technique has been evaluated for many metals such as Cd, Cu, Fe and Pb [20–23] but, to our knowledge, its application for Hg in soil has never been reported. Although Na-thiosulfate was used in a phytoextraction method to increase Hg availability to plants [24], it is never applied for soil-Hg extraction according to speciation aspect. Therefore, it is particularly interesting to investigate this approach in order to provide more information on soil-Hg mobility.

According to our previous work concerning the choice of a reagent for soil-Hg extraction, several powerful reagents were investigated [25]. Hg from our samples is strongly bound to the soil organic matter fraction and only Na-thiosulfate seemed to have the potential for extracting it due to its high stability constant reported in the literature [12,13]. Detailed experiments were investigated in this paper to establish appropriate conditions for achieving an accurate interpretation of soil-Hg behaviour. The first aim of this work was to optimize and evaluate a soil-Hg extraction procedure using Na-thiosulfate as a single reagent. Several experimental parameters such as concentration, pH and the mass–volume ratios were investigated and optimized in order to consider Hg mobilization under equilibrium conditions. The second objective was to apply a kinetics extraction study of Hg so as to provide a more accurate interpretation of soil-Hg lability. It is well known that the redox transformation of Hg(II) to Hg(0) significantly modifies the fate of Hg in soil. Given that Na-thiosulfate may react as a reductant, our third objective was to determine the production of Hg(0) during the soil-Hg extraction when using this reagent.

2. Materials and methods

2.1. Samples

Soil samples (PC01 and PC25) were obtained from the Pierrelaye site, located 29 km to the north-west of Paris, France. For several decades these soils were contaminated by agricultural processes and have known higher levels of Hg. The soils were stored in clean black plastic bags which prevented their exposure to light and moisture. Before being used in this study, the soils were homogenized, sieved (<2 mm) and ground. Furthermore, a soil standard reference material SS-2 (EnviroMat) was also used. All soil characteristics are given in Table 1.

Table 1
Soil characteristics.

	PC01	PC25	SS-2
Organic matter ($g\,kg^{-1}$)	112.45	71.98	–
Organic C ($g\,kg^{-1}$)	65.37	41.83	–
S ($mg\,kg^{-1}$)	952	–	2254
Hg ($mg\,kg^{-1}$)	3.92	3.14	0.34
Cr ($mg\,kg^{-1}$)	80.7	97.72	58
Cu ($mg\,kg^{-1}$)	292.3	299.17	198
Ni ($mg\,kg^{-1}$)	53.6	27.09	59
Zn ($mg\,kg^{-1}$)	858.9	1052.95	509
Co ($mg\,kg^{-1}$)	17.04	5.85	14
Pb ($mg\,kg^{-1}$)	431.6	567.74	148
Cd ($mg\,kg^{-1}$)	5.16	7.1	2
Tl ($\mu g\,kg^{-1}$)	369.4	248.19	0.6
Al (%g)	2.17	1.14	4.49
Ca (%g)	2.26	2.07	11.87
Fe (%g)	1.8	1.24	2.91
K (%g)	0.6	0.41	1.81
Mg (%g)	0.29	0.21	1.42
Mn ($mg\,kg^{-1}$)	378.1	184.07	577
Na (%g)	0.14	0.1	1.25

2.2. Chemical reagents

In all experiments, nitric acid (HNO_3), a standard Hg solution of inorganic Hg(II), a standard iron(II) solution, and a standard calcium(II) solution of analytical quality were used (Merck, USA). Sodium-thiosulfate (Na-thiosulfate) of AnalaR NORMAPUR quality was obtained from VWR Prolabo, Belgium. Water of high purity obtained from a Millipore apparatus (resistivity = 18 MΩ cm) was used (Millipore, USA). Standard Hg solutions of inorganic Hg(II) were prepared by stepwise dilution from a standard stock solution containing $1000 \pm 2\,mg\,L^{-1}$ Hg as $Hg(NO_3)_2\cdot H_2O$. All standards were freshly prepared prior to use.

2.3. Total mercury

In order to determine total Hg in soils, 0.5 g of samples were added to 5 mL of HNO_3. The samples were digested with concentrated HNO_3, heated to 95 °C during 2 h by using a *Digi*PREP Jr. apparatus (SCP Science, Canada). A final volume of the digested samples was made to 30 mL using deionised water prior to Hg determination by cold vapour atomic absorption spectrometry (CV-AAS) (see “CV-AAS detection”).

2.4. Mineralization of the soil-extracted solution

Soil-extracted solutions, outlined in the “Experimental procedures”, were digested using concentrated HNO_3 in order to improve the CV-AAS signal as well as to eliminate the interference induced by the reagent used and the soil matrix. 5 mL sample extractions were mixed with 10 mL HNO_3 and placed into digesting tubes suitable for *Digi*PREP Jr. apparatus for digest temperature control. The *Digi*PREP Jr. apparatus is manufactured under an ISO 9001: 2000 certified quality program. The solutions were digested at 80 °C during 3 h. To prevent the lost of Hg from volatilization, a polyethylene cap (*digi*Cap) was used during heating so as to create a closed system of each digesting tube. After digestion, deionised water was added to the digesting tubes prior to CV-AAS detection to a final volume of 30 mL. Mineralization required a volume ratio (1:2 (v/v)) of the extracted solution and HNO_3. The use of higher ratios was highly unrecommended as the analytical instrument (CV-AAS) would be damaged by the increased acidity of the solution to be analyzed.

In addition, the accuracy of Hg analysis after the mineralization of the extracted solution with Na-thiosulfate was also tested by a standard addition method. The similarity in the results obtained between the standard addition and the direct procedure proves the absence of any interference during the analysis.

2.5. CV-AAS detection

Cold vapour atomic absorption spectrometry (CV-AAS) is one of the most widely used techniques for Hg determination because of its high sensitivity, absence of spectral interferences due to radiation overlapping of the light source, relatively low operational costs, simplicity and speed. Hg was analyzed by a Varian atomic absorption spectrometer (Palo Alto, CA, Model SpectrAA 250Plus) with a quartz absorption cell. A high intensity Hg hollow cathode lamp was operated as the radiation source with a lamp current of 3 mA. The 253.7 nm resonance line of Hg was selected as the analytical line. Hg vapour was generated by employing a Varian vapour generator accessory (Model VGA-77) under a continuous flow of sample solutions and the reductant, $SnCl_2$. The generated Hg vapour was carried out by a flow of nitrogen gas on a continuous flow mode, sent to the non-heated absorption cell for Hg analysis. The reproducibility of CV-AAS detection has been verified with replicated measurements of Hg standard solution diluted in different concentrations by water of high purity obtained from a Millipore apparatus (water resistivity = 18 MΩ cm). The standard deviations obtained were satisfactory and ranged from 2 to 6% ($n = 10$).

