

**SNOWMAN NETWORK** Knowledge for sustainable soils

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Enhanced knowledge in mercury fate and transport for Improved Management of Hg soil contamination

# Mercury fate and transport in soil systems – Conceptual and mathematical model development and sensitivity study

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# Summary

This report presents a reactive model of mercury (Hg) transport and fate in soil systems. Chapter 1 briefly introduces the concept of reactive transport modelling and existing codes.

The main sources and sinks of Hg in soils, and dominant processes affecting Hg contamination from anthropogenic origin were identified in a previous report (Leterme and Jacques, 2014). Following this, a conceptual model is developed (Chapter 2), which includes those important processes and different Hg forms. In parallel, a specific thermodynamic database is built for Hg (excluding reactions with organic molecules) and verified against existing literature by drawing predominance diagrams (Chapter 3).

The model is then numerically implemented in the HP1 code (Chapter 4), accounting for transport processes, Hg speciation, Hg sorption to soil organic matter (SOM; distinguishing thiol groups and humic and fulvic acids), and Hg reduction and volatilization. Initial Hg contamination can be as a solid phase (e.g. cinnabar), as elemental (non-aqueous phase liquid; NAPL) Hg, or as an aqueous species. Kinetic dissolution of solid phase Hg or NAPL releases Hg into the aqueous phase. Dissolved organic matter (DOM), an important ligand of aqueous Hg species, is brought to the system via rain water and can itself sorb to the soil mineral phase.

Virtual simulation cases are designed to test the numerical model (Chapter 5). The basic scenario consists of 50 years of daily atmospheric input (temperate climate) and free drainage bottom boundary condition (deep groundwater, oxidising conditions) on a 1-m sandy soil profile with a grass cover. SOM is uniformly distributed in the top 30 cm, and the initial Hg contamination is assumed to be found in the top 10 cm.

A set of seven base case simulations are examined in Chapter 6, in which the initial Hg source is either in a unique form (solid, NAPL, aqueous Hg), or a combination of several forms. Results are evaluated (typically after 5, 25 and 50 years) in terms of volatilized Hg, Hg leached at the bottom of the soil profile, and Hg still present in the soil in or below the horizon of initial contamination.

To get a better understanding of Hg fate, a detailed sensitivity analysis is performed (Chapter 1). Firstly, a one-at-a-time (local) method is applied, using parameter ranges from the literature or userdefined. Secondly, the elementary effects (global) method is applied, in order to gain insights into linear and additive effect of parameter sensitivity, as well as non-linear effects and interactions between parameters.

Processes and parameters identified as critical based on the sensitivity analyses are found to depend on the pollution type (solid Hg, NAPL, aqueous Hg), on the indicator assessed (leached Hg, Hg in soil horizon originally polluted...) and on time (after 5, 25 or 50 years). However, DOM concentration in rain/soil water is generally the most critical parameter. Other important parameters are those related to Hg sorption on SOM (thiols, and humic and fulvic acids), and to Hg complexation with DOM.

Finally, potential applications of the model for the study and remediation of Hg contaminated sites are briefly discussed in Chapter 1. This Chapter also identifies shortcomings of the present modelling study and gives recommendations about further developments.

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# 1 Reactive transport modelling

Reactive transport modelling solves governing equations of water and solute transport and allows at the same time aqueous geochemical reactions. A detailed discussion of the concepts and applications of reactive transport modelling can be found in Steefel et al. (2005).

A number of softwares have been recently developed that fall into this category of models, including MIN3P (Mayer et al., 2002), PHT3D (Prommer et al., 2003), HYDROGEOCHEM (Yeh et al., 2004), PHWAT (Mao et al., 2006), HP1 (Jacques and Šimůnek, 2005, 2010), CRUNCHFLOW (Steefel, 2009), PHAST (Parkhurst et al., 2010), RICH-PHREEQ (Wissmeier and Barry, 2010). Among these, MIN3P, HYDROGEOCHEM, HP1, CRUNCHFLOW and RICH-PHREEQ can simulate variably-saturated flow.

In the present study, HP1 is chosen because it is flexible enough to represent the key processes identified for Hg modelling (cf. Chapters 2 and 4); and it is based on two softwares that have been extensively used and validated : HYDRUS-1D (Šimůnek et al., 2008) for water and solute transport and PHREEQC (Parkhurst and Appelo, 1999) for geochemical calculations. Moreover, code access and high level of support are ensured as HP1 code developer D. Jacques is member of the IMaHg project.

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# 2 Conceptual model

## 2.1 Introduction

Figure 1 is taken as a reference for processes and phases of mercury in soils. Given the context within which the model is developed (i.e. focus on the vadose zone and management of industrial contaminated land), some of these processes need to be accounted for, while others can be neglected (see Table 1).



#### Figure 1 – Mercury sources (in blue), sinks (in orange) and phases in soil (in grey). Source: Leterme and Jacques (2014).

The conceptualization of the processes identified as important for modeling mercury fate and transport is presented in sections 2.2 to 2.10. Section 2.11 summarizes phase transitions and Hg speciation in the conceptual model.

Process included in conceptual model	Justification
Aqueous speciation and complexation	Determines Hg mobility in soils.
Sorption / desorption	Major process influencing Hg mobility in soils. Mercury strongly sorbs to organic matter, and to mineral surfaces (oxides, hydroxides, oxyhydroxides of Fe/Mn/Al).
Leaching	Advective-dispersive and diffusive transport processes influence the mobility of dissolved Hg species.
Hg <sup>II</sup> precipitation / dissolution	Mercury is frequently found in solid phase (mainly as Hgs(s) or HgO(s)) in contaminated soils. Therefore dissolution is potentially an important source of Hg in the aqueous phase. Probably not relevant as geogenic source for most applications in the vadose zone.
	Precipitation may play a role depending on Hg concentration (precipitated HgS identified as Hg transport process in Slowey et al., 2005). Solid Hg is sometimes observed on contaminated sites even when thermodynamic shows that it all should be dissolved.
NAPL dissolution	As a dense liquid, with relatively low viscosity, mercury can flow through the vadose zone (high mobility; see Gerhard et al., 2007). However, after long drainage period, residual and entrapped mercury are still present in the " residual mercury saturation for mercury of 0.04 and 0.08 (= volume of mercury trapped in the pores relative to its void space) for coarse and fine sand, respectively. Contamination of the subsurface from NAPL can happen through dissolution and volatilization. Direct NAPL volatilization is neglected in the conceptual model, but is considered indirectly as Hg <sup>II</sup> reduction to Hg <sup>0</sup> and volatilization is included (see below).
Hg volatilization from soils	Rinklebe et al. (2010) measured a maximum emission rate of 0.85 $\mu$ g m <sup>-2</sup> h <sup>-1</sup> Hg from heavily polluted floodplain soils. For a 30 cm thick surface horizon with a bulk density of 1.3 g cm <sup>-3</sup> and assuming no limitation of Hg source for volatilization, one can estimate that Hg concentration in soil would decrease by less than 0.01 mg kg <sup>-1</sup> per year. This is negligible compared to the concentrations found on sites of anthropogenic contamination (~10 <sup>0</sup> -10 <sup>4</sup> mg kg <sup>-1</sup> ).
	However, Schlüter (2000) reported in his review maximum emission rates of $3.4 \times 10^5 \mu g  m^{-2}  h^{-1}$ at 1 km of a cinnabar mine. Using the assumptions above, this gives approximately a decrease of 70 mg kg <sup>-1</sup> per year. Other values reported for contaminated areas are ~2×10 <sup>5</sup> $\mu g  m^{-2}  h^{-1}$ emission from soils with contamination of ~50-200 mg kg <sup>-1</sup> . Such emission rates are not negligible.
Colloid transport	Identified as an important transport process in several case studies (e.g. Santoro et al., 2010).
Methylation/demethylation	Lesser priority because not often important in terms of quantities (MMHg is usually less than 2% of the total mercury concentration in oxic conditions), but may be important in terms of toxicity. Main methane source is wetlands, but in oxic soils it is $CH_4$ from atm. (Le Mer and Roger, 2001) ( $CH_4$ in atm. ~1.82 ppm).
Process neglected in conceptual model	Justification
Atmospheric wet and dry deposition	Minor Hg sources compared to concentrations encountered on contaminated sites. If necessary though, atmospheric wet deposition may easily be included in the solution used as top boundary condition (for example in the case where anthropogenic contamination has been found to occur via Hg volatilization and deposition)
NAPL migration and entrapment	HP1 does not include transport of a NAPL phase. Furthemore, for remediation of contaminated sites, it can be expected that only residual and entrapped NAPL are present. Therefore it may not be necessary to simulate NAPL migration in the unsaturated zone. If needed, NAPL concentration may be measured in the field for a given application; or simple models of NAPL migration (see Annex 6.1 in report "Part 1 – Literature review") may be used before geochemical modeling to define initial/boundary conditions
Vegetation uptake and litterfall	Hg uptake is very low in general (Schuster, 1991; Pant et al., 2010); litterfall can be an important Hg source in forests (Obrist et al., 2011) but is a minor source of contamination compared to anthropogenic sources

# Table 1 – Selection and justification of the processes to include in the conceptual model of mercury fate and transport in soil systems.

## 2.2 Transport processes

Transport of aqueous species of Hg is described by the advection-dispersion equation. The spatial and temporal variable advective term governed by the Darcy water flux is obtained from the Richards equation for variably saturated water flow taking into account precipitation, soil evaporation and transpiration (or root water uptake). Diffusion in the water phase is not considered because this transport mechanism is small compared to the hydrodynamic dispersion component. Diffusion of  $Hg^{0}(g)$  in the gas phase is also included; in such a way, volatilization processes can be simulated based on an exchange process between the gaseous and aqueous phases following Henry's law.

## 2.3 Speciation of Hg

The Hg speciation in the soil mainly includes two oxidation states of Hg (Hg<sup>0</sup> and Hg<sup>II</sup>). The focus of this study is on well-drained soil conditions, so we first consider oxidising conditions only (i.e. deep water table). Under these conditions, the forms of methylmercury and dimethylmercury are not considered here (see section 2.4 in Leterme and Jacques (2014), and section 2.10). We can distinguish the following relevant groups of species:

- Free Hg<sup>0</sup> both as an aqueous and a gaseous species;
- Organic and inorganic ligands forming aqueous complexes with Hg<sup>II</sup>;
- Sorbed Hg<sup>II</sup> species on soil organic matter;
- Hg incorporated as Hg<sup>II</sup> or Hg<sup>0</sup> in solid phases.

The database IM003\_THERMODDEM (Blanc et al., 2012a) is used for aqueous complexation, augmented with some Hg speciation data from Skyllberg (2012). This is further detailed in Chapter 3.

Given the strength of Hg<sup>II</sup>-DOM (Dissolved Organic Matter) interactions, Hg<sup>II</sup> binding by DOM should dominate over inorganic speciation under all except extreme conditions of contamination (Haitzer et al., 2003; Skyllberg, 2012). Therefore the main challenge is to adequately model of Hg<sup>II</sup> complexation with DOM and SOM (see also section 2.4). Organic matter heterogeneity, electrostatic effects, and the paucity of stability constants for Hg–DOM complexes cause difficulties for model parameterisation (Ravichandran, 2004).

Complexation with organic compounds is not considered in IM003\_THERMODDEM. Four organic compounds (three representing FA and HA, and one representing thiols) are therefore added directly in HP1 input files. Interactions between Hg and these dissolved organic ligands are modelled as aqueous complexation reactions.

Finally, one issue for mercury in polluted areas is that speciation can be very different even with same source compound but different local conditions. For instance in gold mine tailings, predominant Hg species vary considerably from one site to another. Certain processes in contaminated sites may be very specific due to local circumstances and thus may not be consistent with predictions of thermodynamics. Therefore, some processes need to be modelled independently of the thermodynamic database to be possible to occur in the simulations (e.g. a certain amount of Hg<sup>II</sup> reduction to Hg<sup>0</sup> even in oxic conditions; see section 4.6).

## 2.4 Hg sorption to DOM

Different approaches have been used to characterise SOM (Soil Organic Matter) (and DOM) in geochemical models. For example, in applications using the WHAM VI database (Tipping, 2007; Feyte et al., 2010) (see Annex 9.1), four strongly-acid groups (type A; mainly carboxylic acid groups) and four weaker acid groups (type B; e.g. phenolic acids) are modelled. Metal binding at the type A and B sites is described with equilibrium constants ( $K_{MA}$ ,  $K_{MB}$ ) and associated "spread factors" (around the mean)  $\Delta LK_{A1}$  and  $\Delta LK_{B1}$ . Additional binding site heterogeneity is generated by a parameter,  $\Delta LK_2$ , that characterises the tendency of the metal to interact with "softer" ligand atoms. This feature ( $\Delta LK_2$ ) increases the binding constants for a small number of bidentate and tridentate sites and was found critical in modelling Hg and MeHg speciation (Tipping, 2007).

In Visual Minteq (see Annex 9.2), the Stockholm Humic Model (SHM ; Gustafsson, 2001) uses a similar procedure, with the empirical parameter  $\Delta$ LK2 accounting for binding site heterogeneity of humic and fulvic acids.

In PHREEQC (and hence HP1), Hg sorption to SOM may be modelled using either a surface complexation model or exchange sites. The default surface-complexation model uses a generalized two-layer model with no explicit calculation of the diffuse-layer composition. Alternatively, an electrostatic double layer model with explicit calculation of the diffuse-layer composition may be used; or a non-electrostatic model may be selected (Parkhurst and Appelo, 1999). Ion-exchange equilibria are included in PHREEQC through heterogeneous mass-action equations and mole-balance equations for exchange sites (Parkhurst and Appelo, 1999). PHREEQC allows multiple exchangers, termed an "exchange assemblage".

It is expected that choosing surface complexation or exchange sites does not have a significant impact in the present case, as Hg affinity for DOM and SOM will be much higher than for other ligands. Implementing a surface complexation model of the type of WHAM or SHM is possible in PHREEQC but falls outside of the scope of the present modelling approach.

Table 2 summarizes the kinetics of Hg sorption in soil derived from a number of batch experiments. Rapid initial sorption dominates; equilibrium Hg sorption to SOM may confidently be assumed in the present study given the fact that daily simulation time steps are used.

Sorption site	Information on kinetics	Reference
5 different soils	Equilibrium reached between 24 and 48h	Amacher et al. (1990) cited by Liao et al. (2009)
3 sandy loam and 1	Biphasic patterns:	Yin et al. (1997)
Storry loan Solis	- Sorption: within 2 min Hg sorbed is 4- 38% of Hg sorbed after 5h	
	<ul> <li>Desorption: within 100 min Hg desorbed is 62-81% of Hg released after 8h</li> </ul>	
3 different soils	- Sorption: >90% within 24h	Liao et al. (2009)
	<ul> <li>Desorption: depends on soil type (a few days)</li> </ul>	
River sediments	- Rapid initial sorption within 1h	Parkpoin et al. (2001)
	- Equilibration within 24h	
HA, Ferrih-HA, SW- Ferrih, HA	No detailed information on kinetics, batch equilibration in 24h	Cruz-Guzmán et al. (2003)
Kaolinite Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	<ul> <li>Influence of thiols and caroboxylic groups on desorption is pH dependent: 10% vs. &gt;90% within 2h at pH 7 vs. pH 3</li> </ul>	Senevirathna et al. (2011)
	<ul> <li>Thiols inhibit desorption at early times (first 80 min only 20% desorption) due to formation of ternary complexes</li> </ul>	

Table 2 – Kinetics of Hg sorption in soils derived from batch experiments.

## 2.5 Colloid transport

Colloids facilitating Hg transport may be of three types: clay minerals, metal oxides and organic matter (humic and fulvic acids). Among these, organic matter will play the main role given mercury greater affinity for humic and fulvic acids.

The majority of models that consider colloid-facilitated transport of heavy metals use distribution coefficients to account for the interactions between colloids and contaminants (e.g. Li et al., 2004; Kim and Kim, 2007). However, these models often consider flow and transport only in saturated groundwater systems, usually for steady-state flow (Šimůnek et al., 2006). Flury and Qiu (2008) reviewed conceptual models used to describe colloid-facilitated contaminant transport in the vadose zone, i.e. accounting for colloid interactions with the air–water interface.

HYDRUS-1D includes a package describing colloid-facilitated transport in the unsaturated zone (Šimůnek et al., 2006). However, for the present case, little or no literature data, nor experimental results were available to confidently assign values to the (many) parameters of this package. Using default values or best guessed parameters would only increase modelling uncertainty and the number of parameters to include in the sensitivity analysis without much benefit to understanding processes. As Flury and Qiu (2008) noted, "the modelling of colloid-facilitated contaminant transport in the vadose zone has mostly been theoretical, and tested only with column experiments; field applications are still lacking".