2.6. Soil major elements determination

Determination of the major elements, Fe and Ca, were performed by flame atomic absorption spectrometry (FAAS). We used a Hitachi Z-5000 polarized Zeeman atomic absorption spectrometer equipped with an air-acetylene flame and a micro sampling kit. In this technique, 80–100 μL of sample solution were introduced for each measurement. The reproducibility of the micro sampling technique was verified in replicated measurements for the standard and soil solutions. The standard deviations obtained were satisfactory and ranged from 3 to 5% ($n = 6$).

2.7. Experimental procedures

2.7.1. Optimization of experimental parameters

To evaluate the reagent concentration effect, 10 mL of different concentrations of Na-thiosulfate solutions (ranging from 0.001 to 0.1 mol L^{-1}) were added to 1 g of soil in polyethylene bottles. An end-over-end stirrer was used overnight (21 ± 3 h) to ensure an achieved equilibrium system. Afterwards the samples were centrifuged for 10 min at 6000 rpm (Hettich Zentrifugen model EBA-21®) and filtrated through a 0.45 μm filter with HVLP type membranes (Millipore®, USA). The extracted solutions were mineralized in HNO_3 at 80 °C during 3 h before CV-AAS analysis. It should be noted that the efficiency of this mineralization procedure has previously been verified [25]. All experiments were carried out in triplicate. Once the suitable Na-thiosulfate concentration was determined, the effect of soil mass to extractant volume ratios (m/v) was compared using the ratios of 1:5, 1:10, 1:20 and 1:50. A successive extraction method, in which the residual soil was rinsed twice with deionised water before being re-extracted with the same Na-thiosulfate concentration, was performed to provide the efficiency of the reagent used. The pH effect was also studied by adjusting the pH of Na-thiosulfate solution with a small volume of concentrated HNO_3 or sodium hydroxide (NaOH) solutions before adding to soil.

2.7.2. Kinetic extraction protocol

The study of the kinetic extraction of Hg from soil was performed in separate polyethylene bottles, each containing 1 g of soil and 10 mL of extracting solution. These bottles were stirred with an end-over-end shaker for different time periods, ranging from 5 min to 24 h. Samples were then processed for the evaluation of the reagent concentration effect mentioned above. The obtained results, called the extraction rate data, were needed to mathematically determine several kinetic parameters such as the quantity of desorbed Hg from different compartments of soil at a given time and their associated rate constants. This information can be modelled by using Sigma Plot® software (SSI, USA). In addition, it should be noted that models of multiple first-order reactions have often been used to fit the experimental results. This model gives information with real physicochemical meaning when different first-order reactions are attributed to discrete types of binding sites available in soil. Thus, a target metal may be classified into fractions associated with the specific soil compartments to which it is bound.

The extraction rate data obtained was fitted to a two first-order reaction model using Sigma Plot software in order to classify the soil-Hg into three fractions. These were the readily extractable fraction (labile), a less extractable fraction (slowly labile) and an un-extractable fraction. Each fraction was associated with its own rate constant. Accordingly, an equation related to a two first-order reaction model: $Q_{\text{ext}} = Q_1^0\,(1 - \exp(-k_1 t)) + Q_2^0(1 - \exp(-k_2 t))$ was applied [13–16]. By definition, Q_{ext} was the amount of total extracted Hg (mg kg^{-1}), Q_1^0 and Q_2^0 (mg kg^{-1}), respectively, represent the readily extractable Hg fraction and the less extractable Hg fraction. Therefore, the un-extractable Hg fraction, noted Q_3^0, can be deduced by the difference between the total amounts of Hg in soil, noted Q_{tot}, and the concentration of Hg extracted at equilibrium (Q_{ext}). Once the extraction rate data was fitted to the equation using Sigma Plot software, four kinetic parameters (Q_1^0, Q_2^0, k_1, and k_2) could be obtained.

2.7.3. Study of the reduction of soil-Hg(II) to Hg(0)

A semi-automatic apparatus piloted by a control box was used for measuring Hg(0). This apparatus was specifically developed by CREA-automatism Company. Fig. 1 shows the assembly line, including amalgamation, for the preceding Hg(0) analysis. The analytical sequence contains five phases: (i) golden trap sweeping; (ii) degassing (bubbling of N_2); (iii) golden trap sweeping; (iv) measurement; and (v) cooling the trap. Two concentrations of Na-thiosulfate, 0.001 and 0.05 mol L^{-1}, were used for comparing their effects on the reduction of soil-Hg(II) to Hg(0). 10 mL of the solution was added to 1 g of soil and introduced into the degassing cell. During a given time of reaction and degassing, the reduced Hg was amalgamated onto a golden trap. The trap was then heated, and the Hg vapour produced was measured by atomic absorption spectrometry (AAS). All experiments were protected from daylight through the use of aluminium foil.

Furthermore, a calibration curve for determining the quantity of reduced Hg was performed. For this purpose, different concentrations of Hg(II) (0, 2, 5, 10, 20, 40 and 80 μg mL^{-1}) were prepared by stepwise dilution from a standard stock solution containing 1000 ± 2 mg L^{-1} Hg as $Hg(NO_3)_2 \cdot H_2O$. 0.5 mL of Selenium Chloride ($SnCl_2$) were then added to 10 mL of the prepared solutions prior to their introduction into the degassing cell. The linear equation of this calibration system is $y = 4.956x + 0.1275$, with a linear regression (R^2) of 0.9845. It is important to note that the degassing cell, and all main gas conveyed pipelines, need to be changed for measuring the reduced Hg in the samples in order to avoid the reduction of Hg by $SnCl_2$-traces remaining in the system.

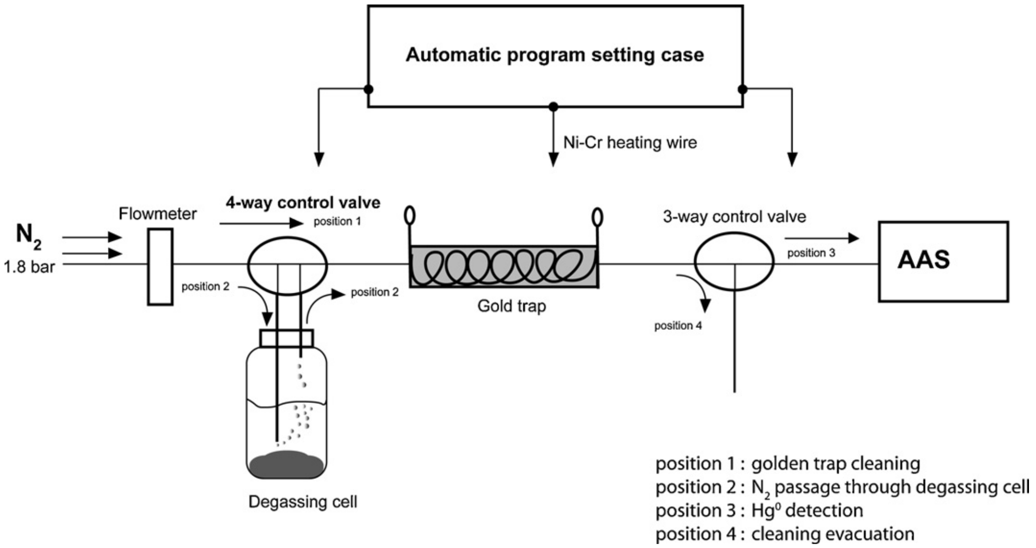

Fig. 1. Diagram of analytical assembly line, included amalgamation, for proceeding Hg(0) analysis.

3. Results and discussion

3.1. Equilibrium conditions study

Based on the Hg content determined by the soil characteristics, the method used for total Hg determination could release 98 ± 3, 104 ± 4 and 99 ± 2% of total Hg content, respectively, for SS-2, PC01 and PC25. These results demonstrated that our procedure, using the *Digi*PREP Jr. apparatus and its equipment, proved to be suitable for Hg determination as the system could prevent volatilized Hg loss. In order to precisely determine the efficiency of Na-thiosulfate as a potential Hg-extracting reagent, a more detailed study is presented here.

3.1.1. Reagent concentration

The optimal concentration of Na-thiosulfate was first established. As shown in Fig. 2, the amount of extracted Hg increased as the concentration of Na-thiosulfate increased. No significant change in Hg extraction was observed by increasing Na-thiosulfate concentration above 0.01 mol L^{-1}. A slight decrease in Hg extraction at concentrations of Na-thiosulfate greater than 0.01 mol L^{-1} might simply be due to an analysis error corresponding to their standard deviation of measurement. However, this decrease in extracted Hg levels could also indicate Hg loss during the extraction procedure as the reductant characteristic of Na-thiosulfate might reduce Hg(II) to Hg(0).

The efficiency of Na-thiosulfate resulted in 50 ± 5% of total Hg being extracted from both samples (PC01 and PC25) with 0.01 mol L^{-1} of the reagent used. This efficiency was confirmed by a successive extraction experiment. As shown in Fig. 3, we found that only a small amount of Hg (<5% of extracted Hg) remained in the second extraction and further decreased in the third extraction. The small percentage of Hg remaining after the first extraction was considered as not significant compared to the amount of Hg extracted in the first extraction.

Furthermore, as shown in “the kinetic extraction approach”, approximately 90% of extracted Hg from both samples was obtained after 8 h of mixing. Our experiments, applying the equilibrium time of 21 ± 3 h, were therefore considered to be appropriate. This allowed the extractions to proceed in a simple daily rhythm and operated over a time period where moderate differences in the extraction time produced minimal differences in the amount of Hg extracted. At this point we concluded that 0.01 mol L^{-1} of Na-thiosulfate was the suitable reagent concentration for soil-Hg extraction at equilibrium.

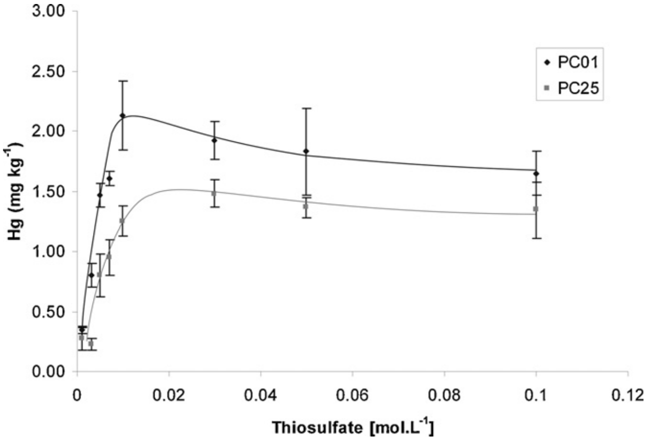

Fig. 2. Hg extracted from soil (PC01 and PC25) using different concentrations of Na-thiosulfate.

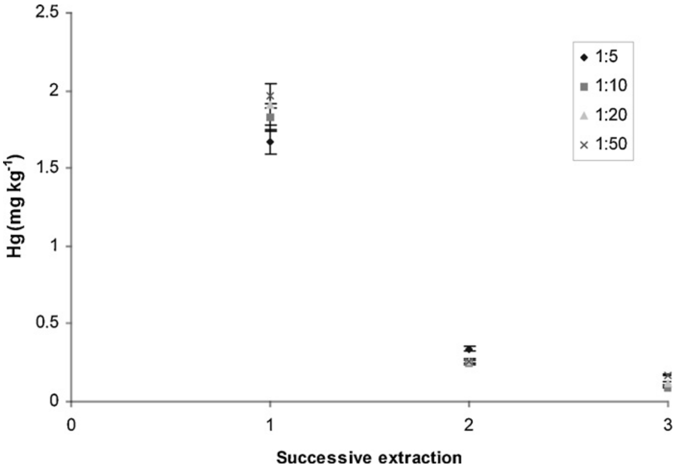

Fig. 3. Determination of soil to Na-thiosulfate ratio (m/v) for optimal Hg extraction, using PC01 and 0.01 mol L^{-1} Na-thiosulfate.