Instead, colloid-facilitated transport was implicitly accounted for by mercury complexation with DOM ligands (see section 2.2). If Hg<sup>2+</sup> is transported mainly as a complex of DOM, then this "colloid" transport can be modelled as a simple solute transport.

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Other possibilities for modelling Hg–colloid interactions may exist in PHREEQC (e.g. "change\_surf" together with "SURFACE" command, to change the status of part of a surface from mobile to immobile or immobile to mobile), and can be explored at a further stage.

## 2.6 Solid phase : dissolution and precipitation

Kinetics have to be used to describe dissolution of Hg solid forms (e.g. cinnabar, montroydite), because they are frequently observed in contaminated sites although this can hardly be explained based on thermodynamic database and reactions only (different redox states etc.).

Dissolution rate of cinnabar was shown to depend on DOC (dissolved organic carbon) (Waples et al., 2005). In HP1, a first order rate equation (based on parameters from Waples et al., 2005) was implemented for describing cinnabar dissolution when Hg solid phase was considered as a contamination source:

$$M(t) = M_0 e^{-\lambda DOC t}$$
<sup>(1)</sup>

where M(t) (M) is cinnabar mass at time t,  $M_{\theta}$  is the initial cinnabar mass in soil, *DOC* (M) is the dissolved organic carbon at time t and  $\lambda$  (T<sup>-1</sup> M<sup>-1</sup>) is the dissolution rate per unit mass DOC.

Alternatively for montroydite, experimental results and kinetics of dissolution are available in Hocsman et al. (2006).

## 2.7 NAPL dissolution

The vast majority of NAPL dissolution models were developed for saturated media (and often for chlorinated DNAPLs – PCE and degradation products). Models for NAPL in groundwater usually quantify the flux of contaminant from the NAPL to the aqueous phase. Several approaches exist for characterizing the relationship between mass flux reduction and mass removal, based on "source-depletion" models or simple "mass-removal" functions (e.g. Jawitz et al., 2005; Basu et al., 2008; Brusseau et al., 2008). However, these models often require specific parameters such as mass transfer coefficient and specific interfacial area between phases, which are currently not available for a Hg<sup>0</sup>-air-water system.

A simple dissolution model with a first-order rate equation (taken from NAPL dissolution models in Zhu and Sykes (2004)) was implemented in HP1 :

$$M(t) = M_0 e^{-\lambda t}$$

where M(t) (M) is Hg NAPL mass at time t,  $M_{\theta}$  is the initial Hg NAPL mass in soil and  $\lambda$  (T<sup>-1</sup>) is the dissolution rate. Due to the paucity of data on Hg NAPL, no dissolution rate could be derived from the literature. Realistic dissolution rates can be approximated to some extent by observed persistence time of Hg NAPL in soils (e.g. Bloom et al., 2003). However, it remains a very uncertain parameter and different values were tested in the sensitivity analysis (Chapter 1).

# 2.8 Hg<sup>II</sup> reduction and volatilization

Sunlight (and heat emitted from sunlight) are considered the most important factors driving Hg<sup>0</sup> volatilization, but also water content plays a role (volatilization increases with increasing water content up to a certain level). However, for soils contaminated with non-volatile mercury species, it can be

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(2)

expected that the production of volatile mercury (i.e. not the meteorological conditions) is the evaporation rate limiting process (Schlüter, 2000).

Starting from Hg<sup>II</sup>(aq), mercury volatilization can be decomposed in two reactions :

$$Hg^{2+} + H_2O \leftrightarrows Hg^0(aq) + \frac{1}{2}O_2 + 2H^+$$
(3)  

$$log k = -20.649$$
  

$$Hg^0(aq) \leftrightarrows Hg^0(g)$$
(4)  

$$log k = 0.924$$

where the log k values are from IM003\_THERMODDEM database. Thermodynamically mercury volatilization seems thus not favoured in the present case under the (assumed) prevailing oxidizing conditions, but Hg(g) emissions are often observed in contaminated sites. Therefore it was decided to implement a (pseudo-first-order) kinetic reaction in HP1 for the reduction of Hg<sup>II</sup> to Hg<sup>0</sup> (Eq. (3)). This reaction was applied only to the top 5 cm of the soil profile (see section 4.6), accounting for the influence of sunlight and heat to the topsoil only.

#### 2.9 DOM sorption to minerals

DOM sorption on soil is largely due to ligand exchange between DOM and hydroxyl groups on the soil mineral surface (Shen, 1999). Al and Fe oxyhydroxides are particularly strong sorption sites for DOM. The strength of the sorption relates to the surface area but more importantly to the surface properties of the sorbing mineral phase and to the chemical structure of the sorbing DOM (Kaiser and Guggenberger, 2000).

The rapid kinetics of sorption processes between the mineral soils and DOM allows steady-state conditions to occur within minutes (Kothawala et al., 2009). Therefore in the present study equilibrium will be considered for DOM sorption to soil minerals. A Langmuir isotherm is chosen (see section 4.7), based on the results of Kothawala et al. (2008) using 52 mineral soil samples.

## 2.10 Methylation / demethylation

Mercury methylation (Eq. (5) and (6)) is included in IM003\_THERMODDEM database, but requires that  $CH_4$  be modelled in the system.

$Hg^{++} + CH_{4,aq} \xrightarrow{Bacteria} CH_3Hg^+ + H^+$	Mono-MetylMercury (MMHg)	(5)
$CH_{3}Hg^{+} + CH_{4,aq} \longrightarrow (CH_{3})_{2}Hg + H^{+}$	Di - MethylMerary (DMHg)	(6)

In an oxic environment, the main methane source is from the atmosphere (Le Mer and Roger, 2001). Similarly to Hg, the partitioning of MMHg will be determined by the binding to thiol groups and in turn its partitioning between SOM and DOM (Skyllberg, 2012).

## 2.11 Conclusion

Figure 2 depicts how mercury speciation is modelled in the solid, aqueous and gas phase in the soil. In this model, mercury contamination source can be in the solid, aqueous and/or non aqueous liquid phase(s). Several kinetic reactions are implemented, notably to include processes observed in contaminated sites but that would not happen in a model solely based on thermodynamic equilibrium assumptions.



Figure 2 – Conceptual model of Hg speciation and reactions in the solid, aqueous and gas phases. Initial mercury contamination can be present in NAPL, solid, and/or aqueous phase (see section 5.1). Note that mercury (de)methylation is not implemented in the current version of the model.

# 3 Building a thermodynamic database for Hg

The thermodynamic database Thermoddem (Blanc et al., 2012) will be updated with data for mercury. This chapter outlines the procedure and the data (text is based on Blanc (2013)).

## 3.1 Technical aspects

#### 3.1.1 Calculation tools

Technically, this work uses the database Thermoddem (Blanc et al., 2012b), updated in 2011-2012. The database is implemented through the codes GWB (Bethke, 2002) and PHREEQC (Parkhurst and Appelo, 1999). The activity model is the Bdot (Parkhurst and Appelo, 1999) and all the thermodynamic relations are detailed in (Blanc et al., 2012b).

#### 3.1.2 Processing the selection

In the Thermoddem selection process, internal consistency is first ensured by selecting elements entropies from the CODATA (Cox et al., 1989) review. Next, the primary species properties are required in order to take into account equilibria in aqueous media. Those are selected from review papers like Baes and Mesmer (1976), in consistency with the selection for the element and the CODATA conventions. This selection is tested by using a simple, oxide/hydroxide, test case:

When available, a set of thermodynamic properties, from direct calorimetric measurements, is selected. Then, the LogK(T) function is calculated by using the previous primary specie properties. If a match is found, then this confirms the selection for both the primary specie and the solid phase properties. From that stage, the speciation in the water – element system may be investigated, followed by other sub-systems.

Thereafter, the verification is held on essentially by drawing predominance diagrams. This way, it is possible to the consistency of the selection by detecting the contradictions or the errors with respect to literature results

## 3.2 Selection of the thermodynamic species

Mercury possesses 3 oxidation degrees: 0, 1 and 2. In solution, it exists mainly as divalent or neutral complexes (Thomassin and Touze, 2003). In reduced environment, It complexes with sulfides under the dominant HgS(aq) form. In oxidized media, it is present as  $Hg^{+2}$  or the neutral Hg(OH)<sub>2</sub>, specie. But as soon as chloride is present it is readily involved in the complexing process to produce new species (Ullrich et al., 2001).

Methylated forms of Hg can also be synthesized by microbial activity. Monomethylmercury forms some quite stable complexes with methyl groups like  $CH_3HgOH$  or  $CH_3HgCI$  when chloride is available. In continental surface water, it happens to represent up to 30% of the total dissolved mercury concentrations, albeit this amount is strongly reduced in soil because of the complexation with organic matter (see Skyllberg, 2012; Leterme and Jacques, 2014). Methylmercury is especially toxic for living beings (Thomassin and Touze, 2003).

In addition, it has to be added that mercury is strongly adsorbed by humic acids (Zhang and Lindberg, 1999), which association may represent the main migration vector of the metal for acid pHs. Skyllberg (2012) states also that the complexation with humic acids may be involved even at higher pHs.

However, it is usually reported that, in near neutral to basic conditions, the adsorption proceeds also onto iron or manganese oxides/hydroxides surfaces (Cossa and Ficht, 1999).

The selection is reported on Table 3 for aqueous species and on

Table 4 for solids and gases.

The case of thiols-humic acids complexes is considered thereafter, in a specific section.

#### 3.2.1 The Hg-O-H<sub>2</sub>O system

According to Thermoddem selection rules, the first set is given by considering Codata (Cox et al., 1989) selection. It includes Hg(I), Hg(g), Hg(aq), Hg(II), Hg<sub>2</sub>(II), HgO<sub>cr</sub>, Hg<sub>2</sub>Cl<sub>2</sub> and Hg<sub>2</sub>SO<sub>4</sub>. Except for Hg(I) and Hg(g), the heat capacity functions Cp(T) are not provided there and are to be completed from other sources.

The main source for the Cp(T) functions of aqueous species is the work of Bessinger and Apps (2005) where HKF parameters (including dependences of the LogK(T) function with respect to T and P) are derived for complexes Hg(aq), Hg(OH)<sub>2</sub>, Hg(HS)- and Hg(HS)<sub>2</sub>. This is completed with other sources when this is possible.

Little verification could be held because of a lack of experimental data. At least we could check the solubility of Hg(I) as a function of temperature. This is reported in Figure 3 and the agreements between calculated LogK(T) and the experimental points allows to justify the selection for the entropy of Hg(I) and the properties of Hg(aq).

Similarly, the solubility of  $HgO_{cr}$  is investigated as function of temperature in order to check the properties of both this solid phase and the main aqueous complex Hg(OH)2,aq. As reported by Baes and Mesmer (1976) the solid has three polymorphs: yellow and red orthorhombic and hexagonal forms. In Figure 4, the LogK(T) function of  $HgO_{cr}$  is calculated using Codata (Cox et al., 1989) selection from calorimetric measurements on red orthorhombic HgO. The experimental points on Figure 4 concern the three phases. Especially for Aurivillius and von Heidenstam (1961) data, the figure reports points corresponding to the red form and the hexagonal form (Montroydite). The points for the yellow form would be located between both series. Even if we only have a few experimental data, it appears that their dispersion, especially as a function of temperature, prevents to make an accurate distinction of the different polytypes. Thus we will consider, for the rest of the study, the solid HgO<sub>cr</sub>, with thermodynamic properties selected from Cox et al. (1989).

For the complex  $Hg(OH)_{2,aq}$ , from Figure 4 we were able to slightly adjust its thermodynamic properties from the original values from Bessinger and Apps (2005), with a modification of the equilibrium constant from -6.17 to -6.08 and of its entropy from 162 to 156 J/mol.K.

Apart from Baes and Mesmer (1976), no recent work is discussing the properties of polynuclear complexes or of complexes more hydroxylated than  $Hg(OH)_{2,aq}$ . There have been evidences that, at pH > 10-11, the solubility of Hg should increase (Hagelberg, 2006). This is the reason why we are including such complexes in the selection. Unfortunately, the data could not be used in order to derive constants. Finally, we have included in the present selection the properties provided by Baes and Mesmer (1976) for Hg<sub>2</sub>(OH)<sup>+</sup>, Hg<sub>2</sub>(OH)<sup>+3</sup> and Hg<sub>3</sub>(OH)<sup>3+</sup><sub>3</sub>.

#### 3.2.2 The Hg-Cl-H<sub>2</sub>O system

This system displays four main complexes HgCl<sup>+</sup>, HgCl<sub>2</sub>, HgCl<sup>3-</sup>, HgCl<sup>4-</sup><sub>2</sub>, whose equilibrium constant are discussed and derived by Baes and Mesmer (1976) and confirmed by Powell et al. (2005). The entropy and HKF coefficients are issued from the compilation of Sverjensky et al. (1997), the only source, to our knowledge. The speciation is completed by an additional hydroxylated complex HgOHCl(aq). The latter may represent a non-negligible part of dissolved mercury, according to Thomassin and Touze (2003). Its properties are issued from the Baes and Mesmer (1976) compilation.

The thermodynamic properties of solid  $HgCl_2$  calomel have been derived, at 25°C by Cox et al. (1989). They are completed by the Cp(T) function, extracted from the selection of Chase et al. (1985).

#### 3.2.3 The Hg-S-H<sub>2</sub>O system

The sulfide system is of special importance for mercury mobility, since its solubility increases strongly in those environments (Thomassin and Touze, 2003).

The main solid phase is cinnabar, with an alpha and a beta form, the polymorphic transition occurring at 618K. The main sources for thermodynamic data are well summarized by Helgeson et al. (1978) including the properties of the phase transition reaction, and confirmed by Bessinger and Apps (2005) and we have adopted those values.

The complexation of sulfides species is more complicated and debated case. The overall tendency is a constant concentration of mercury, in reduced and sulfide dominated environments, up to pH 6. Then the concentration of mercury increases as the pH increases. At low pHs, until pH 6, an agreement is found in the literature (Skyllberg et al., 2003) in considering first Hg(HS)-, then Hg(HS)<sub>2</sub> as the dominant species (Bessinger and Apps, 2005). For pH higher than 6, no agreement could be found concerning the stoichiometry of mercury sulfide complexes (Krupp, 1988). Following Skyllberg et al. (2003), we are adding to the speciation model the complex HgS<sup>2-</sup><sub>2</sub> whose properties are issued from the synthesis of Benoit et al. (1999). Even trying to verify such a model is complicated because the work dedicated to that matter may have undergone some experimental and analytical artefacts (Skyllberg et al., 2003).



Figure 3 – Hg(I) – Hg(aq) equilibrium as a function of temperature. Source: Blanc (2013).



Figure 4 –  $HgO_{cr}$  –  $Hg(OH)_2(aq)$  equilibrium as a function of temperature. Source: Blanc (2013).

For the sulfate system, the main discussion is held by Powell et al. (2005). They provide an equilibrium constant at 25°C for the  $Hg(SO_4)_{aq}$  specie formation, at 0.5M NaClO<sub>4</sub>, LogK = 1.4. Thermodynamic properties of  $Hg_2SO_{4,cr}$  are discussed and extracted by Cox et al. (1989) and completed, for the Cp(T) function, with data provided by Barin et al. (1977).

#### 3.2.4 Mercury carbonates and phosphates

In that case the Powell et al. (2005) discussion allows getting a clear idea of the available data and their quality.

The solid HgCO<sub>2</sub>.2HgO seems to be the most reliable carbonated solid phase, bearing mercury. It comes along with a set of three complexes: HgCO<sub>3</sub>, Hg(OH)CO<sub>3</sub><sup>-</sup> and HgHCO<sub>3</sub><sup>+</sup>. For all those complexes and the solid phase, the authors provides the 25°C equilibrium constant but no enthalpy of reaction, nor entropy seems to be available, so far.

For mercury phosphates, the synthesis from Powell et al. (2005) provides a suite of equilibrium constants at 25°C and 3M NaClO<sub>4</sub>. We were unable to find more reliable data, especially extended to infinite dilution, nor we could find any data allowing to extend the LogK(T) functions to temperature other than 25°C. The species concerned are: HgHPO<sub>4</sub>,aq, HgPO<sup>4</sup>, Hg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>,s, (HgOH)<sub>3</sub>PO<sub>4</sub>,s and HgHPO<sub>4</sub>,s. The constants are reported in Table 3 and

#### Table 4.

#### 3.2.5 Methylmercury

Methylmercury is a strongly toxic complex that accumulates in the muscles and various living tissues of living organisms. After Thomassin and Touze (2003) the methylation of mercury is favored in anoxic environment by the presence of sulfato reductive bacteria and of sulfur. Generally speaking, the methylation reaction proceeds that way:

$Hg^{++} + CH_{4,aq} \xrightarrow{Bacteria} CH_3Hg^+ + H^+$	Mono-MetylMercury (MMHg)
$CH_{3}Hg^{+} + CH_{4,aq} \xrightarrow{Bacteria} (CH_{3})_{2}Hg + H^{+}$	Di-MethylMercury (DMHg)

The dimethyl products are found as both aqueous complexes (in basic solutions) or even under its gaseous form. Methylation of mercury may be reversed. Its degradation is favored by light.