3.1.2. Mass–volume ratio

The mass–volume ratios of soil and reagent (solid-to-liquid ratio) were tested by comparing the ratios of 1:5, 1:10, 1:20 and 1:50. In theory, it is better to utilize the lowest solid-to-liquid ratio possible to better fully leach the Hg species. In practice, the ratio is limited by real-world sample heterogeneity and the ability to accurately weigh very small sample mass. We found that the quantity of extracted Hg appeared to increase with decreasing reagent ratios. Furthermore, while applying two successive extractions, the majority of the extractable Hg was released in the first extraction. As shown in Fig. 3, the differences of extracted Hg at all ratios were ambiguous with overlapping analytical errors. Therefore, the solid-to-liquid ratio of 1:10 was applied to our experiments as the difference in the amount of extracted Hg between the solid-to-liquid ratio of 1:10 and 1:50 was insignificant (less than 6%) and it has been routinely practiced in our laboratory for studying metals in soil.

3.1.3. The effect of final pH

In order to study the final pH effect on Hg extraction using Na-thiosulfate as an extraction reagent, we adjusted its pH to obtain a soil-extracted solution with a pH ranging between 5.5 and 6.0. This was achieved by using a small volume of concentrated HNO_3 and NaOH prior to mineralization. It should be noted that without adjustment the pH of the Na-thiosulfate solution ≅5.0. The buffer effect of soil samples drove the final pH of the extracted solution to 7.5–8.5. Regarding this buffer effect, it is difficult to predetermine the final pH of the extracted solution. However, the efficiency of Na-thiosulfate for complexing with Hg is pH independent and only soil components were responsible for the final pH of the extracted solution [25]. Finally, the reagent was adjusted to pH 1.5 in order to obtain the desired final pH of 5.5–6.0 for our soil-extracted solutions.

As shown in Fig. 4, the results derived from experiments performed in triplicate demonstrated that the extraction efficiency increased with decreasing pH. This effect was particularly noticeable at lower concentrations of Na-thiosulfate. Differences between the three replicated experiments were less than 8%. Furthermore, no significant difference in Hg extraction was observed that at high concentrations of Na-thiosulfate (0.01 and 0.05 mol L^{-1}) or between soil-extracted solutions with and without pH adjustment. This may be explained by the stability of Hg present in soil. As the stability of soil-Hg complexes seemed to decrease with decreasing pH, the amount of the immobilized metal should be strongly dependent on the complex stability with only very stable Hg complexes being able to exist at low pH. Due to the effects of competition, the influence of pH becomes less important with increasing ligand concentration (0.01 and 0.05 mol L^{-1} of Na-thiosulfate). The final pH of the extracted soil solutions tending towards an alkaline pH indicated a soil environment favouring Hg fixation. However, to ensure Na-thiosulfate as a potential reagent for releasing Hg from our soil samples and to prevent acidic damage to the apparatus, experiments have been done without pH adjustment. Furthermore, as shown in Fig. 2, the suitable Na-thiosulfate concentration for releasing the soil-Hg was relatively high. Due to the small differences in extracted Hg with and without pH adjustment, experiments using high concentrations of the reagent were considered appropriate.

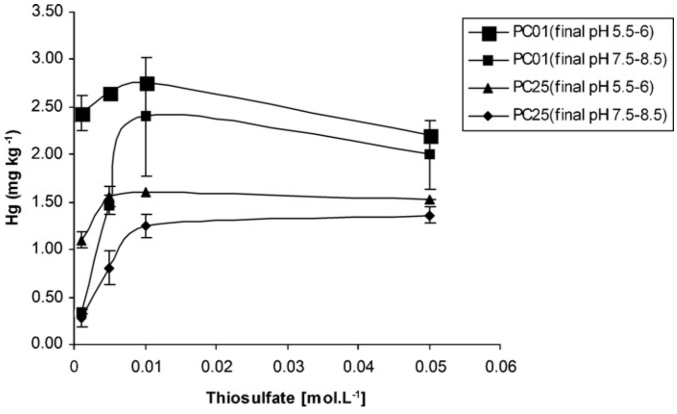

Fig. 4. pH effect on soil-Hg extraction using Na-thiosulfate.

3.2. Kinetic approach

Although equilibrium reactions of soil-Hg have been extensively studied, the kinetics of these reactions rarely appear in the literature. In most cases, due to the mobility of a soil solution, the retention and/or release reaction of the metal in soil is time dependent. This indicates the importance of kinetic extraction studies in order to predict the transport and fate of Hg extracted from soil.

The kinetic approach was based on the study of the desorption fluxes of Hg from the soil samples caused by the action of one specifically added chemical reagent. The results presented in Fig. 5 show similar curves of extracted Hg from both soil samples by using two concentrations of Na-thiosulfate, 0.001 and 0.05 mol L^{-1}. At equilibrium (24 h), 0.001 mol L^{-1} of Na-thiosulfate released 38 and 27% total Hg from the samples PC01 and PC25. At the higher reagent concentration, 50 ± 5% of total Hg was extracted from both soils (Fig. 2). Considering these proportions as the total extracted Hg, approximately 80% of Hg in all samples was obtained in the first

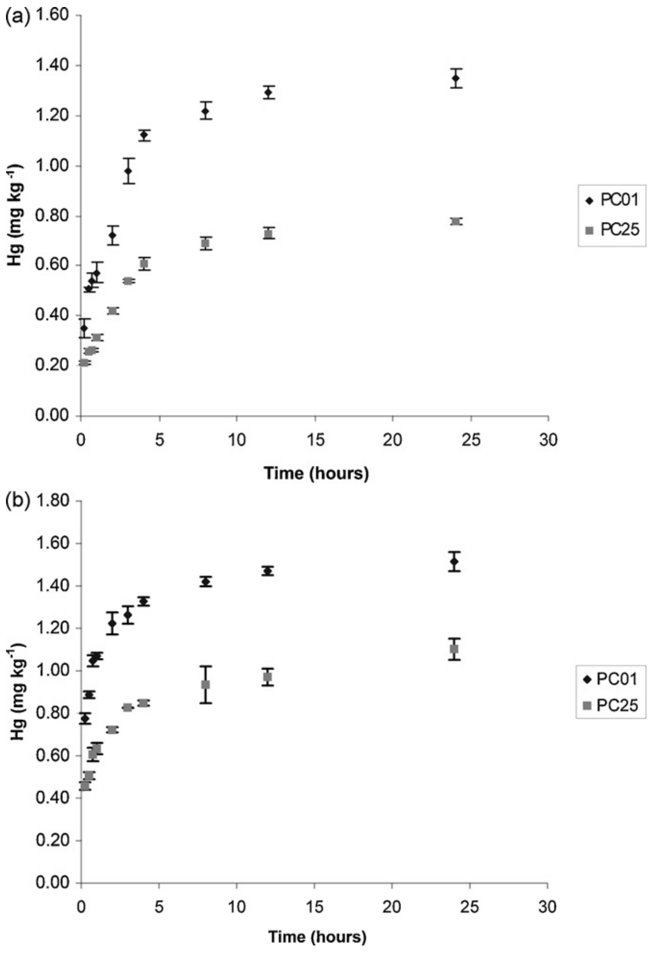

Fig. 5. Extraction kinetics of soil-Hg using Na-thiosulfate as a reagent (a) 0.001 mol L^{-1} of Na-thiosulfate and (b) 0.05 mol L^{-1} of Na-thiosulfate.