The thermodynamic parameters associated to those reactions have been collected and discussed by Stumm and Morgan (1995) and Skyllberg (2012), for various chemical systems, at 25°C only. Alderighi et al. (2003) have measured, by calorimetry, the heat exchanged during various complexation reactions involving methylmercury. From these measurements, we were able to calculate the entropy of complexes, which are reported in Table 3, as well as their Gibbs energies of formation, extracted from equilibrium constants at 25°C.

Other than aqueous we have included in the present selection an additional gas phase,  $Hg(CH_3)_{2,g}$ . It represents an extreme stage of the methylation process (Thomassin and Touze, 2003) and can be reverted, depending on pH conditions.

Espèce	LogK	∆G°f	∆H°f	S°	Ср	a1	a2	a3	a4	c1	c2	ω	V	Références
		kJ/mol	kJ/mol	J/mol.K	J/mol.K								cm³/mo I	
Hg <sub>aq</sub>	20.65	37.12		-6.65	410.74	17.93	11.21	19.71	-12.09	263.83	70.97	-0.22	18.54	Bessinger and Apps (2005)
Hg⁺²			170.21	-36.19		-2.2	-38.0	39.0	-10.1	75.6	-10.8	4.8		Cox et al. (1989); Shock and Helgeson (1988)
Hg <sup>2+</sup> 2	-12.21		166.87	65.74		16.8	8.6	20.7	-12.0	91.2	-0.9	3.4		Cox et al. (1989); Shock et al. (1997)
Hg(OH)⁺	-3.40			69.87		5.2	-19.7	31.7	-10.8	151.4	26.9	1.3	93.97	Baes and Mesmer (1976) ; Shock et al. (1997)
Hg(OH) <sub>2,aq</sub>	-6.08			156.00	73	45.3	78.0	-6.5	-14.9	67.0	2.1	-0.2	66.3	Blanc (2013); Bessinger and Apps (2005)
Hg(OH) <sup>3-</sup> / HHgO <sup>2-</sup>	-21.10			9.62		7.6	-14.0	29.6	-11.0	15.7	-37.6	6.7		Baes and Mesmer (1976); Shock et al. (1997)
Hg <sub>2</sub> (OH) <sup>+3</sup>	-3.33		67.39											Baes and Mesmer (1976); Arnek et al. (1967)
Hg <sub>3</sub> (OH) <sup>3+</sup> <sub>3</sub>	-6.42													Baes and Mesmer (1976)
HgOHCI	4.06			129.76										Baes and Mesmer (1976)
HgCl⁺	7.21			48.83		10.4	-7.1	26.8	-11.3	136.0	20.6	1.6		Baes and Mesmer (1976); Sverjensky et al. (1997)

#### Table 3 – Thermodynamic properties for aqueous complexes. Source: Blanc (2013).

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Espèce	LogK	∆G°f	∆H°f	S°	Ср	a1	a2	a3	a4	c1	c2	ω	V	Références
		kJ/mol	kJ/mol	J/mol.K	J/mol.K								cm³/mo I	
HgCl <sub>2</sub>	13.98			103.09		25.2	28.9	12.7	-12.8	203.5	49.6	-0.2		Baes and Mesmer (1976); Sverjensky et al. (1997)
HgCl³⁻	15.06			127.65		43.9	74.7	-5.3	-14.7	326.5	76.2	4.9		Baes and Mesmer (1976); Sverjensky et al. (1997)
HgCl <sup>4-</sup> 2	15.48			118.66		65.2	126.7	-25.8	-16.9	458.4	100.4	11.7		Baes and Mesmer (1976); Sverjensky et al. (1997)
Hg(HS)₂		-37.79		207.94	59.11	111.78	-19.70	-16.25	110.52	17.31	-0.16	59.11	90.44	Bessinger and Apps (2005)
HgS(HS) <sup>-</sup>		-2.80		150.88	43.14	72.79	-4.42	-14.64	98.44	-1.87	4.50	43.14	59.80	Bessinger and Apps (2005)
HgS <sup>2-</sup> 2		44.58												Benoit et al. (1999)
$HgSO_{4,aq}$		-587.33												Powell et al. (2005)
$HgCO_{3,aq}$		-428.17												Powell et al. (2005)
Hg(OH)CO <sup>3-</sup>		-630.24												Powell et al. (2005)
HgHCO <sup>3+</sup>		-452.89												Powell et al. (2005)
HgHPO <sub>4,aq</sub>		-981.55												Powell et al. (2005)
HgPO <sup>4-</sup>		-949.87												Powell et al. (2005)
HgF⁺			-165.34	-18.77		-0.21	-33.05	37.02	-10.26	156.06	24.24	2.60		Sverjensky et al. (1997)

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Espèce	LogK	∆G°f	∆H°f	S°	Ср	a1	a2	a3	a4	c1	c2	ω	v	Références
		kJ/mol	kJ/mol	J/mol.K	J/mol.K								cm³/mo I	
CH₃Hg⁺			113.09		20.25									Stumm and Morgan (1995)
CH₃HgOH			-96.53		65.05									Alderighi et al. (2003)
$(CH_3Hg)_2OH^+$		3.32		75.69										Alderighi et al. (2003)
CH₃HgS⁻			85.38											Alderighi et al. (2003)
CH₃HgSH			42.57											Alderighi et al. (2003)
CH₃HgCl			-47.87		97.05									Alderighi et al. (2003)

Minerals	LogK	ΔG <sup>0</sup> <sub>f</sub>	ΔH⁰ <sub>f</sub>	S⁰	Cp 25°C	а	b*10 <sup>3</sup>	c*10⁻⁵	V	References
	(25°C)	(kJ/mol)	(kJ/mol)	(J/mol.K)	(J/mol.K)	(J/mol.K)	(J/mol.K²)	(J/mol/K)	cm³/mol	
Hg, <sub>I</sub>		0.000	0.00	75.90	20.786					Cox et al. (1989); Chase (1998)
Hg <sub>.g</sub>			61.38	174.97	20.786					Cox et al. (1989)
HgO <sub>cr</sub>			-90.79	70.25	44.06	42.09	21.93	-4.06	19.32	Cox et al. (1989); Chase (1998)
HgS <sub>cr</sub> (Cinnabar)		-45.73	-53.35	82.82	48.41	46.22	15.52	-2.17	28.42	Helgeson et al. (1978)
HgS <sub>cr</sub> (Metacinnabar)		-43.53	-48.98	89.68	46.37	49.21	11.95	-5.69	30.17	Helgeson et al. (1978)
HgCl2 <sub>cr</sub> (Calomel)			-265.37	191.60	101.97	97.19	26.28	-2.71	32.94	Cox et al. (1989); Chase et al. (1985)
Hg <sub>2</sub> SO <sub>4</sub>			-743.09	200.70	132.33	103.97	131.08	-9.53	65.77	Cox et al. (1989); Barin et al. (1977)
HgCO <sub>3</sub> .2HgO(s)		-572.91								Powell et al. (2005)
$Hg_3(PO_4)_2(s)$		-1838.38								Powell et al. (2005)
(HgOH) <sub>3</sub> PO <sub>4</sub> (s)		-1367.06								Powell et al. (2005)
HgHPO <sub>4</sub> (s)		-1006.09								Powell et al. (2005)
Hg(CH <sub>3</sub> ) <sub>2.g</sub>			94.39	306	83.30					Wagman et al. (1982)

#### Table 4 – Thermodynamic properties for minerals and gases. Source: Blanc (2013).
#### 3.2.6 Organic thiol complexes

Some recent studies have demonstrated the importance of the organic matter in complexing mercury through thiols groups. The synthesis proposed by Skyllberg (2012) indicates two types of organic matter that could be involved in such complexes: low molecular mass (LMM) molecules (e.g. cysteine, glutathione, ...) and natural organic matter (NOM) usually associated to humic acids. Skyllberg (2012) proposes a list of equilibrium constants that could reproduce the complexation with both types of organic matter. Considering RS as the organic radical holding the thiol group, the complexation reaction reported by the author are:

(LoaK = 42.0)

-	$RS^{-} + Hg^{+2} = HgSR^{+}$	(LogK = 22.7)

			(==9:====)
-	RS <sup>-</sup> + OH <sup>-</sup> +	Hg <sup>+2</sup> = HgOHSR	(LogK = 32.2)

- HgOHSR +  $CI^{-}$  = HgCISR +  $OH^{-}$  (LogK = -3.7)

Technically, the Thermoddem management system implies to define chemically all the compounds. In the present case, this cannot apply to the SR radical which is not precisely defined, from a chemical or structural point of view. In addition, any modeling work using these reactions will have to define the "amount" of SR radicals in the system, which could not be a simple issue to address. However, we are proposing the equilibrium constant reported by Skyllberg (2012) as the most relevant for the formation of organic thiols complexes.

## 3.3 Verification

 $2RS^{-} + Hq^{+2} = Hq(SR)_{2}$ 

By drawing predominance diagrams, it is possible to somehow check the consistency of the selection. The aim, at this stage, is to detect by using such type of diagrams, if the relations between phases or complexes, contradicts or not what is usually found in literature.

#### 3.3.1 The Hg-O-H<sub>2</sub>O system

A first diagram is drawn in the system Hg-O- $H_2O$ , at saturation with respect to mercury and at 25°C (Figure 5). The result is very similar to the diagram drawn by Takeno (2005) using the SUPCRT database.



Figure 5 – Predominance diagram in the Hg-O-H<sub>2</sub>O system, at 25°C. Source: Blanc (2013).

The essential difference with respect to Brookins (1988) representation is that no HHgO<sup>2-</sup> (similar to Hg(OH)<sup>3-</sup>) stability field appears, in agreement with Baes and Mesmer (1976) speciation model and calculations in high pH domains. A second diagram is presented, in the same system, by ignoring the equilibrium with solid phases (Figure 6). Therefore appears clearly the dominant species in the speciation model, very conform to what is obtained by Baes and Mesmer (1976).



Figure 6 - Predominance diagram in the Hg-O-H<sub>2</sub>O system, at 25°C without solid phases. Source: Blanc (2013).

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## 3.3.2 The Hg-O-CI-H<sub>2</sub>O system

Adding chloride to the chemical system allows presenting a new diagram in Figure 7. Chloride species (Calomel  $Hg_2CI_{2,s}$  and  $HgCI_{2,aq}$ ) appears in the same domain than what is reported by Brookins (1988). Actually, they depend on the total concentration in dissolved chloride.



Figure 7 - Predominance diagram in the Hg-O-Cl-H<sub>2</sub>O system, at 25°C, [Cl]<sub>T</sub> =  $10^{-2}$ M. Source: Blanc (2013).

On Figure 8 are displayed the dominant complexes in the Hg-Cl-O-H<sub>2</sub>O sub system, at 25°C. It is essentially consistent with Powell et al. (2005) calculations in the same context, including the HgOHCl,aq complex which stability domains lies between that of HgCl<sub>2</sub>,aq and Hg(OH)<sub>2</sub>,aq, after Baes and Mesmer (1976).



Figure 8 - Predominance diagram in the Hg-O-Cl-H<sub>2</sub>O system, at 25°C without solid phases,  $[Cl]_T = 10^{-2}M$ . Source: Blanc (2013).

#### 3.3.3 The Hg-S-CI-O-H2O system

The original Brookins (1988) diagram includes sulfur in the chemical system. It has been added for the diagram on Figure 9. With the exception of the  $HHgO_2^-$  specie, the features displayed in this work are in agreement with Brookins (1988) stability field, especially for cinnabar.

The sulfide speciation was also tested against the experimental data gathered by Skyllberg (2012) with calculations performed using PhreeqC. The results were consistent with the experimental solubility data, given their few numbers and their spreading.



Figure 9 - Predominance diagram in the Hg-O-Cl-H<sub>2</sub>O system, at 25°C,  $[S]_T = [Cl]_T = 10^{-3}M$ . Source: Blanc (2013).

#### 3.3.4 The Hg-C-S-O-H<sub>2</sub>O system, including methylmercury

A representation is devoted to the investigation of carbon speciation in the Hg-O-C-H2O system (Figure 10). The carbonate stability domains are in agreement with the calculation by Powell et al. (2005). As for methylmercury species, they are dominated by  $CH_3Hg^+$ ,  $(CH_3Hg)_2OH^+$  and  $CH_3HgOH$  complexes and located in the reduced part of the predominance diagram. The equilibrium with dissolved carbonate species strongly reduces the stability domain of methylmercury. However, this is difficult to evaluate since this is the first time, to our knowledge, that such a diagram involving both methylmercury and carbonates species is drawn.

Two last representations of the stability of methylmercury complexes are provided in Figure 11 and Figure 12, for the system Hg-Cl-C-S-O-H<sub>2</sub>O, at 25°C. , reported in. Figure 11 displays a transition between sulfide and hydroxylated species for a total concentration in sulfides close to  $10^{-12}$  mol/L, whereas Boszke et al. (2002) evaluated it close to  $10^{-11}$  mol/L. On the other hand the transition between chlorinated and hydroxylated methyl complexes occurs accordingly Boszke et al. (2002) calculation at pH = 7 and for a chloride concentration of about  $10^{-3}$  mol/L, as seen in Figure 12.



Figure 10 - Predominance diagram in the Hg-C-O-H<sub>2</sub>O system, at 25°C, [C]<sub>T</sub> =  $10^{-4}$ M. Source: Blanc (2013).



Figure 11 - Predominance diagram of the methyl-mercuric complexes in the CH<sub>3</sub>Hg-S-O-H<sub>2</sub>O system, at 25°C. Source: Blanc (2013).



Figure 12 - Predominance diagram of the methyl-mercuric complexes in the CH<sub>3</sub>Hg-S-CI-O-H<sub>2</sub>O system, at 25°C and pH=7. Source: Blanc (2013).

#### 3.4 Conclusion

This chapter (from Blanc, 2013) presents a selection of the thermodynamic properties for different mercury bearing species, from aqueous complexes to solid phases, including gases.

The selection is based on a gathering of the most reliable sources: the Codata database (Cox et al., 1989), the IUPAC (Powell et al., 2005), Baes and Mesmer (1976) selection or Bessinger and Apps (2005) synthesis work. However, few workable verification cases could be found in the literature in spite of the quantity of work concerning mercury.

The case of methylmercury is a specific hindrance, being the first time we get involved with actual organo metallic species. From this point of view, the work presented here represents a first stage. Few verification could be proposed. The reliability of the selection ought to be tested, be taking care of the kinetic aspect (possibly involving microbial interactions) of the methylation or demethylation processes.

This also applies to the formation of mercury complexes with organic thiols groups.

#### 4 Mathematical model

#### 4.1 Transport processes in soil systems

The water flow equation is based on conservation of mass within a given soil volume and on the summation of fluxes in and out of this volume. The fluxes are described with the Darcy-Buckingham law relating the flux in the unsaturated soil to the pressure head gradient in the soil and a moisture dependent proportionality factor. The resulting Richards equation for water flow in soils is:

$$\frac{\partial \theta(h)}{\partial t} = \frac{\partial}{\partial x} \left[ K(h) \left( \frac{\partial h}{\partial x} + \cos \alpha \right) \right] - S(h)$$
(7)

where *h* is the soil water pressure head [L],  $\theta$  is the volumetric water content [L<sup>3</sup>L<sup>-3</sup>], *t* is time [T], *x* is the spatial coordinate [L] (positive upward), *S* is the sink term to represent root water uptake [L<sup>3</sup>L<sup>-3</sup>T<sup>-1</sup>],  $\alpha$  is the angle between the flow direction and the vertical axis, and *K* is the unsaturated hydraulic conductivity [LT<sup>-1</sup>]. To describe the relations between  $\theta - h$  and K - h, the van Genuchten equations (van Genuchten, 1980) are used:

$$\theta(h) = \theta_r + \frac{\theta_s - \theta_r}{\left(1 + |\alpha h|^n\right)^m}$$
(8)

and

$$K(h) = K_s S_e^l \left[ 1 - \left( 1 - S_e^{1/m} \right)^m \right]^2$$
(9)

where  $\theta_r$  is the residual water content  $[L^3L^{-3}]$ ,  $\theta_s$  is the saturated water content  $[L^3L^{-3}]$ ,  $\alpha [L^{-1}]$ , n [-] and m (= 1 - 1/n) [-] are shape parameters, l is a pore connectivity parameter [-],  $K_s$  is the saturated hydraulic conductivity  $[LT^{-1}]$ , and  $S_e = (\theta - \theta_r)/(\theta_s - \theta_r)$  is the effective saturation. A typical sandy soil texture is used, with the following hydraulic parameters :  $\theta_s = 0.43 \text{ cm}^{-3}$ ,  $\theta_r = 0.045 \text{ cm}^{-3}$ ,  $\alpha = 0.145 \text{ cm}^{-1}$ , n = 2.68 and  $K_{sat} = 712.8 \text{ cm} \text{ day}^{-1}$  (Šimůnek et al., 2008).