4 h of reaction times for both concentrations of Na-thiosulfate. The remaining 20% of total extracted Hg was released over the following period of 20 h (4 h < t < 24 h).

The experimental data demonstrated in Fig. 5 was first checked for the pertinence of the kinetic first-order model application (single or multiple first-order compartment(s)). The results were expressed in terms of Hg-removal rates per unit of time. Accordingly, the amount of Hg extracted per weight unit of soil (mg kg^{-1}) between extraction initiation time (t_i) and termination time (t_{i-1}) can be defined as:

$$\mathrm{Hg}(t_{i-1} < t < t_i) = [\mathrm{Hg}(t_i) - \mathrm{Hg}(t_{i-1})] \times \left[\frac{V}{m}\right] \tag{1}$$

where Hg concentration is determined as a function of the volume of extractant solution (V), and the sample mass (m) at a given time (t).

The removal rate (R_{Hg}) per unit of time, (t), between t_i and t_{i-1} can be written as:

$$R_{\mathrm{Hg}}(t_{i-1} < t < t_i) = \frac{\mathrm{Hg}_{(t_{i-1}<t<t_i)}}{t_i - t_{i-1}} \tag{2}$$

The mean values of $R_{\mathrm{Hg}}(t)$ were calculated and plotted in a semi-log diagram, which was another way to represent the data originally reported in Fig. 5. It appeared that the evolution of $R_{\mathrm{Hg}}(t)$ of both soils, in both reagent concentrations, occurred as two distinct linear segments with different non-null slopes as shown by the crossing of the intercepts on the Y-axis. Fig. 6 shows an example of the Hg extraction rate with 0.05 mol L^{-1} of Na-thiosulfate from soils PC01 and PC25. This difference of behaviour through time allowed the variable $R_{\mathrm{Hg}}(t)$ to be modeled by the sum of two distinct fractions occurring simultaneously, each of them followed an exponential decreasing function:

$$R_{\mathrm{Hg}}(t) = A_1(0)\mathrm{e}^{-k_1 t} + A_2(0)\mathrm{e}^{-k_2 t} \tag{3}$$

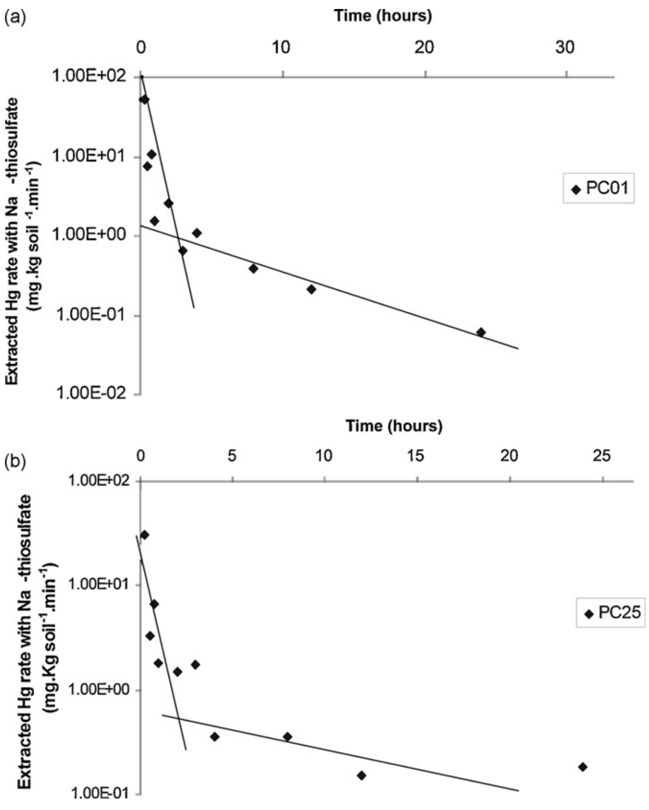

Fig. 6. Extracted Hg rate with 0.05 mol L^{-1} of Na-thiosulfate from both soil samples: (a) PC01 and (b) PC25.

where $A_1(0)$ and $A_2(0)$ are the initial Hg-removal rates (at $t = 0$) of the two fractions and k_1 and k_2 are their apparent rate constants.

In other words, the model used in the present work was simplified to a two first-order reaction model in order to classify the soil-Hg into three fractions that are the readily extractable (labile) fraction, the less extractable (slowly labile) fraction and the non-extractable fraction. Each fraction was associated with its own rate constant. Therefore, at time t, the total amount of Hg extracted, noted as $Q(t)$, was obtained by integrating $R_{\mathrm{Hg}}(t)/dt$:

$$Q(t) = \left[\left(\frac{A_1(0)}{k_1}\right)(1 - \mathrm{e}^{-k_1 t})\right] + \left[\left(\frac{A_2(0)}{k_2}\right)(1 - \mathrm{e}^{-k_2 t})\right] \tag{4}$$

or

$$Q(t) = Q_1^0(1 - \exp(-k_1 t)) + Q_2^0(1 - \exp(-k_2 t)) \tag{5}$$

where $(A_1(0)/k_1)$ and $(A_2(0)/k_2)$ were replaced by Q_1^0 and Q_2^0 (mg kg^{-1}) which corresponded, respectively, to the readily extractable Hg (labile) fraction and the less extractable (slowly labile) Hg fraction. Therefore, the un-extractable Hg fraction, noted as Q_3^0, was then deduced by the difference between the total concentration of Hg in soil, noted Q_{tot}, and the concentration of Hg extracted at equilibrium ($Q_1^0 + Q_2^0$). Sigma Plot software was used for fitting the experimental data presented in Fig. 5 to Eq. (5) in order to obtain the four kinetic parameters (Q_1^0, Q_2^0, k_1, and k_2) mentioned above. The amount of extracted Hg at equilibrium was the sum of its labile and slowly labile fractions released as a function of time. From a kinetic point of view, it should be mentioned that a two-compartment model has been reported to reveal the fractionation of trace metals in soil associated with two kinetically different compartments of soil for providing the information of metal bioavailability [26]. The feasibility of the two-compartment model has been successfully evaluated for many metals such as Cd, Cu, Fe and Pb [13–16] but, to our knowledge, no data for Hg in soil are available.

As previously noted, two extraction regimes corresponding to two different kinetic fractions could be obtained for PC01 and PC25 samples. Accordingly, the parameters Q_1^0, Q_2^0, k_1, k_2, the coefficient of correlation r, and the standard error of estimate S.E. for Hg in both soil samples using 0.001 and 0.05 mol L^{-1} of Na-thiosulfate are shown in Table 2. The values of Q_1^0 and Q_2^0 all have relative standard deviation values (R.S.D.) lower than 10%. The P value associated to each fit was always lower than 0.0001 and the coefficient of correlation was always higher than 0.97. Fig. 7 demonstrates representative curves calculated from the two first-order reactions model that fitted the extraction rate data of Hg in our experiments. Furthermore, the un-extractable Hg fraction, Q_3^0, could be deduced by the difference between the total concentration of Hg in soil and the concentration of Hg extracted at equilibrium ($Q_1^0 + Q_2^0$). As shown in Fig. 8, the distribution between Q_1^0, Q_2^0 and Q_3^0 of the

Table 2
Two first-order kinetic parameters of studied soils.

Sample	Parameters	Na-thiosulfate (mg kg^{-1})	
		0.001	0.05
PC01	Q_1^0 (mg kg^{-1})	1.01 ± 0.07	0.91 ± 0.05
	Q_2^0 (mg kg^{-1})	0.32 ± 0.07	0.58 ± 0.05
	k_1	8.8607	5.9087
	k_2	0.3260	0.3283
	r	0.986	0.987
	S.E. (mg kg^{-1})	0.0531	0.034
PC25	Q_1^0 (mg kg^{-1})	0.59 ± 0.02	0.54 ± 0.05
	Q_2^0 (mg kg^{-1})	0.17 ± 0.02	0.52 ± 0.05
	k_1	0.3048	5.9237
	k_2	0.1675	0.2161
	r	0.994	0.973
	S.E. (mg kg^{-1})	0.021	0.043

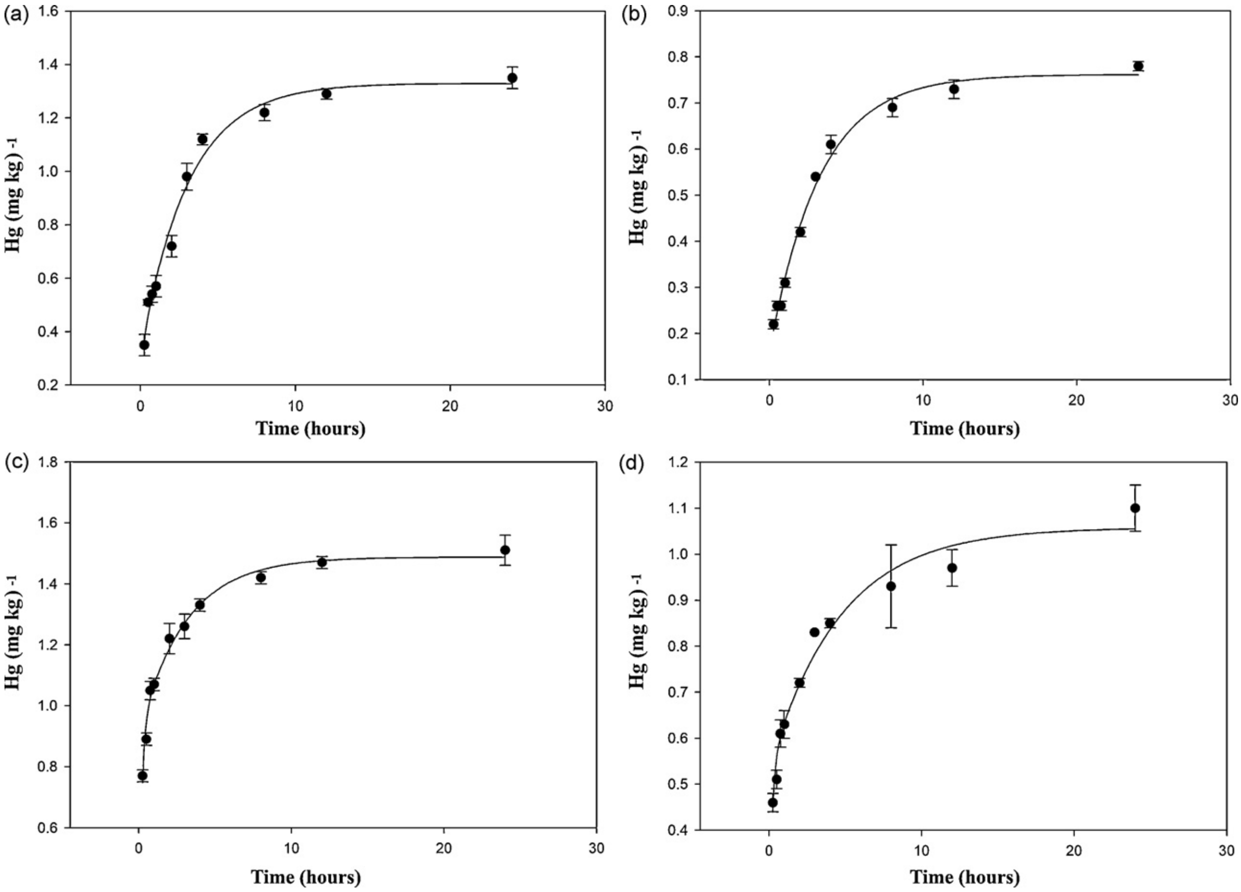

Fig. 7. Representative curves calculated from the two first-order reactions model, given by Sigma Plot software: (a) PC01/0.001 mol L^{-1} of Na-thiosulfate; (b) PC25/0.001 mol L^{-1} of Na-thiosulfate; (c) PC01/0.05 mol L^{-1} of Na-thiosulfate; (d) PC25/0.05 mol L^{-1} of Na-thiosulfate.

soil samples indicated that the Q_2^0 fraction was always lower than Q_1^0 fraction and that 60% of total Hg in all soils was un-extractable by 0.05 mol L^{-1} of Na-thiosulfate. The latter fraction, Q_3^0, might involve an insoluble form of Hg frequently present in soil such as HgS. For this purpose we used the protocol of Fernández-Martínez et al. [27] to determine HgS concentration by calculating the difference between total Hg and Hg extracted by 50% (v/v) HNO_3, a small portion of Q_3^0 could be defined as HgS, represented as Q_3^{HgS} in Fig. 8. Although 10% of the non-extractable fraction was different from those found in the "Equilibrium conditions study", this corresponded with the error gaps presented in Fig. 2. Thus, the stability of analytical solutions needs further investigating in order to confirm the efficiency of Na-thiosulfate throughout the soil-Hg extraction.