Solute transport is only calculated for so-called primary species for which the total concentration is defined as:

$$C_{j} = c_{j} + \sum_{i=1}^{N_{s_{a}}} v_{ji} c_{i}$$
(10)

where  $C_j$  is the total concentration of the primary species *j*,  $c_j$  is the concentration of the aqueous species *j*,  $c_i$  is the concentration of the *i*th secondary aqueous species,  $n_{ji}$  is the stoichiometric coefficient of the primary species *j* in the *i*th secondary species and  $N_{sa}$  is the number of secondary aqueous species. For a species-independent diffusion coefficient, solute transport in the aqueous phase is described by the advective-dispersive equation:

$$\frac{\partial \theta C_j}{\partial t} = \frac{\partial}{\partial x} \left( \theta D^{\mathbf{W}} \frac{\partial C_j}{\partial x} \right) - \frac{\partial q C_j}{\partial x} - S C_{\mathbf{r},j} + R_{\mathbf{o},j}$$
(11)

where *S* is the sink term in the water flow equation  $[L^{3}L^{-3}T^{-1}]$ ,  $C_{r,j}$  is the total concentration of the sink term  $[ML^{-3}]$ ,  $D^{w}$  is the dispersion coefficient in the liquid phase  $[L^{2}T^{-1}]$ , and  $R_{o,j}$  is the source/sink term that represents various heterogeneous equilibrium and kinetic reactions (e.g., cation exchange, surface complexation, mineral dissolution) and homogeneous kinetic reactions (e.g., degradation reactions in the aqueous phase)  $[ML^{-3}T^{-1}]$ . In the gaseous phase, diffusion is the only transport process:

$$\frac{\partial \theta C_j}{\partial t} = \frac{\partial}{\partial x} \left( \theta D^{\mathbf{a}} \frac{\partial C_j}{\partial x} \right) + R_{\mathbf{o},j}$$
(12)

The dispersion coefficients  $D^{w}$  and  $D^{a}$  in Eqs. (11) and (12) respectively are given by:

$$\theta D_i^{w} = D_L |q| + \theta D_{i,w} \tau_w$$

$$\theta_a D_i^{a} = \theta_a D_{i,a} \tau_a$$
(13)

where  $D_{i,w}$  and  $D_{i,a}$  are the molecular diffusion of the  $i^{tn}$  aqueous species in free water and gaseous species in the gas phase, repsectivley  $[L^2T^{-1}]$ ,  $D_L$  is the longitudinal dispersivity [L], and  $\tau_w$  and  $\tau_w$  are the tortuosity factors in the liquid and gaseous phases, respectively [-] which are related to the water content by the model of Millington and Quirk (1961).

#### 4.2 Speciation of Hg

Initial soil solution and rainwater composition is taken from the Dutch "National Precipitation Chemistry Network" (Stolk, 2001):

```
solution 1001
-units mmol/kgw
pH 5.22 charge
Ca .0055
Mg .006
K .0038
Na .047
Cl .052
F .00105
N(5) .036 mmol/kgw as NO3-
N(-3) .084 mmol/kgw as NH4+
O(0) 1 02(g) -0.68
[...]
```

Aqueous speciation of Hg is solved using a version of the IM003\_THERMODDEM database (Blanc et al., 2012b) specifically augmented with mercury species (see Chapter 3).

Complexation of Hg<sup>2+</sup> with DOM was added to the database via the input files of HP1, using four reactants symbolising humic and fulvic acids (Ya, Yb and Yc) and thiols (Ys) :

HYa + .5Hg++ = Hg0.5Ya + H+ log k -1.1

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HYb + .5Hg++ = Hg0.5Yb + H+ log\_k -7.6 HYc + .5Hg++ = Hg0.5Yc + H+ log\_k -1.8 HYa + HgOH+ = HgOHYa + H+ log\_k -3 HYb + HgOH+ = HgOHYb + H+ log\_k 1.8 HYc + HgOH+ = HgOHYc + H+ log\_k 2.0

The reaction constants used for Hg complexation with DOM are from Bessinger and Marks (2010) for fulvic and humic acids, and from Skyllberg (2008) for thiols, obtained by converting exchange constants (section 4.3) to complexation constants conforming to the Gapon Convention (Gapon, 1933).

For diffusion of  $Hg^{0}(g)$  in the gas phase, a molecular diffusion coefficient in soil air of 0.119 cm<sup>2</sup> s<sup>-1</sup> is used (Massman, 1999). A boundary layer of 5 cm at the top of the soil profile is chosen, with a background  $Hg^{0}(g)$  concentration in atmosphere of 1 ng m<sup>-3</sup> (Lin and Pehkonen, 1999; Gabriel et al., 2005).

## 4.3 Hg sorption to SOM

Interactions between mercury and immobile, solid organic matter are described using a combination of multiple H-exchangers (HA and FA, and thiol sites) with proton/cation exchange to account for background electrolyte concentration effects. Interactions between cations and reactive surface sites were treated as ion exchange reactions.

SOM is represented as cation exchange sites (similarly to Bessinger and Marks, 2010), using four different reactive sites : Xa, Xb, Xc (representing oxygen sites of fulvic and humic acids) and Xs (representing thiols). For fulvic and humic acids, H<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Hg<sup>2+</sup> and HgOH<sup>+</sup> sorption to exchange sites was included in HP1 simulations. For example, for Xa:

```
Hg++ + 2Xa- = HgXa2
log_k 3.5
                           # Bessinger and Marks (2010)
HgOH+ + Xa- = HgOHXa
log k 7.7
                           # Bessinger and Marks (2010)
H+ + Xa- = HXa
log k 1
Ca++ + 2Xa- = CaXa2
log k 1
Mg++ + 2Xa- = MgXa2
log k 1
Na+ + Xa- = NaXa
log k 0
K+ + Xa- = KXa
log k 0.5
```

For thiols, exchange with cations  $H^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ ,  $Na^+$  and  $Hg^{2+}$  is simulated :

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```
Ca++ + 2Xs- = CaXs2

log_k 1

Mg++ + 2Xs- = MgXs2

log_k 1

Na+ + Xs- = NaXs

log_k 0

K+ + Xs- = KXs

log_k 0.5
```

Calculation of the exchange capacity assumes a soil bulk density of 1.5 g cm-3, a uniform SOM content of 1% in the top 30 cm of the profile, and a number of sites of 5.3 meq gOC-1 (oxygen sites; Bessinger and Marks, 2010) and 0.047 meq gOC-1 (thiol sites; Skyllberg, 2008). In soils with mercury background concentrations thiols are always in excess compared to Hg. However, this may not be the case in highly contaminated sites and/or low OM environments1. With the assumptions above regarding number of sites, soil bulk density and SOM content, thiol (bidentate) exchange sites will be saturated for mercury contamination higher than ~50 mg Hg kg-1.

In HP1, Hg sorption to SOM is coded using PHREEQC "exchange" reaction as:

## 4.4 Cinnabar dissolution

Waples et al. (2005) found cinnabar dissolution rate in the range  $2.31 \times 10^{-13}$  to  $7.16 \times 10^{-12}$  mol Hg (mg C)<sup>-1</sup> m<sup>-2</sup> s<sup>-1</sup>. A rate law has been implemented in HP1 (as in Bessinger and Marks, 2010), assuming cinnabar surface area of 0.23 m<sup>2</sup> g<sup>-1</sup> (Waples et al., 2005) and multiplying the rate by the porosity. This gives in the additions to the thermodynamical DB :

#### RATES

<sup>&</sup>lt;sup>1</sup> Skyllberg et al. (2006) noted that at Hg conc. of 0.1 mg/kg, only about 1% of thiols were saturated by Hg. Bessinger and Marks (2010) in a batch experiment observed saturation of sorption sites from > Hg 100-200 mg/kg.

## 4.5 NAPL dissolution

No literature data is available for the dissolution rate of residual Hg NAPL. Therefore, an arbitrary rate was fixed so that approximately all residual NAPL was dissolved in 20 to 25 years. This gives in the additions to the thermodynamic DB:

```
RATES
HgNAPL
-start
10 rate = m * parm(1)
20 save rate * time
-end
and in the geochemical model :
KINETICS 1-11
HgNAPL
-formula Hg(1) 1.0
-m0 1e-3
-parms 8.64e-4  # in 1/day (time unit of HP1 simulations)
```

Due to the uncertainty on the dissolution rate, this parameter is added to the list of the parameters included in the sensitivity analysis (section 5.1).

## 4.6 Hg<sup>II</sup> reduction and volatilization

A new species Hg\_zero is added to the database to simulate the kinetic reduction of Hg<sup>II</sup> to Hg<sup>0</sup> in HP1, using PHREEQC "RATES" and "KINETICS" commands:

In the additions to the thermodynamic DB:

```
RATES
HgII_reduction
-start
10 Hg_two = totmole("Hg")
20 if (Hg_two <= 0) then goto 100
30 moles = Hg_two * parm(1) * time
100 save moles
-end</pre>
```

and in the geochemical model :

KINETICS 1-6 HgII\_reduction -formula Hg\_zero 1.0 Hg -1.0 -parms 6.91e-6 **# in 1/day** 

The reduction rate constant is from Scholtz et al. (2003), who chose it to match values measured by Carpi and Lindberg (1998) over background soils (between  $1.2 \times 10^{-2}$  and  $4.5 \times 10^{-2} \ \mu g \ m^{-2} \ h^{-1}$  over open field soil). The parameter value may be changed to reflect values measured over contaminated sites that can vary over several orders of magnitude : e.g.  $8.5 \times 10^{-1} \ \mu g \ m^{-2} \ h^{-1}$  (Rinklebe et al., 2010) to  $3.4 \times 10^{5} \ \mu g \ m^{-2} \ h^{-1}$  (Schlüter, 2000).

PHREEQC allows three ways of modelling a gas-liquid interaction: (i) fixed partial pressure, (ii) fixedpressure multicomponent gas phase, and (iii) fixed-volume multicomponent gas phase. In the present study, fixed-volume was applied (volume of air phase is fixed by the porosity and the water content).

## 4.7 DOM production and sorption to minerals

DOM production is considered as flowing in the soil profile with rain water, i.e. it is included in the initial and boundary solution composition (see section 4.1):

[...] # units mmol/kgw Ya .23333 # with 50 mg/L, and 5.3 meq gOC<sup>-1</sup> (Bessinger and Marks, 2010) Yb .03 Yc .00167 Ys .00235 # Skyllberg 2008

An alternative could be the use of a rate law (Chow, 2006). Full modeling of DOM cycle in the soil was not implemented but could be considered as future improvement to the model given its importance in Hg fate.

The PHREEQC command "SURFACE" and a Langmuir isotherm were used to represent DOM sorption to mineral surfaces. Parameters fitted by Kothawala et al. (2008) for DOC sorption to a Ah soil horizon were used. They found that a Langmuir isotherm (with final concentration in the formulation) gave the best fit to their experimental data:

$$DOC_{Sor} = \frac{K_L S_{max} DOC_f}{1 + K_L DOC_f} - b$$
(14)

where  $DOC_{Sor}$  (mg kg<sup>-1</sup>) is the amount of DOC sorbed,  $K_L$  (-) is the coefficient of binding affinity,  $S_{max}$  (mg kg<sup>-1</sup>) is the maximum adsorption capacity,  $DOC_f$  (mg kg<sup>-1</sup>) is the final equilibrium concentration and *b* (mg kg<sup>-1</sup>) is a desorption term. It was assumed that all DOC-fractions sorb in the same way.

In HP1, the desorption term b (correcting for native adsorbed DOC on minerals) was not implemented.

```
SURFACE SPECIES
Smax = Smax
log k 0.0
Smax + Ya- = SmaxYa-
                            # kL = 1/k from (Kothawala et al., 2008) ; log10(kL) = -2.252
log k -2.252
Smax + Yb- = SmaxYb-
log k -2.252
Smax + Yc- = SmaxYc-
log k -2.252
Smax + Ys- = SmaxYs-
log k -2.252
Geochemical model:
SURFACE 1-101
                            # complete soil profile
Smax 1.06e-3 1.0 1e100
                            # max. number of sites (mol/1000cm<sup>3</sup>) in Langmuir equation, 1
m2/g, 1e100 g
-equilibrate with 1001
                            # equilibrate with soil solution
-no edl
                            # non-electrostatic model
```

The non-electrostatic model (" $-no\_edl$ ") does not consider the effects of the development of surface charge on the formation of surface complexes, with the result that surface complexes are treated like aqueous complexes without activity coefficient terms (Parkhurst and Appelo, 1999).

end;

# 4.8 Methylation / demethylation (currently not implemented in the model)

If we add CH4 as such to the system (via the atm), it will probably just oxidize to C(4). If we include it, we have to define just a completely different component (which may or may not transform to CO2) and then kinetically or in equilibrium reacts with Hg.

```
1CH4 + 1Hg++ = CH3Hg+ + 1H+
       log k 3.000
SOLUTION MASTER SPECIES
Met MetH 0.0 Met 16.04
SOLUTION SPECIES
# Methane
2MetH + 1H2O + 2Hg++ = (MetHg)2OH+ + 3H+

      -llnl_gamma
      3.0

      log_k
      3.499

      -delta_H
      -49.047
      kJ/mol # References :n/a

      -analytic
      1.9165512e+021.7962199e-02-2.0532670e+03
      -7.3196995e+01

       -4.8935945e+05
1MetH + 1F- + 1H+ + 0.502 = MetF + 1H20
       -llnl_gamma 3.0
log_k 25.490

        -delta_H
        -121.664
        kJ/mol # References :01sch/sho

        -analytic
        4.2830231e+027.2437400e-02-1.4879704e+04
        -1.5637320e+02

       1.1052880e+06
1MetH + 1Hg++ = MetHg+ + 1H+
        -llnl gamma 3.0
       log_k 3.000
-delta_H
                               -26.481
                                            kJ/mol # References :n/a
       -analytic 8.4002822e+019.0151964e-03 -3.6929630e+02 -3.2219364e+01
       -2.4243902e+05
1CH4 + 1Cl - + 1Hq++ = CH3HqCl + 1H+
       -llnl gamma 3.0
       log_k 8.210
                      -50.197 kJ/mol # References :n/a
       -delta H
       -analytic 6.2558916e+029.8694663e-02-2.8309923e+04 -2.2975818e+02
       1.4817335e+06
1MetH + 1H2O + 1Hq++ = MetHqOH + 2H+
       -llnl gamma 3.0
       log_k -1.821
       -delta H
                      -6.458 kJ/mol # References :n/a
       -analytic 1.0815427e+028.9470024e-03-2.5253605e+03 -4.0977631e+01
       -2.4692043e+05
1MetH + 1HS - + 1Hg + = MetHgS - + 2H +
       -llnl gamma 3.0
       log_k 10.000
-analytic 1.000000e+010.000000e+000.000000e+00
       0.0000000e+00
#
      References DGf or LogK 12sky ; DHf n/a ; S° n/a ; Cp n/a
```

```
1MetH + 1HS - + 1Hg++ = MetHgSH + 1H+
         -llnl gamma 3.0
         log_k 17.500
-analytic 1.7500000e+010.0000000e+000.0000000e+00
         0.0000000e+00
#
        References DGf or LogK 12sky ; DHf n/a ; S° n/a ; Cp n/a
PHASES
MetH(g)
         MetH = 1MetH

        log_k
        -2.858

        -delta_H
        -876.620
        kJ/mol # References :98cha

        -analytic
        1.9803838e+023.4578373e-02-1.2491896e+04
        -7.3027856e+01

         1.0129196e+06
Hg(Met)2(g)
         Hg(Met)2 + 2H + = 1Hg + + 2MetH
         log_k 8.818

        -delta_H
        -1827.166
        kJ/mol # References :82wag/eva

        -analytic
        1.1862599e+022.4722556e-02-6.5145222e+03
        -4.4108205e+01