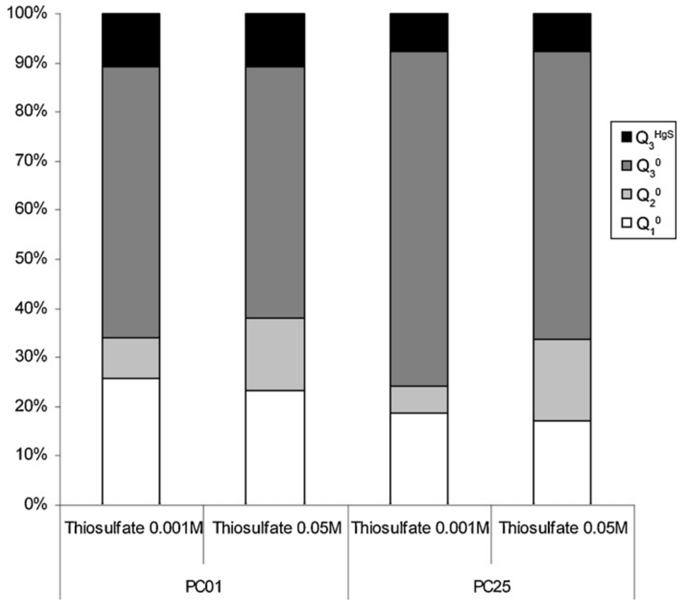

Fig. 8. Distribution of soil-Hg fractions in the soil samples between Q_1^0, Q_2^0, Q_3^0 and Q_3^{HgS} (NB: Q_1^0 = labile fraction; Q_2^0 = slowly labile fraction; Q_3^0 = un-extractable fraction; Q_3^{HgS} = un-extractable feaction defined as HgS).

As has been widely reported in the literature, in most cases, total Hg level found in soils corresponds to organic matter content (OM). We also observed the correlation between Q_1^0, Q_2^0 fractions and the amount of OM (112.45 and 71.98 g kg^{-1} for PC01 and PC25, respectively) presented in Table 1. Accordingly, the values of Q_1^0 and Q_2^0 of PC01 were higher than those of PC25. For a given soil sample, the Q_1^0 fraction was not significantly different at both concentrations of Na-thiosulfate, while the Q_2^0 fraction increased with increasing concentration of the applied reagent. All applied concentrations of Na-thiosulfate in this present work could extract the labile Hg fraction. The difference in quantities of the slowly labile Hg fraction resulting from the extracted Hg at equilibrium, were released as a function of the reagent concentrations.

It is well known that Hg has a strong affinity for sulphur and Skyllberg et al. quantified six different groups of sulphur functionalities in organic substances. These were in turn considered as major factors controlling the adsorption and desorption of Hg in soil [28–30]. Among these groups, reduced organic sulphur has been reported to play an important role in Hg retention in soil. They are supposed to be the strongest Hg fixation sites [12,13,31,32]. Regarding the stability constants of Hg and SOM proposed in liter-

Table 3
Quantity of calcium and iron extracted by different concentrations of Na-thiosulfate.

Na-thiosulfate [mol L^{-1}]	Ca [mg kg^{-1}]		Fe [mg kg^{-1}]	
	PC01	PC25	PC01	PC25
0.001	217.33 ± 13.25	271.17 ± 1.53	33.33 ± 5.45	55.30 ± 1.11
0.003	293.00 ± 34.39	322.67 ± 11.06	29.70 ± 3.90	43.27 ± 2.81
0.005	333.33 ± 71.19	354.40 ± 13.39	23.50 ± 2.72	37.83 ± 1.33
0.007	304.93 ± 5.29	397.95 ± 19.14	24.73 ± 2.06	33.47 ± 3.40
0.01	369.75 ± 7.80	460.89 ± 18.18	26.27 ± 1.37	30.47 ± 3.59
0.03	515.24 ± 33.21	643.42 ± 8.90	14.53 ± 1.74	21.03 ± 1.60
0.05	525.78 ± 15.20	686.68 ± 5.27	10.90 ± 0.66	14.82 ± 4.29

ature, the Hg fraction extracted by Na-thiosulfate might especially concern reduced sulphur groups contained in SOM [12,24,33]. Consequently, it seemed that the Hg present in our soil samples should involve the reduced organic sulphur contained in SOM as several powerful reagents (i.e. EDTA, DTPA and cysteine) other than Na-thiosulfate extracted lesser than 5% of total Hg content in the samples [results not shown]. It is worth noting that almost all Hg contained in the samples was strongly bounded to Hg fixation sites. However, it seemed that all high affinity sulphur sites present in PC01 and PC25 were unsaturated by total soil-Hg contents. Thus, the two Hg sub-fractions, binding with two different SOM-compartments resulting from the kinetic approach, could represent two different sites of the reduced sulphur groups extracted by Na-thiosulfate. Furthermore, our results were in agreement with the work of Skyllberg et al. in which two reduced organic sulphur groups contained in SOM had been determined to be complexed with Hg [32].

3.3. Reduction of soil-Hg to Hg(0) study

In soil, the redox transformation of Hg(II) to Hg(0) has been wildly studied. This process reveals the main cycle of Hg between the soil and the atmosphere, as well as the limitation of the remaining soil-Hg(II) concentration that is available for groundwater transportation and methylation. As the main objective of our work concerned soil-Hg extraction by Na-thiosulfate, the reductant characteristic of this reagent leads us to suppose that the production of Hg(0) may occur and introduce a bias in the determination of extracted Hg. Furthermore, it has been reported that, in an anoxic environment (reductant medium), the sorption of Fe(II) to mineral surfaces might enhance the reduction rate of soil-Hg(II) species [34–37]. This may also correspond to our study of soil-Hg extraction with Na-thiosulfate, as Fe(II) is considered as a major element in the medium. Therefore, in order to complete our experiments, the presence of produced Hg(0) was verified.