         1.2279840e+06
```

## 5 Virtual simulation cases

#### 5.1 Initial forms of mercury

To test the impact of different Hg phases at a contaminated site on Hg fate and leaching, three different Hg phases were tested:

1) Solid phase

Cinnabar (HgS(s)) was used as an example. Other solid phase forms of mercury encountered in polluted sites are:

- Montroydite HgO(s);
- $\circ$  Corderoite Hg<sub>3</sub>S<sub>2</sub>Cl<sub>2</sub>(s);
- $\circ$  Mercury chloride HgCl<sub>2</sub>(s).
- 2) Mercury NAPL

Residual NAPL mercury Hg<sup>0</sup>(I)

3) Aqueous forms of mercury (Hg<sup>II</sup>)

 $HgCl_2(aq)$ ,  $Hg^{II}$  hydroxides,  $Hg^{II}$  bound to OM...

For the sensitivity analysis, the initial concentration of mercury in soil could be arbitrarily set, because results are mainly reported in terms of percentages of the initial contamination (see section 0). Therefore initial concentration of Hg in the top 10 cm of the soil profile is set to  $1 \times 10^{-3}$  mol dm<sup>-3</sup> (HP1 input units), which corresponds to a contamination of ~135 mg Hg kg<sup>-1</sup>. This is in the range of Hg contamination reported for example by Bloom et al. (2003) for samples from different source areas : from 37.2 to 78400 mg Hg kg<sup>-1</sup>. However, given that observed Hg concentrations range over several orders of magnitude, the initial concentration was added in the sensitivity analysis (section5.3).

Different combinations of initial mercury phases were tested (Table 5).

Code	Solid phase Hg <sup>ll</sup>	Liquid phase (NAPL) Hg <sup>0</sup>	Aqueous phase Hg <sup>ll</sup> (HgCl₂(aq))		
А	100%				
В		100%			
С			100%		
D	50%	50%			
E		50%	50%		
F	50%		50%		
G	33.33%	33.33%	33.33%		

## 5.2 Indicators

Figure 13 and the table next to it show the indicators retained for comparing different model runs in the sensitivity analysis. All indicators are expressed in percentage of the initial amount of mercury present in the soil, so that different simulations where the initial contamination is in a different phase can be compared. They are reported after 5, 25 and 50 years.



Figure 13 – Indicators calculated from model output for the sensitivity analysis.

#### 5.3 Parameters and processes

The basic scenario consists of:

- 50 years of daily climatic data at Dessel, Belgium (= 2×25 year time series);
- Atmospheric top boundary condition (with 1 cm ponding surface layer) and free drainage bottom boundary condition (deep groundwater, oxidising conditions);
- Rainwater composition (except DOM);
- Sandy soil type (this a priori corresponds to the coarse textured types of soil more likely to be encountered on polluted sites (mine tailings, etc.));
- Grass cover (30 cm rooting depth);
- SOM uniformly distributed in the top 30 cm;
- Initial Hg contamination uniformly spread in the top 10 cm;
- Background atmospheric Hg(g) concentration 1 ng m<sup>-3</sup>.

Table 6 gives the parameters included in the sensitivity analysis, together with their initial values (for base case simulations) and lower and upper bounds.

Parameter / process	Units	Initial value	Low value	High value
Initial Hg concentration	mg kg <sup>−1</sup>	135	-	1350 13500
NAPL dissolution rate	day <sup>-1</sup>	8.64×10 <sup>-4</sup>	8.64×10 <sup>-5</sup>	8.64×10 <sup>-3</sup>
Cinnabar dissolution rate	day <sup>-1</sup> g <sub>oc</sub> <sup>-1</sup>	7.33×10 <sup>-3</sup>	4.59×10 <sup>-4(a)</sup>	1.42×10 <sup>-2</sup> (a)
Hg <sup>II</sup> reduction rate	day <sup>-1</sup>	6.91×10 <sup>-6 (b)</sup>	6.91×10 <sup>-7</sup>	6.91×10 <sup>-5</sup>
DOM (in rainwater boundary solution)	mg L <sup>−1</sup>	50	9 <sup>(c,d)</sup>	90 <sup>(c,d)</sup>
Exchange capacity of HA and FA (SOM top 30 cm) $$	meq dm <sup>-3</sup>	79.5 <sup>(f)</sup>	7.95	159
Exchange capacity of thiols (SOM top 30 cm)	meq dm $^{-3}$	0.705 <sup>(e)</sup>	0.0705	1.41
log k complexation Hg-DOM (HA and FA)	-	$\begin{array}{c} HgYa_{2}:-1.1 \stackrel{(f)}{=} \\ HgYb_{2}:-7.6 \stackrel{(f)}{=} \\ HgYc_{2}:-1.8 \stackrel{(f)}{=} \\ HgOHYa:-3.0 \\ \stackrel{(f)}{=} \\ HgOHYb:1.8 \end{array}$	-2.2 -15.2 -3.6 -6.0 0.9 1.0	-0.55 -3.8 -0.9 -1.5 3.6 4.0
		HgOHYc : 2.0		
log k complexation Hg-DOM (thiols)	-	HgYs <sub>2</sub> : 22.0 <sup>(e)</sup>	11.0	44.0
log k sorption Hg-SOM (HA and FA)	-	$\begin{array}{c} \text{HgXa}_2:3.5\stackrel{(\text{f})}{}\\ \text{HgXb}_2:4.3\stackrel{(\text{f})}{}\\ \text{HgXc}_2:5.08\stackrel{(\text{f})}{}\\ \text{HgOHXa}:7.7\stackrel{(\text{f})}{}\\ \text{HgOHXb}:7.7\stackrel{(\text{f})}{}\\ \text{HgOHXc}:10.2\stackrel{(\text{f})}{}\\ \end{array}$	1.75 2.15 2.54 3.85 3.85 5.1	7.0 8.6 10.16 15.4 15.4 20.4
log k sorption Hg-SOM (thiols)		HgXs <sub>2</sub> : 15.4 <sup>(f)</sup>	7.7	30.8
$K_L$ sorption DOM to soil minerals	-	5.6×10 <sup>-3 (g)</sup>	5.6×10 <sup>-4</sup>	1.23×10 <sup>-2</sup> (g)
$\mathcal{S}_{\text{max}}$ max. adsorption capacity of DOM to minerals	mg kg <sup>−1</sup>	355 <sup>(g)</sup>	109 <sup>(g)</sup>	601 <sup>(g)</sup>

#### Table 6 – List of parameters included in the sensitivity analysis.

<sup>(a)</sup> Waples et al. (2005)

<sup>(b)</sup> Scholtz et al. (2003)

<sup>(c)</sup> Mertens et al. (2007)

<sup>(d)</sup> Don and Schulze (2008)

<sup>(e)</sup> Skyllberg (2008)

<sup>(f)</sup> Bessinger and Marks (2010)

<sup>(g)</sup> Kothawala et al. (2008)

## 5.4 Applications

Very few Hg speciation models have been validated by actual data from soils, sediments, or waters (Skyllberg, 2012). A full (experimental) validation is beyond the scope of the present work. However, a "plausibility" check can be implemented, by performing a sensitivity analysis on a number processes and parameters. This will help to identify (and quantify) the most important features determining mercury fate in the vadose zone. The sensitivity of processes and parameters may depend on the type of contamination. Therefore test simulations will be performed with different initial forms of mercury (section 5.1) and a number of indicators are calculated from the model outputs (section 0).

Chapter 6 discusses in detail the simulation results and indicators of the seven base cases (initial value in

Table 6) with different initial contamination speciation. In addition, two types of sensitivity analysis were done : (i) a one-at-a time sampling design to investigate the impact of bounding values on model results (section 7.1), and (ii) a elementary effects method to quantify more precisely which input factors are negligible or play an import role in the model (section 7.2).

## 6 Base case simulations

Table 7 provides the results of the 7 base cases (A01, B01 ... G01, Table 5) for the four indicators defined in section 0. Indicator 1 is reported in column "Hg to atm."; indicator 2 is given in column "Hg leached"; the sum of the next 6 columns (in Top 10 cm) constitutes indicator 3 (percentage of Hg still present in the horizon of initial contamination); and the last 4 columns (excluding "TOTAL") provide the percentage of Hg present in the soil under the horizon of initial contamination (indicator 4).

For all base case simulations indicator **①** was equal to 0% (no Hg volatilized). Hg volatilization will be discussed further in the results of the sensitivity analyses (Chapter 1).

In the base case, the percentage of Hg leached at the bottom of the soil profile after 50 years (indicator 2) varied between 19.1% (all cinnabar) and 32.1% (all HgCl<sub>2</sub>(aq)) (see Table 10). Leaching is more important when HgCl<sub>2</sub>(aq) is present at the start of the simulation period, because all HgCl<sub>2</sub>(aq) is in the liquid phase from the start and available for transport, while cinnabar and NAPL involve dissolution kinetics.

The results are further discussed in the following paragraphs.

Table 7 – Results of base case simulations (7 groups corresponding to different forms of Hg initial contamination) after 0, 5, 25 and 50 years. Results are given in percentage of the initial Hg contamination. The mercury mass balance is reported in terms of "Hg to atm." = Hg<sup>0</sup>(g) volatilized to the atmosphere, Hg leached (at the bottom of the 1-m soil profile), HgS = cinnabar, Hg NAPL = non-aqueous liquid phase Hg<sup>0</sup>, Hg SOM = Hg sorbed to SOM, Hg DOM = aqueous Hg complexed to organic species, Hg Inorg = aqueous Hg complexed to inorganic species, Hg Inorg = aqueous Hg complexed t

					Top 10 cm						11-100 cm				
		Time (yr)	Hg to atm.	Hg leached	HgS	Hg NAPL	Hg SOM	Hg DOM	Hg inorg	Hg(g)	Hg SOM	Hg DOM	Hg inorg	Hg(g)	TOTAL
-	T.	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Α	01	0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0
Α	01	5	0.0	0.2	93.6	0.0	4.2	0.0	0.0	0.0	2.0	0.0	0.0	0.0	100.0
Α	01	25	0.0	6.6	70.7	0.0	11.7	0.0	0.0	0.0	11.0	0.0	0.0	0.0	100.0
А	01	50	0.0	19.1	50.0	0.0	10.1	0.0	0.0	0.0	20.7	0.1	0.0	0.0	100.0
в	01	0	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0
В	01	5	0.0	0.3	0.0	20.6	74.4	0.0	0.0	0.0	4.7	0.0	0.0	0.0	100.0
в	01	25	0.0	7.3	0.0	0.0	72.3	0.0	0.0	0.0	20.3	0.0	0.0	0.0	100.0
В	01	50	0.0	20.5	0.0	0.0	45.0	0.0	0.0	0.0	34.4	0.1	0.0	0.0	100.0
С	01	0	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	100.0
С	01	5	0.0	1.6	0.0	0.0	42.0	0.0	0.0	0.0	56.4	0.0	0.0	0.0	100.0
С	01	25	0.0	13.7	0.0	0.0	23.8	0.0	0.0	0.0	62.4	0.1	0.0	0.0	100.0
С	01	50	0.0	32.1	0.0	0.0	1.8	0.0	0.0	0.0	66.0	0.1	0.0	0.0	100.0
D	01	0	0.0	0.0	50.0	50.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0
D	01	5	0.0	0.3	46.8	10.3	38.6	0.0	0.0	0.0	4.1	0.0	0.0	0.0	100.0
D	01	25	0.0	7.2	35.3	0.0	40.8	0.0	0.0	0.0	16.6	0.0	0.0	0.0	100.0
D	01	50	0.0	20.3	25.0	0.0	26.3	0.0	0.0	0.0	28.4	0.1	0.0	0.0	100.0
Ε	01	0	0.0	0.0	0.0	50.0	0.0	0.0	50.0	0.0	0.0	0.0	0.0	0.0	100.0
Ε	01	5	0.0	0.5	0.0	10.3	74.1	0.0	0.0	0.0	15.1	0.0	0.0	0.0	100.0
Ε	01	25	0.0	8.4	0.0	0.0	62.7	0.0	0.0	0.0	28.8	0.1	0.0	0.0	100.0
Ε	01	50	0.0	22.4	0.0	0.0	36.5	0.0	0.0	0.0	41.1	0.1	0.0	0.0	100.0
F	01	0	0.0	0.0	50.0	0.0	0.0	0.0	50.0	0.0	0.0	0.0	0.0	0.0	100.0
F	01	5	0.0	0.5	46.8	0.0	38.1	0.0	0.0	0.0	14.7	0.0	0.0	0.0	100.0
F	01	25	0.0	8.4	35.3	0.0	31.0	0.0	0.0	0.0	25.2	0.1	0.0	0.0	100.0
F	01	50	0.0	22.3	25.0	0.0	17.3	0.0	0.0	0.0	35.3	0.1	0.0	0.0	100.0
G	01	0	0.0	0.0	33.3	33.3	0.0	0.0	33.3	0.0	0.0	0.0	0.0	0.0	100.0
G	01	5	0.0	0.3	31.5	6.9	57.3	0.0	0.0	0.0	4.9	0.0	0.0	0.0	100.9
G	01	25	0.0	7.5	23.8	0.0	51.2	0.0	0.0	0.0	18.4	0.0	0.0	0.0	100.9
G	01	50	0.0	20.8	16.8	0.0	32.3	0.0	0.0	0.0	31.0	0.1	0.0	0.0	100.9

## 6.1 A01

In the base case simulation A01 with all mercury initially present as cinnabar, 50% of the initial cinnabar is still present in the top 10 cm after 50 years (Figure 14a and Table 7). Besides, 10% of the initial Hg that has dissolved from cinnabar is still present in the same horizon, principally sorbed to SOM (Table 7). An integrated view in the space-time domain of the evolution of Hg speciation is given in Figure 14. This figure plots for a given species (cinnabar and other Hg species in Figure 14a and Figure 14b, respectively) the cumulative depth distribution from the top to the bottom over time. For example for cinnabar, at time zero, 100% of the initial Hg contamination is present as cinnabar in the top 10 cm. However, after 50 years, about 50% of the initial Hg contamination is still present as cinnabar in the top 10 cm, about 10 % is present in any other form of Hg in the top 10 cm and between the surface and a depth of 30 cm, about 31% is present. About 19% of the initial mercury leached from the profile because 50% of cinnabar and 31% of other Hg species are present in the top 100 cm. Also after 50 years, most of the dissolved Hg (except from the part being leached) is still present in the layers just below 10 cm depth (see also Figure 15).

Figure 15 shows the same data, but in absolute Hg concentrations (mg[Hg]/kg[soil]) at discrete times : after 0, 5, 10, 25 and 50 years. The vertically non uniform dissolution of cinnabar in Figure 15a is explained by the influence of DOM on the dissolution rate (cf. Eq. (1) in section 2.6). The profile of Hg concentration in Figure 15b reflects that (i) Hg source is in the top 10 cm, and (ii) SOM is present only in the top 30 cm. It is interesting to note that in the timeframe of the simulation (50 years) maximum Hg concentration is found at the bottom of the horizon initially contaminated. The top 10 cm act as a continuous source of Hg in the aqueous phase, and the dominant process is then Hg<sup>II</sup> mobilization by DOM and sorption to SOM.

Complexes of Hg with DOM and inorganic species play an important role in mercury leaching but do not represent a high amount of mercury at a particular time. The absence of SOM between 30 and 100 cm has the consequence that no mercury is present in that interval, except a small amount of aqueous species (0.1% of the initial Hg; mainly in the form of Hg-DOM complexes).



## Figure 14 – Cumulative depth distribution over time of (a) cinnabar and (b) other Hg species (in % of total initial Hg) for base case simulation A01.

Figure 16 shows Hg<sup>II</sup> flux at the bottom of the soil profile for simulation A01. Mercury leaching at 1 m depth starts after ~2 years. Using a moving average (red line in Figure 16) on daily simulated values, some correlation between Hg flux and precipitation is observed. Because the same atmospheric

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forcings were used for all simulations, they all display the same bottom flux variations, i.e. only the absolute values of the flux change but the dynamics are the same. In some instances, the timing at which leaching begins may also vary (see for example base case C01).



Figure 15 – Depth distribution of Hg (a) in solid phase (HgS) and (b) sorbed to SOM at t = 0, 5, 10, 25 and 50 years for base case simulation A01. Note that for clarity the y-axis stops at 50 cm depth.



Figure 16 – Hg(II) flux at the bottom of the soil profile over time for simulation A01. Grey dots are daily simulated fluxes at the bottom of the soil profile. Red line is the result of a moving average (window 31 days) on the daily data. Grey bars show the surface precipitation input (averaged every two months for clarity). Note that the y-scale is logarithmic for the solute flux.

### 6.2 B01

In the base case B01 (initial contamination 100% as a residual NAPL), the source of Hg NAPL is completely after slightly more than 10 years (Figure 17a and Table 7). After dissolution, Hg(0) is almost instantly oxidized to  $Hg^{II}$  and sorbs to SOM. Over time, Hg leaching occurs, together with resorption to SOM below the horizon originally contaminated (Figure 17b and Table 7). In the base case, 20.5% of the initial mercury has leached after 50 years.

Figure 21 shows the same data at discrete times: after 0, 5, 10, 25 and 50 years. The vertical profile of NAPL dissolution is uniform (Figure 21a) as it depends on time only (cf. Eq. (2) in section 2.7). In the timeframe of the simulation, maximum Hg concentration is found at the bottom of the horizon initially contaminated, similarly to what was observed in base case A01. The top 10 cm act as a continuous source of Hg (after NAPL dissolution and oxidation to Hg<sup>II</sup>), and the dominant process is then Hg<sup>II</sup> mobilization by DOM and sorption to SOM.

Figure 19 shows Hg<sup>II</sup> flux at the bottom of the soil profile for simulation B01. The value of indicator **2** for B01 (20.5%) is close to the value calculated for A01 (19.1%). The percentage of leaching is slightly higher for B01 because leaching started before what was simulated in base case A01. Afterwards, both curves (Figure 16 and Figure 19) are almost identical.

Complete dissolution of NAPL within the timeframe of the simulation, as opposite to what was simulated for cinnabar, does not seem to affect the amount of leaching. The mechanism of leaching and the most sensitive parameters will be further investigated in the sensitivity analyses (Chapter 1).



Figure 17 – Cumulative depth distribution over time of (a) NAPL and (b) other Hg species (in % of total initial Hg) for base case simulation B01.



Figure 18 – Depth distribution of Hg (a) as NAPL and (b) sorbed to SOM at t = 0, 5, 10, 25 and 50 years for base case simulation B01. Note that for clarity the y-axis stops at 50 cm depth.



Figure 19 – Hg(II) flux at the bottom of the soil profile over time for simulation B01. Grey dots are daily simulated fluxes at the bottom of the soil profile. Red line is the result of a moving average (window 31 days) on the daily data. Grey bars show the surface precipitation input (averaged every two months for clarity). Note that the y-scale is logarithmic for the solute flux.

#### 6.3 C01

Amongst the seven base cases, C01 (Hg initial present in soluble form) is the one with highest value of indicator 2 (% Hg leached) after 50 years (32.1%). This is explained by the absence of any kinetic constraint of release of Hg<sup>II</sup> by dissolution processes, i.e. all Hg is immediately available for mobilization and sorption/desorption to/from SOM as opposed to the other base cases. Therefore leaching starts earlier than in other base cases. In the case of HgCl<sub>2</sub>(aq) as a pollution source, Hg almost instantly sorbs to SOM.

Figure 20a shows that from the initial amount of  $HgCl_2(aq)$  only 23.3% is still present in liquid phase after introduction in the top 10 cm. The rest has been spread either as aqueous Hg species deeper in

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the soil profile (14.4%) or as Hgs orbed to SOM (62.3%; Figure 20b). Closer inspection of the results reveals that the fraction of aqueous Hg complexes becomes negligible compared to Hg-SOM after a few days only. Figure 20b clearly shows the gradual leaching of Hg from the top soil (here mimicked by the amount of sorbed Hg).

Figure 21 shows the same data at discrete times: after 0, 5, 10, 25 and 50 years. It should be noted that "initial" profile of Hg-SOM is taken after 1 day of model run, because at 0 day no Hg is input in the soil profile yet. Still, even after 1 day, Hg sorption to SOM has already occurred until about 20 cm depth (Figure 21a). Over time, Hg sorbed to SOM is progressively leached (or resorbed deeper) due to continuous infiltration of DOM via rainwater. After 50 years, only 1.8% of the initial Hg is still present in the top 10 cm, and 32.1% has leached at the bottom of the soil profile. A zoom in Figure 21b allows to see in details the concentration profile of Hg aqueous species. Hg-DOM complexes can be viewed as the "carriers" of Hg in the soil and are therefore more present in the zones where Hg is being desorbed or is accumulating.

It is also for base case C01 that the smallest value of indicator ③ and highest value of ④ are found (note that the indicator values are correlated as they have to sum to 100%).

Figure 22 shows that leaching starts almost immediately in base case simulation C01. After a few years the curve closely resembles what was calculated for base cases A01 and B01 above. This confirms that the temporal dynamics (not the absolute values) of leaching are mainly driven by the climate.



Figure 20 – Cumulative depth distribution over time of Hg (a) in aqueous phase and (b) sorbed to SOM (in % of total initial Hg) for base case simulation C01.



Figure 21 – Depth distribution of Hg (a) sorbed to SOM and (b) in aqueous phase at t = 0, 5, 10, 25 and 50 years for base case simulation C01. Note that for clarity the y-axis stops at 50 cm depth.



Figure 22 – Hg(II) flux at the bottom of the soil profile over time for simulation C01. Grey dots are daily simulated fluxes at the bottom of the soil profile. Red line is the result of a moving average (window 31 days) on the daily data. Grey bars show the surface precipitation input (averaged every two months for clarity). Note that the y-scale is logarithmic for the solute flux.

#### 6.4 D01

In this simulation, the source is divided between cinnabar and NAPL (50% each). Figure 23 (a,b) shows dissolution over time for cinnabar and NAPL, respectively. As noted for base cases A01 and B01, NAPL dissolution is faster due to the higher rate chosen for the base case simulations.

Leaching after 50 years is 20.1% of initial Hg, i.e. an intermediate value between A and B base cases. Also for other indicators, base case D01 can be considered as intermediate between A01 and B01 cases (cf. Table 7).

Figures 23c shows that the percentage of Hg sorbed to SOM in the top 10 cm reaches a maximum after ~10-15 years (at the end of NAPL dissolution). DOM transports Hg deeper in the soil profile, where it is resorbed to SOM or eventually leaches at the bottom of the 1-m profile. Maximum concentration of Hg in the soil profile is reached at the end of the 50 years, at the bottom of the top horizon (Figure 24c).



Figure 23 – Cumulative depth distribution over time of Hg (a) in solid phase (HgS), (b) as NAPL, and (c) in other Hg species (in % of total initial Hg) for base case simulation D01.



Figure 24 – Depth distribution of Hg (a) in solid phase (HgS), (b) as NAPL, and (c) sorbed to SOM at t = 0, 5, 10, 25 and 50 years for base case simulation D01. Note that for clarity the y-axis stops at 50 cm depth.

### 6.5 E01

In this simulation, the source is divided between NAPL and  $HgCl_2(aq)$  (50% each). Simulation results are displayed in Figures 25 and 26. Complete dissolution of NAPL occurs after slightly more than 10 years, as in B01 simulation (rate is used independently of initial concentration).

Similarly to base case C01, rapid initial sorption of Hg from the aqueous source (until ~20 cm depth) is observed (Figures 25b and 26b). The percentage of Hg (other than NAPL) in the top horizon continues to increase until ~10-15 years (Figure 25b), due to NAPL dissolution followed by oxidation and sorption to SOM. Maximum concentration of Hg-SOM is reached after 25 years (Figure 26b) due to leaching and resorption of the mercury close to the surface.

After 50 years 36.5% of the initial Hg is still present in the topsoil. Values of all indicators are intermediate between B01 and C01 cases (see Table 7).



Figure 25 – Cumulative depth distribution over time of Hg (a) as NAPL and (b) in other Hg species (in % of total initial Hg) for base case simulation E01.



Figure 26 – Depth distribution of Hg (a) as NAPL and (b) sorbed to SOM at t = 0, 5, 10, 25 and 50 years for base case simulation E01. Note that for clarity the y-axis stops at 50 cm depth.

#### 6.6 F01

In this simulation, the source is divided between cinnabar and  $HgCl_2(aq)$  (50% each). Simulation results are presented in Figures 27 and 28. Cinnabar dissolution is incomplete over the simulation period (Figures 27a and 28a), but slightly higher close to the soil surface due to the influence of DOM (cf. case A01).

Compared to base case E01, slower dissolution of the solid phase causes a less important increase of Hg-SOM concentrations in the horizon originally polluted (up to ~80 mg[Hg]/kg[soil] for F01 after 50 years compared to ~115 mg[Hg]/kg[soil] for E01 after 25 years.

Compared to A01 and C01 cases (see Table 7), a higher percentage of Hg (other than HgS) is retained in the topsoil after 50 years (17.3%). If total Hg is considered, indicator 3 for F01 (42.3%) is intermediate between A01 (60.1%) and C01 (1.8%) base cases.



Figure 27 – Cumulative depth distribution over time of Hg (a) in solid phase (HgS) and (b) in other Hg species (in % of total initial Hg) for base case simulation F01.



Figure 28 – Depth distribution of Hg (a) in solid phase (HgS) and (b) sorbed to SOM at t = 0, 5, 10, 25 and 50 years for base case simulation F01. Note that for clarity the y-axis stops at 50 cm depth.

## 6.7 G01

In this simulation, the source is split between cinnabar, NAPL and  $HgCl_2(aq)$  (one third each). Simulation results are shown in Figures 29 and 30. Dissolution rates of cinnabar and NAPL are the same (see Figure 29a, b) as in the other base cases. Mercury transport and redistribution processes are averaging the dominant features of base cases A01, B01 and C01.

After 50 years, 20.8% of the initial Hg has leached and around 49% of the mercury is still present (mainly as cinnabar and Hg-SOM) in the horizon initially contaminated. Maximum Hg concentration in the soil profile is reached after 50 years at the bottom of the top horizon (~105 mg[Hg]/kg[soil]; Figure 30 (c)).

Figure 31 presents  $Hg^{II}$  flux at the bottom of the soil profile. As already mentioned, climatic forcings determine the shape of the leaching flux and thus this Figure is very similar to corresponding Figures previously shown. In the present case however, very early leaching as in base case C01 (Figure 22) does not occur, because  $HgCl_2(aq)$  initial concentration was not high enough to initiate it.



Figure 29 – Cumulative depth distribution over time of Hg (a) in solid phase (cinnabar), (b) as NAPL and (c) in other Hg species (in % of total initial Hg) for base case simulation G01.

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Figure 30 – Depth distribution of Hg (a) in solid phase (HgS), (b) as NAPL, and (c) sorbed to SOM at t = 0, 5, 10, 25 and 50 years for base case simulation G01. Note that for clarity the y-axis stops at 50 cm depth.



Figure 31 – Hg(II) flux at the bottom of the soil profile over time for simulation G01. Grey dots are daily simulated fluxes at the bottom of the soil profile. Red line is the result of a moving average (window 31 days) on the daily data. Grey bars show the surface precipitation input (averaged every two months for clarity). Note that the y-scale is logarithmic for the solute flux.
### 7 Sensitivity analysis

### 7.1 One-at-a-time analysis

### 7.1.1 Method

The sensitivity analysis was first implemented in a one-at-a time form. Because of the long simulation time series and HP1 relatively high computational requirements, a global method seems a priori difficult to implement. However, the one-at-a-time sensitivity analysis can provide useful information and can serve later as a basis for a more detailed sensitivity/uncertainty analysis (Saltelli et al., 2008). The one-at-a time sensitivity analysis designed here investigates model response with the bounding values of input parameters. It is important to note that the sensitivity analysis performed here was not a local analysis, i.e. the different parameter sets are not small changes around the base case values, but rather bounding values of the parameter range were tested.

In section 7.2 another method of sensitivity analysis (Morris "elementary effects") is implemented, quantifying more precisely the relative effect of different parameters on the model output.

Parameters in the sensitivity analysis were varied one-at-a-time, plus some simultaneous variations of (i) NAPL and cinnabar dissolution rates; (ii) exchange capacity of HA and FA and of thiols; (iii) log k complexation of HA and FA and of thiols; and (iv) log k sorption of HA and FA and of thiols. Table 8 summarizes all combinations tested for a given pollution source. Some combinations of initial contamination forms and parameter variations are not relevant (e.g. initial Hg 100% NAPL and changing cinnabar dissolution rate). In total, the sensitivity analysis consisted of 230 simulation runs.

### Table 8 – Parameter variations in the one-at-a time sensitivity analysis. Analysis performed for each contamination (defined in section 5.1).



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### 7.1.2 Results

Two simulation runs (C21 and C23) failed due to convergence problem in the geochemical calculations. These simulation runs were characterized by a high log k for Hg-DOM complexation (thiols).

The following paragraphs discuss the simulation results for the four different indicators defined in section 0.

#### 7.1.2.1 **1** Volatilization

In the different scenarios of mercury pollution tested, simulated volatilization does not appear to be an important process. Table 9 shows that the percentage of Hg volatilized to atmosphere is ~0% in all cases, except in cases D02, D03, G02 and G03 where both HgS and Hg NAPL are initially present at high concentrations (×10 and ×100 base case concentration).

In group G of the SA simulations, a high NAPL dissolution rate had also a slightly noticeable impact (0.4 to 0.6% Hg volatilized).

# Table 9 – Hg volatilized to the atmosphere (in % of initial contamination) in the different simulation cases of the sensitivity analysis, after 5, 25 and 50 years.

1	Hg volatilized to atm. (% of initial contamination)			Α			В			С			D			Е			F			G				
			:	1-0-0		C	0 - 1 - 0			0-0-1		0.5	5-0.5-0	)	0 -	0.5 - 0.	5	0.5	-0-0.5	5	0.33 -	0.33-0	0.33	(HgS - NAPL - HgCl <sub>2</sub> )		
Simul	SA parameter		5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	years		
1	Base case	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0		Color	legend
2	Initial Hg conc.	×10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.7	4.4	4.4	0.0	0.0	0.0	0.0	0.0	0.0	2.0	2.3	2.3			>10 × base case
3	Initial Hg conc.	×100	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.5	2.2	2.4	0.0	0.0	0.0	0.0	0.0	0.0	2.0	2.6	2.6			>2 ×base case
4	NAPL dissolution rate	÷10				0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0				0.0	0.0	0.0			<0.5×base case
5	NAPL dissolution rate	×10				0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0				0.4	0.4	0.4			<0.1×base case
6	Cinnabar dissolution rate	low	0.0	0.0	0.0							0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0			
7	Cinnabar dissolution rate	high	0.0	0.0	0.0							0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0			
8	Hg <sup>II</sup> reduction rate	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
9	Hg <sup>II</sup> reduction rate	×10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0			
10	DOM (in rainwater boundary solution)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
11	DOM (in rainwater boundary solution)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
12	Exchange capacity of HA and FA (SOM top 30 cm)	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
13	Exchange capacity of HA and FA (SOM top 30 cm)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
14	Exchange capacity of thiols (SOM top 30 cm)	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
15	Exchange capacity of thiols (SOM top 30 cm)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
16	Exchange capacity of HA, FA, thiols (SOM top 30 cm)	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
17	Exchange capacity of HA, FA, thiols (SOM top 30 cm)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