Based on the calibration curve of the reduced Hg obtained from different concentrations of a standard Hg solution, the estimation of the reduced Hg concentration from the soil samples using Na-thiosulfate as a reagent was determined. Hg(0) detection under the same conditions as in the "Equilibrium conditions study" was unsuccessful. This may be due to quantities of Hg(0) produced being smaller than the detection limit of the AAS apparatus, inappropriate accumulation times, or that there is no Hg(0) production.

Due to the reductive characteristics of Na-thiosulfate we believe that there is a strong probability that process is occurring. The Hg(0) production may however need other catalytic process to release it into the atmosphere. Therefore, a degassing process using N_2 was further performed. The soil PC01 was used for testing the production of Hg(0), using 0.001 and 0.05 mol. L^{-1} of Na-thiosulfate. The produced Hg(0) was accumulated during 4 and 8 h on the gold trap (amalgamation), with the flow rate degassing of 150 mL min^{-1}, before measuring its absorbance by atomic absorption spectrometry (AAS). The results showed the absorbance (abs) of 0.393 and 0.668 which respectively correspond to 0.054 and 0.11 mg kg^{-1} of Hg(0) during 4 and 8 h of accumulation by using 0.001 mol L^{-1} of Na-thiosulfate. At the higher concentration of the reagent, 0.05 mol L^{-1}, 0.25 and 0.43 mg kg^{-1} of Hg(0) were obtained for the accumulation times of 4 and 8 h, respectively. It is important to note that the experiment for Hg(0) determination was performed under extreme conditions in the degassing cell that should not be directly compared with previous fractionation results. The estimated Hg(0) produced should be considered as a higher threshold of vapour Hg that could be produced within our defined equilibrium conditions. The reductive characteristics of Na-thiosulfate have however been shown to be occurring as the production of Hg(0) increased with increasing concentrations of Na-thiosulfate, and increased of accumulation time. Consequently, it seemed reasonable to assume that a small amount of Hg(0) might be found in both equilibrium and kinetics extractions and that a sealed reaction vessel is therefore necessary.

To study the influence of Fe on Hg(0) production, two soil elements were investigated as a supplementary experiment beside the study of the reagent concentration effect on soil-Hg extraction. The first one was calcium (Ca) which represents a major soil element and the other one was iron (Fe) because its presence in soil had been reported to induce the reduction of Hg(II) to Hg(0) [34–37]. The complexation constants (log K) between the thiosulfate ligand and these two elements, Ca and Fe, were, respectively, 3.49 and 2.17 [33]. It had been expected that the extraction curves of these two elements would have the same tendency as the extracted Hg curve (Fig. 2). Our results showed that the quantity of extracted Ca increased with increasing Na-thiosulfate concentration while, as shown in Table 3, the amount of Fe decreased. The unexpected extraction curve of Fe could be explained by the adsorption of Fe(II) on soil particles according to the equation proposed in the work of Charlet et al. [34]:

$$\equiv \mathrm{SOH} + \mathrm{Fe}^{2+} + \mathrm{H_2O} \leftrightarrow \equiv \mathrm{SOFeOH} + 2\mathrm{H}^+ \qquad (6)$$

$$\equiv \mathrm{SOFeOH} + 1/2\mathrm{Hg(OH)}_{2(aq)} + \mathrm{H_2O} \leftrightarrow \equiv \mathrm{SOH} + \mathrm{Fe(OH)_3} + 1/2\mathrm{Hg^0}_{(aq)} \qquad (7)$$

where ≡SOFeOH is defined as surface complex of soil particles.

Therefore, the experiment performed in the "Equilibrium conditions study" seemed to enhance the reaction in Eq. (6) at higher concentrations of the reagent. The decrease in Fe with increasing Na-thiosulfate concentration might suggest the formation of Fe(II), induced by the reductive characteristic of the reagent, that should be strongly adsorbed on soil particles (≡SOFeOH). Furthermore, Table 3 showed that by using Na-thiosulfate, the quantity of extracted Ca increased with increased concentrations of the reagent. These results confirm the adsorption of Fe on soil particles as their surface complex-sites became more available for the Fe to be adsorbed. Accordingly, the experimental conditions for optimizing the extraction of soil-Hg at equilibrium might be favourable to oxidize the soil-adsorbed Fe(II) to Fe(III) (hydr)-oxides for providing the formation of Hg(0) as described in Eq. (7). As mentioned earlier, a small amount of Hg(0) may occur in our previous studies the "Equilibrium conditions study" and the "Kinetic approach", this could be probably be induced by the soil-adsorbed Fe(II). However, more detail research concerning the reduction of soil-Hg(II) to Hg(0) by the presence of Fe in the medium needs to be investigated.

4. Conclusion

We demonstrated here that 50 ± 5% of total Hg in the samples could be released by 0.01 mol L^{-1} of Na-thiosulfate without pH adjustment, using a solid-to-liquid ratio of 1:10. Above this concentration no further significant change was observed in the quantity of extracted Hg. Extracted Hg obtained by the use of Na-thiosulfate has been proposed to be strongly bound in soils as it could not be released by other powerful reagents such as EDTA, DTPA, and cysteine. Accordingly, Na-thiosulfate is an effective reagent for soil-Hg single extractions, especially when the metal is strongly bound to specific sites of organic matter. The non-extractable Hg remaining in the samples might correspond to the crystalline form of Hg frequently presented in soil such as HgS.

Results obtained from a kinetic extraction procedure were fitted to a two-compartment model and revealed the Hg fractionation associated with two kinetically different compartments of soil. Results obtained from this two-compartment model analysis indicate the presence of two Hg fractions binding with two different sites of the reduced sulphur groups contained in SOM. The efficiency of the kinetic extraction methodology should be considered as a specific tool of soil-Hg mobility for providing more information in the speciation field. Furthermore, according to the reductant characteristic of Na-thiosulfate, the loss of volatilized Hg during the soil-Hg extraction procedure was verified. Although the results implied an insignificant amount of Hg(0) that might occur during the extraction processes, the possibility of iron(II) present in soil for reducing Hg(II) to vapour Hg was observed. Thus, it should be considered that the risk of Hg mobility in soil increases in the reductive medium, especially with the presence of iron(II). Therefore, the reduction of Hg by Fe needs further investigation in order to better understand the dynamic of the metal in soil.

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