18	log k complexation Hg-DOM (HA and FA)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
19	log k complexation Hg-DOM (HA and FA)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
20	log k complexation Hg-DOM (thiols)	÷2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
21	log k complexation Hg-DOM (thiols)	×2	0.0	0.0	0.0	0.0	0.0	0.0	NaN	NaN	NaN	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
22	log k complexation Hg-DOM (HA, FA, thiols)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
23	log k complexation Hg-DOM (HA, FA, thiols)	high	0.0	0.0	0.0	0.0	0.0	0.0	NaN	NaN	NaN	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
24	log k sorption Hg-SOM (HA and FA)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
25	log k sorption Hg-SOM (HA and FA)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
26	log k sorption Hg-SOM (thiols)	÷2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
27	log k sorption Hg-SOM (thiols)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
28	log k sorption Hg-SOM (HA, FA, thiols)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
29	log k sorption Hg-SOM (HA, FA, thiols)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
30	K <sub>L</sub> sorption DOM to soil minerals	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
31	K <sub>L</sub> sorption DOM to soil minerals	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
32	S <sub>max</sub> max. adsorption capacity of DOM to minerals	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
33	S <sub>max</sub> max. adsorption capacity of DOM to minerals	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
34	NAPL and cinnabar dissolution rates	low										0.0	0.0	0.0							0.0	0.0	0.0			
35	NAPL and cinnabar dissolution rates	high										0.0	0.0	0.0							0.6	0.6	0.6			
36	Initial Hg conc.	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			

#### 7.1.2.2 **2** Leaching

Independently of the contamination phase, the highest impact on Hg leaching in the range of parameters tested appeared to come from:

- initial Hg concentration: the higher the initial concentration, the higher the leaching fraction because Hg sorption sites are saturated except for group A where incomplete dissolution of cinnabar over the whole simulation period causes an inverse relationship);
- DOM concentration in rainwater boundary condition: i.e. higher DOM leads to more leaching because Hg-DOM complexes are the main conveyor of Hg towards the bottom of the soil profile;
- Parameters related to Hg complexation with thiols: exchange capacity of thiols (in SOM), log k complexation of Hg-DOM and Hg-SOM (thiols).

The importance of DOM concentration for Hg fate and transport is illustrated by the sorption isotherm shown in Figure 32. This isotherm was calculated using a hypothetical batch reaction in PHREEQC, with parameters similar to the base case. It can be seen that higher DOM concentrations increase the amount of mobile Hg (i.e. aqueous inorganic and organic complexes of Hg).

In cases C16 and E16, the percentage of Hg leached after 50 years was ~100%. These simulation cases correspond to a lower exchange capacity in the top 30 cm SOM (for both thiol and humic and fulvic acid sites), with all (C16) or half (E16) the initial contamination in the form of  $HgCl_2(aq)$ .

Also in cases C36 and E36 the percentage of Hg leached reached 100% after 50 years. Due to a lower initial concentration of Hg, complete leaching of mercury can occur through complexation and transport with DOM (thiols); which is the most favoured speciation reaction (cf. initial values in

Table 6).



Figure 32 – Mercury sorption isotherm showing the effect of DOC concentration for a system with Hg, SOM and DOM (both concentrations of Hg and SOM are fixed). Top figure shows the % Hg sorbed to SOM and the amount of Hg in the aqueous phase (inorganic and organic complexes of Hg). Bottom figure shows the distribution ratio (Kd) between sorbed Hg (on SOM, mol/kg) and aqueous Hg (inorganic and organic complexes of Hg, mol/l).

2	Hg leached (% of initial contamination)			А			В			С			D			E			F			G				
				1-0-0		(	0-1-0			0-0-	1	0.5	- 0.5 -	0	0 -	0.5 - 0.	5	0.5	5-0-0	5	0.33	-0.33	-0.33	(HgS - NAPL - HgCl <sub>2</sub> )		
Simulation	SA parameter		5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	years		
1	Base case	-	0.2	6.6	19.1	0.3	7.3	20.5	1.6	13.7	7 32.1	0.3	7.2	20.3	0.5	8.4	22.4	0.5	8.4	22.3	0.3	7.5	20.8			
2	Initial Hg conc.	×10	0.0	0.7	2.0	0.1	1.2	3.2	81.1	83.3	1 85.6	0.0	0.8	2.2	34.2	36.3	38.9	33.9	35.9	38.3	18.7	20.7	23.2		Color	legend
3	Initial Hg conc.	×100	0.0	0.1	0.2	53.3	61.6	63.5	95.2	96.2	2 96.2	17.3	19.5	21.3	68.5	71.1	72.5	46.8	47.1	47.7	40.7	42.2	43.7			>2 ×base case
4	NAPL dissolution rate	÷10				0.2	6.9	19.7				0.2	6.8	19.5	0.5	8.4	22.3				0.3	7.5	20.7			>1.1×base case
5	NAPL dissolution rate	×10				0.3	7.6	21.1				0.3	7.4	20.5	0.5	8.4	22.4				0.3	7.5	20.9			<.9 × base case
6	Cinnabar dissolution rate	low	0.1	1.8	3.9							0.3	7.2	20.3				0.5	8.4	22.3	0.3	7.5	20.8			<0.5×base case
7	Cinnabar dissolution rate	high	0.2	6.9	19.6							0.3	7.2	20.3				0.5	8.4	22.3	0.3	7.5	20.8			
8	Hg <sup>II</sup> reduction rate	÷10	0.2	6.6	19.1	0.3	7.3	20.5	1.6	13.7	7 32.1	0.3	7.2	20.3	0.5	8.4	22.4	0.5	8.4	22.3	0.3	7.5	20.8			
9	Hg <sup>II</sup> reduction rate	×10	0.2	6.6	19.1	0.3	7.3	20.5	1.6	13.7	7 32.1	0.3	7.2	20.3	0.5	8.4	22.4	0.5	8.4	22.3	0.3	7.5	20.8			
10	DOM (in rainwater boundary solution)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	4 1.7	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.0			
11	DOM (in rainwater boundary solution)	high	1.6	19.5	48.3	1.8	20.5	50.0	4.2	29.7	7 65.9	1.8	20.4	49.7	2.3	22.1	52.7	2.3	22.1	52.6	1.9	20.9	50.7			
12	Exchange capacity of HA and FA (SOM top 30 cm)	÷10	0.2	6.6	19.1	0.3	7.4	21.6	2.3	16.4	4 37.2	0.3	7.2	20.5	0.5	8.6	23.8	0.5	8.6	22.8	0.3	7.6	21.4			
13	Exchange capacity of HA and FA (SOM top 30 cm)	×2	0.2	6.6	19.1	0.3	7.3	20.5	1.4	13.0	30.8	0.3	7.2	20.3	0.5	8.3	22.2	0.5	8.3	22.2	0.3	7.5	20.8			
14	Exchange capacity of thiols (SOM top 30 cm)	÷10	1.8	16.0	37.3	2.0	16.6	38.2	44.8	63.6	5 87.3	2.0	16.5	38.0	10.8	29.1	52.0	10.8	29.1	52.0	3.9	21.7	44.4			
15	Exchange capacity of thiols (SOM top 30 cm)	×2	0.0	3.9	13.3	0.1	4.5	14.7	0.2	5.9	9 17.3	0.0	4.4	14.5	0.1	4.6	14.9	0.1	4.6	14.9	0.1	4.7	14.9			
16	Exchange capacity of HA, FA, thiols (SOM top 30 cm)	÷10	1.8	16.1	39.1	2.0	18.7	76.6	67.5	93.4	4 100	2.0	17.6	63.5	24.6	49.9	99.1	24.4	47.8	74.8	11.7	35.3	80.5			
17	Exchange capacity of HA, FA, thiols (SOM top 30 cm)	×2	0.0	3.9	13.3	0.1	4.5	14.7	0.2	5.9	9 17.2	0.0	4.4	14.5	0.1	4.6	14.9	0.1	4.6	14.9	0.1	4.7	14.9			
18	log k complexation Hg-DOM (HA and FA)	low	0.2	6.6	19.1	0.3	7.3	20.5	1.6	13.7	7 32.1	0.3	7.2	20.3	0.5	8.4	22.4	0.5	8.4	22.3	0.3	7.5	20.8			
19	log k complexation Hg-DOM (HA and FA)	high	0.2	6.6	19.1	0.3	7.3	20.5	1.6	13.7	7 32.1	0.3	7.2	20.3	0.5	8.4	22.4	0.5	8.4	22.3	0.3	7.5	20.8			
20	logk complexation Hg-DOM (thiols)	÷2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
21	log k complexation Hg-DOM (thiols)	×2	4.3	22.0	44.3	4.4	22.1	44.4	NaN	NaN	NaN	4.4	22.1	44.4	4.4	22.1	44.4	4.4	22.1	44.4	4.4	22.3	44.8			
22	logk complexation Hg-DOM (HA, FA, thiols)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
23	logk complexation Hg-DOM (HA, FA, thiols)	high	4.3	22.0	44.3	4.4	22.1	44.4	NaN	NaN	NaN	4.4	22.1	44.4	4.4	22.1	44.4	4.4	22.1	44.4	4.4	22.3	44.8			
24	log k sorption Hg-SOM (HA and FA)	low	0.2	6.6	19.1	0.3	13.1	33.9	3.5	20.0	0 41.8	0.3	7.5	21.5	0.8	14.7	35.7	0.5	8.9	23.4	0.4	8.9	24.8			
25	logksorption Hg-SOM (HA and FA)	high	0.0	2.8	10.5	0.0	3.3	11.6	0.0	3.3	3 11.7	0.0	3.2	11.4	0.0	3.4	11.7	0.0	3.3	11.6	0.0	3.4	11.8			
26	logksorption Hg-SOM (thiols)	÷2	4.3	21.9	44.2	4.3	22.0	44.3	18.6	36.3	58.7	4.3	22.0	44.3	4.4	22.1	44.4	4.4	22.1	44.4	4.4	22.3	44.7			
27	logksorption Hg-SOM (thiols)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3	1 0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
28	logksorption Hg-SOM (HA, FA, thiols)	low	4.3	21.9	44.2	4.3	22.2	48.0	23.1	41.0	63.3	4.3	22.0	44.3	4.4	23.1	50.5	4.4	22.1	44.4	4.4	22.3	44.7			
29	logksorption Hg-SOM (HA, FA, thiols)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
30	$K_L$ sorption DOM to soil minerals	÷10	0.2	6.6	19.1	0.3	7.3	20.5	1.6	13.7	7 32.1	0.3	7.2	20.3	0.5	8.4	22.4	0.5	8.4	22.3	0.3	7.5	20.8			
31	$K_L$ sorption DOM to soil minerals	×2	0.2	6.6	19.1	0.3	7.3	20.5	1.6	13.7	7 32.1	0.3	7.2	20.3	0.5	8.4	22.4	0.5	8.4	22.3	0.3	7.5	20.8			
32	$\boldsymbol{S}_{\max}\max$ . adsorption capacity of DOM to minerals	low	0.2	6.6	19.1	0.3	7.3	20.5	1.6	13.7	7 32.1	0.3	7.2	20.3	0.5	8.4	22.4	0.5	8.4	22.3	0.3	7.5	20.8			
33	S $_{\rm max}$ max. adsorption capacity of DOM to minerals	high	0.2	6.6	19.1	0.3	7.3	20.5	1.6	13.7	7 32.1	0.3	7.2	20.3	0.5	8.4	22.4	0.5	8.4	22.3	0.3	7.5	20.8			
34	NAPL and cinnabar dissolution rates	low										0.2	6.7	19.2							0.3	7.5	20.7			
35	NAPL and cinnabar dissolution rates	high										0.3	7.4	20.6							0.3	7.5	20.9			
36	Initial Hg conc.	÷10	0.9	25.3	48.4	2.3	68.3	100	3.0	72.0	0 100	2.1	62.4	74.4	2.9	71.1	100	2.9	63.0	74.4	2.8	69.6	82.9			

Table 10 – Hg leached (in % of initial contamination) in the different simulation cases of the sensitivity analysis, after 5, 25 and 50 years.

#### 7.1.2.3 **3** Hg still present in the soil horizon originally contaminated (top 10 cm)

Mercury contamination is initially uniformly distributed in the top 10 cm of the soil profile. Tables 11 to 16 give the amount of mercury still present in the top 10 cm after 5, 25 and 50 years for different (groups of) Hg phases and species : cinnabar (HgS), NAPL, Hg sorbed to SOM, Hg complexed with organic and inorganic ligands, and gaseous Hg. Most of the mercury in the top 10 cm is either in the initial contamination phase (HgS(s) and/or NAPL), or sorbed to SOM.

### Logically given the model conceptualization (see Figure 2), dissolution rates have an impact on the amount of HgS (Table 11) and NAPL (

# Table 12). For cinnabar, DOM infiltrating with rainwater is also a sensitive parameter, because in the model the dissolution rate is actually dependent on DOC following the conceptualization of (Waples et al., 2005) (see rate equation in section 4.4).

Due to mercury high sorption on SOM, Hg-SOM is the dominant Hg form (following HgS and/or NAPL dissolution) in the top 10 cm. Similarly to what was found for the fraction of Hg leached from the soil profile, the most sensitive parameters affecting Hg-SOM in the top 10 cm are DOM in rainwater and parameters linked to thiol groups. Hg complexes with DOM and inorganic ligands and gaseous Hg are in all SA runs ~0% of the initial Hg contamination. Therefore, practically all Hg in the top 10 cm is distributed between HgS and/or NAPL initially present and Hg sorbed to SOM.

3	Hg top 10 cm (% of initial contamination)			Α			В			С			D			E			F			G				
Species :	HgS			1-0-0		(	0-1-0			0-0-1		0.	5 - 0.5 -	0	0 - 0	0.5 - 0.5		0.	5 - 0 - 0.	5	0.33	-0.33 -	0.33	(HgS - NAPL - HgCl <sub>2</sub> )		
Simulation	SAparameter		5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	years		
1	Base case	-	93.6	70.7	50.0	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8			
2	Initial Hg conc.	×10	93.6	70.7	49.9	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8		Color	legend
3	Initial Hg conc.	×100	93.6	70.7	49.9	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8	;		>2 ×base case
4	NAPL dissolution rate	÷10				0.0	0.0	0.0				46.8	35.3	25.0	0.0	0.0	0.0				31.5	23.8	16.8	;		>1.1×base case
5	NAPL dissolution rate	×10				0.0	0.0	0.0				46.8	35.3	25.0	0.0	0.0	0.0				31.5	23.8	16.8	:		<.9 × base case
6	Cinnabar dissolution rate	low	99.6	97.9	95.7							49.8	48.9	47.9				49.8	48.9	47.9	33.5	32.9	32.2			<0.5×base case
7	Cinnabar dissolution rate	high	87.9	51.1	26.2							44.0	25.5	13.1				44.0	25.5	13.1	29.6	17.2	8.8	-		
8	Hg <sup>II</sup> reduction rate	÷10	93.6	70.7	50.0	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8	;		
9	Hg <sup>II</sup> reduction rate	×10	93.6	70.7	50.0	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8	;		
10	DOM (in rainwater boundary solution)	low	98.8	93.9	88.2	0.0	0.0	0.0	0.0	0.0	0.0	49.4	47.0	44.1	0.0	0.0	0.0	49.4	47.0	44.1	33.2	31.6	29.7			
11	DOM (in rainwater boundary solution)	high	88.7	53.6	28.7	0.0	0.0	0.0	0.0	0.0	0.0	44.4	26.8	14.4	0.0	0.0	0.0	44.4	26.8	14.4	29.8	18.0	9.7			
12	Exchange capacity of HA and FA (SOM top 30 cm)	÷10	93.6	70.7	50.0	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8	:		
13	Exchange capacity of HA and FA (SOM top 30 cm)	×2	93.6	70.7	50.0	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8	;		
14	Exchange capacity of thiols (SOM top 30 cm)	÷10	93.6	70.7	50.0	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8	;		
15	Exchange capacity of thiols (SOM top 30 cm)	×2	93.6	70.7	50.0	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8	:		
16	Exchange capacity of HA, FA, thiols (SOM top 30 cm)	÷10	93.6	70.7	50.0	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8			
17	Exchange capacity of HA, FA, thiols (SOM top 30 cm)	×2	93.6	70.7	50.0	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8	:		
18	log k complexation Hg-DOM (HA and FA)	low	93.6	70.7	50.0	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8	;		
19	log k complexation Hg-DOM (HA and FA)	high	93.6	70.7	50.0	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8	:		
20	log k complexation Hg-DOM (thiols)	÷2	93.6	70.7	50.0	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8	;		
21	log k complexation Hg-DOM (thiols)	×2	93.6	70.7	50.0	0.0	0.0	0.0				46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8			
22	log k complexation Hg-DOM (HA, FA, thiols)	low	93.6	70.7	50.0	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8	:		
23	log k complexation Hg-DOM (HA, FA, thiols)	high	93.6	70.7	50.0	0.0	0.0	0.0				46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8	:		
24	log k sorption Hg-SOM (HA and FA)	low	93.6	70.7	50.0	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8			
25	log k sorption Hg-SOM (HA and FA)	high	93.6	70.7	50.0	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8			
26	log k sorption Hg-SOM (thiols)	÷2	93.6	70.7	50.0	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8			
27	log k sorption Hg-SOM (thiols)	×2	93.6	70.7	50.0	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8			
28	log k sorption Hg-SOM (HA, FA, thiols)	low	93.6	70.7	50.0	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8			
29	log k sorption Hg-SOM (HA, FA, thiols)	high	93.6	70.7	50.0	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8			
30	K <sub>L</sub> sorption DOM to soil minerals	÷10	93.6	70.7	50.0	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8			
31	K <sub>L</sub> sorption DOM to soil minerals	×2	93.6	70.7	49.9	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8			
32	S <sub>max</sub> max. adsorption capacity of DOM to minerals	low	93.6	70.7	50.0	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8			
33	S <sub>max</sub> max. adsorption capacity of DOM to minerals	high	93.6	70.7	50.0	0.0	0.0	0.0	0.0	0.0	0.0	46.8	35.3	25.0	0.0	0.0	0.0	46.8	35.3	25.0	31.5	23.8	16.8			
34	NAPL and cinnabar dissolution rates	low						-				49.8	48.9	47.9				-		_	33.5	32.9	32.2			
35	NAPL and cinnabar dissolution rates	high										44.0	25.5	13.1							29.6	17.2	8.8			
36	Initial Hg conc.	÷10	93.3	69.6	48.4	0.0	0.0	0.0	0.0	0.0	0.0	46.6	34.8	24.2	0.0	0.0	0.0	46.6	34.8	24.2	31.1	23.2	16.1			

### Table 11 – Cinnabar (HgS) still present in the top 10 cm of the soil profile (in % of initial contamination), after 5, 25 and 50 years.

B	Hg top 10 cm (% of initial contamination)			Α			В			С			D			E			F			G				
Species :	NAPL		:	1-0-0			0-1-0			0-0-1		0.5	5-0.5-	0	0 -	0.5 - 0.5	5	0.5	5-0-0.	5	0.33	-0.33-0	0.33	(HgS - NAPL - HgCl <sub>2</sub> )		
Simulation	SAparameter		5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	years		
1	Base case	-	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
2	Initial Hg conc.	×10	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0		Color	legend
3	Initial Hg conc.	×100	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			>2×base case
4	NAPL dissolution rate	÷10				85.4	44.1	19.4				42.7	22.0	9.7	42.7	22.0	9.7				28.7	14.8	6.5			>1.1×base case
5	NAPL dissolution rate	×10				0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0				0.0	0.0	0.0			<.9×base case
6	Cinnabar dissolution rate	low	0.0	0.0	0.0							10.3	0.0	0.0				0.0	0.0	0.0	6.9	0.0	0.0			<0.5×base case
7	Cinnabar dissolution rate	high	0.0	0.0	0.0							10.3	0.0	0.0				0.0	0.0	0.0	6.9	0.0	0.0			
8	Hg <sup>II</sup> reduction rate	÷10	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
9	Hg <sup>II</sup> reduction rate	×10	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
10	DOM (in rainwater boundary solution)	low	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
11	DOM (in rainwater boundary solution)	high	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
12	Exchange capacity of HA and FA (SOM top 30 cm)	÷10	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
13	Exchange capacity of HA and FA (SOM top 30 cm)	×2	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
14	Exchange capacity of thiols (SOM top 30 cm)	÷10	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
15	Exchange capacity of thiols (SOM top 30 cm)	×2	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
16	Exchange capacity of HA, FA, thiols (SOM top 30 cm)	÷10	0.0	0.0	0.0	2.1	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
17	Exchange capacity of HA, FA, thiols (SOM top 30 cm)	×2	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
18	log k complexation Hg-DOM (HA and FA)	low	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
19	log k complexation Hg-DOM (HA and FA)	high	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
20	log k complexation Hg-DOM (thiols)	÷2	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
21	log k complexation Hg-DOM (thiols)	×2	0.0	0.0	0.0	20.6	0.0	0.0				10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
22	log k complexation Hg-DOM (HA, FA, thiols)	low	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
23	log k complexation Hg-DOM (HA, FA, thiols)	high	0.0	0.0	0.0	20.6	0.0	0.0				10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
24	log k sorption Hg-SOM (HA and FA)	low	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
25	log k sorption Hg-SOM (HA and FA)	high	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
26	log k sorption Hg-SOM (thiols)	÷2	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
27	log k sorption Hg-SOM (thiols)	×2	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
28	log k sorption Hg-SOM (HA, FA, thiols)	low	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
29	log k sorption Hg-SOM (HA, FA, thiols)	high	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
30	K, sorption DOM to soil minerals	÷10	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
31	K <sub>1</sub> sorption DOM to soil minerals	×2	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
32	S <sub>max</sub> max. adsorption capacity of DOM to minerals	low	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
33	S <sub>max</sub> max. adsorption capacity of DOM to minerals	high	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			
34	NAPL and cinnabar dissolution rates	low										42.7	22.0	9.7							28.7	14.8	6.5			
35	NAPL and cinnabar dissolution rates	high										0.0	0.0	0.0							0.0	0.0	0.0			
36	Initial Hg conc.	÷10	0.0	0.0	0.0	20.6	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	10.3	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0			

### Table 12 – Hg NAPL still present in the top 10 cm of the soil profile (in % of initial contamination), after 5, 25 and 50 years.

# Table 13 – Mercury sorbed to SOM (thiol and humic and fulvic acid sites) in the top 10 cm of the soil profile (in % of initial contamination), after 5, 25 and 50 years.

ß	Hg top 10 cm (% of initial contamination)			А			В			С			D			Е			F			G				
Species	Hg-SOM			1-0-0			0 - 1 - 0			0-0-1		0.	5 - 0.5 -	0	0	- 0.5 - 0.	.5	0.	5 - 0 - 0.	5	0.33	-0.33 -	0.33	(HgS - NAPL - HgCl <sub>2</sub> )		
Simulation	SAparameter		5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	years		
1	Base case	-	4.2	11.7	10.1	74.4	72.3	45.0	42.0	23.8	1.8	38.6	40.8	26.3	74.1	62.7	36.5	38.1	31.0	17.3	57.3	51.2	32.3			
2	Initial Hg conc.	×10	6.0	25.2	39.0	61.2	73.8	66.0	7.7	5.7	3.2	39.8	54.5	56.6	41.7	46.1	39.7	9.5	17.9	23.4	33.3	42.0	42.0		Color	legend
3	Initial Hg conc.	×100	6.2	26.9	44.3	16.8	28.1	27.1	2.0	1.7	1.3	18.6	37.2	44.7	14.2	21.2	20.2	4.5	14.5	22.6	15.7	28.1	32.7			>2×base case
4	NAPL dissolution rate	÷10				11.6	34.8	34.5				7.8	22.8	21.7	42.1	43.6	30.7				35.7	38.1	28.2			>1.1×base case
5	NAPL dissolution rate	×10				91.7	69.4	42.6				48.2	40.0	25.6	82.6	61.3	35.2				63.9	50.8	31.9			<.9 ×base case
6	Cinnabar dissolution rate	low	0.1	0.1	0.1							35.6	27.9	5.8				35.1	18.0	0.2	55.3	42.5	18.5			<0.5×base case
7	Cinnabar dissolution rate	high	9.3	28.4	28.9							41.3	50.0	36.6				40.9	40.3	27.7	59.2	57.4	39.1			
8	Hg <sup>II</sup> reduction rate	÷10	4.2	11.7	10.2	74.4	72.3	45.0	42.0	23.8	1.8	38.6	40.8	26.3	74.1	62.7	36.5	38.1	31.0	17.3	57.3	51.2	32.3			
9	Hg <sup>II</sup> reduction rate	×10	4.2	11.7	10.1	74.4	72.3	45.0	42.0	23.7	1.8	38.6	40.8	26.2	74.1	62.7	36.4	38.0	31.0	17.3	57.3	51.1	32.2			
10	DOM (in rainwater boundary solution)	low	1.1	5.1	8.8	78.2	93.7	87.9	45.9	42.6	38.4	39.5	48.3	46.6	78.1	83.9	78.5	39.2	38.4	37.0	59.7	63.9	60.8			
11	DOM (in rainwater boundary solution)	high	5.9	10.0	0.5	70.7	52.3	6.3	38.2	5.7	0.0	37.5	30.4	1.0	70.1	42.9	0.5	36.8	20.6	0.1	55.1	37.1	1.8			
12	Exchange capacity of HA and FA (SOM top 30 cm)	÷10	4.2	11.7	10.1	70.1	35.8	6.0	35.7	16.2	0.0	38.5	29.4	11.3	66.6	30.2	3.7	35.7	24.0	8.5	54.3	30.0	8.9			
13	Exchange capacity of HA and FA (SOM top 30 cm)	×2	4.2	11.7	10.1	74.6	74.7	49.8	44.6	26.6	4.2	38.6	41.4	28.1	75.3	65.7	41.3	39.0	32.3	19.4	57.4	52.4	35.1			
14	Exchange capacity of thiols (SOM top 30 cm)	÷10	2.4	6.7	3.0	73.9	68.7	38.4	25.2	6.2	0.0	38.0	37.8	20.5	57.2	44.8	17.4	21.3	13.4	0.1	43.0	35.8	15.5			
15	Exchange capacity of thiols (SOM top 30 cm)	×2	4.7	14.6	15.7	75.0	75.5	51.1	70.3	52.4	30.0	39.2	43.3	31.3	84.6	74.7	50.4	48.5	42.4	30.5	57.8	53.8	37.6			
16	Exchange capacity of HA, FA, thiols (SOM top 30 cm)	÷10	2.4	2.6	0.2	64.4	14.1	0.0	11.0	0.0	0.0	33.2	5.8	0.0	41.8	2.4	0.0	11.1	0.1	0.0	31.2	2.4	0.0			
17	Exchange capacity of HA, FA, thiols (SOM top 30 cm)	×2	4.7	14.6	15.7	75.0	76.1	52.6	71.2	53.4	31.0	39.2	43.3	31.3	84.6	75.5	51.9	48.5	42.4	30.5	57.8	53.8	37.7			
18	log k complexation Hg-DOM (HA and FA)	low	4.2	11.7	10.1	74.4	72.3	45.0	42.0	23.8	1.8	38.6	40.8	26.3	74.1	62.7	36.5	38.1	31.0	17.3	57.3	51.2	32.3			
19	log k complexation Hg-DOM (HA and FA)	high	4.2	11.7	10.1	74.4	72.3	45.0	42.0	23.8	1.8	38.6	40.8	26.3	74.1	62.7	36.5	38.1	31.0	17.3	57.3	51.2	32.3			
20	log k complexation Hg-DOM (thiols)	÷2	6.4	29.3	45.9	77.2	82.5	65.3	45.5	41.0	36.5	42.7	55.7	53.8	76.3	73.4	57.8	41.8	47.6	48.1	60.4	63.8	56.6			
21	log k complexation Hg-DOM (thiols)	×2	2.1	7.2	5.5	74.6	72.2	44.8				38.5	40.8	25.9	74.1	62.7	36.5	38.1	31.0	17.3	57.8	51.5	32.3			
22	log k complexation Hg-DOM (HA, FA, thiols)	low	6.4	29.3	45.9	77.2	82.5	65.3	45.5	41.0	36.5	42.7	55.7	53.8	76.3	73.4	57.8	41.8	47.6	48.1	60.4	63.8	56.6			
23	log k complexation Hg-DOM (HA, FA, thiols)	high	2.1	7.2	5.5	74.6	72.2	44.8				38.5	40.8	25.9	74.1	62.7	36.5	38.1	31.0	17.3	57.8	51.5	32.3			
24	log k sorption Hg-SOM (HA and FA)	low	4.2	11.7	10.1	35.9	21.9	0.9	31.1	13.4	0.0	33.7	23.3	9.4	35.2	20.1	0.2	32.1	20.3	7.1	35.2	22.4	6.1			
25	log k sorption Hg-SOM (HA and FA)	high	5.0	16.2	19.5	75.3	77.3	55.0	94.9	76.3	54.1	39.5	45.7	36.0	85.0	76.6	54.4	49.0	45.0	35.3	58.3	56.1	41.7			
26	log k sorption Hg-SOM (thiols)	÷2	2.1	7.1	4.6	74.6	71.7	43.8	36.1	17.5	0.0	38.4	39.9	24.5	66.3	55.2	29.1	30.2	22.9	9.3	50.3	44.3	25.4			
27	log k sorption Hg-SOM (thiols)	×2	6.4	29.3	35.5	74.9	73.2	46.2	42.0	35.5	35.5	40.9	43.1	35.5	74.1	62.7	37.2	38.1	35.5	35.5	56.9	51.3	35.9			
28	log k sorption Hg-SOM (HA, FA, thiols)	low	2.1	6.7	2.8	35.5	17.4	0.0	28.7	7.7	0.0	32.6	19.1	3.0	34.4	15.0	0.0	27.3	14.9	0.4	34.0	17.6	0.0			
29	log k sorption Hg-SOM (HA, FA, thiols)	high	6.4	29.3	40.7	76.1	78.5	56.6	94.2	76.4	54.5	42.1	49.9	42.6	84.7	77.0	55.1	49.2	47.3	40.4	58.7	58.3	46.3			
30	K <sub>1</sub> sorption DOM to soil minerals	÷10	4.2	11.7	10.1	74.4	72.3	45.0	42.0	23.8	1.8	38.6	40.8	26.3	74.1	62.7	36.5	38.1	31.0	17.3	57.3	51.2	32.3			
31	$K_L$ sorption DOM to soil minerals	×2	4.2	11.7	10.1	74.4	72.3	45.0	42.0	23.8	1.8	38.6	40.8	26.3	74.1	62.7	36.5	38.1	31.0	17.3	57.3	51.2	32.3			
32	$S_{\rm max}$ max. adsorption capacity of DOM to minerals	low	4.2	11.7	10.1	74.4	72.3	45.0	42.0	23.8	1.8	38.6	40.8	26.3	74.1	62.7	36.5	38.1	31.0	17.3	57.3	51.2	32.3			
33	${\rm S}_{\rm max}$ max. adsorption capacity of DOM to minerals	high	4.2	11.7	10.1	74.4	72.3	45.0	42.0	23.8	1.8	38.6	40.8	26.3	74.1	62.7	36.5	38.1	31.0	17.3	57.3	51.2	32.3			
34	NAPL and cinnabar dissolution rates	low										5.2	11.1	3.4							33.7	29.4	14.4			
35	NAPL and cinnabar dissolution rates	high										51.0	49.3	35.9							65.7	57.0	38.8			
36	Initial Hg conc.	÷10	1.8	1.1	0.7	52.9	0.0	0.0	65.1	0.0	0.0	22.4	0.5	0.3	57.7	0.0	0.0	25.1	0.5	0.3	33.9	0.3	0.2			

8	Hg top 10 cm (% of initial contamination)			А			В			С			D			E			F			G				
Species :	Hg-DOM		1	1 - 0 - 0			0 - 1 - 0			0-0-1		0.5	- 0.5 -	0	0 -	0.5 - 0.5	5	0.	5 - 0 - 0.	5	0.33 -	0.33 -	0.33	(HgS - NAPL - HgCl <sub>2</sub> )		
Simulation	SAparameter		5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	years		
1	Base case	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
2	Initial Hg conc.	×10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0		Color	legend
3	Initial Hg conc.	×100	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			>2 ×base case
4	NAPL dissolution rate	÷10				0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0				0.0	0.0	0.0			>1.1×base case
5	NAPL dissolution rate	×10				0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0				0.0	0.0	0.0			<.9 × base case
6	Cinnabar dissolution rate	low	0.0	0.0	0.0							0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0			<0.5×base case
7	Cinnabar dissolution rate	high	0.0	0.0	0.0							0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0			
8	Hg <sup>II</sup> reduction rate	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
9	Hg <sup>II</sup> reduction rate	×10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
10	DOM (in rainwater boundary solution)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
11	DOM (in rainwater boundary solution)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
12	Exchange capacity of HA and FA (SOM top 30 cm)	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
13	Exchange capacity of HA and FA (SOM top 30 cm)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
14	Exchange capacity of thiols (SOM top 30 cm)	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
15	Exchange capacity of thiols (SOM top 30 cm)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
16	Exchange capacity of HA, FA, thiols (SOM top 30 cm)	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
17	Exchange capacity of HA, FA, thiols (SOM top 30 cm)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
18	log k complexation Hg-DOM (HA and FA)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
19	log k complexation Hg-DOM (HA and FA)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
20	log k complexation Hg-DOM (thiols)	÷2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
21	log k complexation Hg-DOM (thiols)	×2	0.0	0.0	0.0	0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
22	log k complexation Hg-DOM (HA, FA, thiols)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
23	log k complexation Hg-DOM (HA, FA, thiols)	high	0.0	0.0	0.0	0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
24	log k sorption Hg-SOM (HA and FA)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
25	log k sorption Hg-SOM (HA and FA)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
26	log k sorption Hg-SOM (thiols)	÷2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
27	log k sorption Hg-SOM (thiols)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
28	log k sorption Hg-SOM (HA, FA, thiols)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
29	log k sorption Hg-SOM (HA, FA, thiols)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
30	K <sub>L</sub> sorption DOM to soil minerals	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
31	K <sub>L</sub> sorption DOM to soil minerals	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
32	S max max. adsorption capacity of DOM to minerals	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
33	S <sub>max</sub> max. adsorption capacity of DOM to minerals	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
34	NAPL and cinnabar dissolution rates	low										0.0	0.0	0.0							0.0	0.0	0.0			
35	NAPL and cinnabar dissolution rates	high										0.0	0.0	0.0							0.0	0.0	0.0			
36	Initial Hg conc.	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			

### Table 14 – Aqueous complex Hg-DOM in the top 10 cm of the soil profile (in % of initial contamination), after 5, 25 and 50 years.

# Table 15 – Aqueous complexes of Hg with inorganic ligands in the top 10 cm of the soil profile (in % of initial contamination), after 5, 25 and 50 years.

B	Hg top 10 cm (% of initial contamination)			А			В			С			D			E			F			G				
Species :	Hg-inorg		1	L-0-0		(	0-1-0		(	0-0-1		0.5	-0.5-0	0	0 -	0.5 - 0.5	5	0.5	5-0-0.5	i	0.33	- 0.33 -	0.33	(HgS - NAPL - HgCl <sub>2</sub> )		
Simulation	SA parameter		5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	years		
1	Base case	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
2	Initial Hg conc.	×10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0		Color	legend
3	Initial Hg conc.	×100	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			>2 ×base case
4	NAPL dissolution rate	÷10				0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0				0.0	0.0	0.0			>1.1×base case
5	NAPL dissolution rate	×10				0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0				0.0	0.0	0.0			<.9×base case
6	Cinnabar dissolution rate	low	0.0	0.0	0.0							0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0			<0.5×base case
7	Cinnabar dissolution rate	high	0.0	0.0	0.0							0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0			
8	Hg <sup>II</sup> reduction rate	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
9	Hg <sup>II</sup> reduction rate	×10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
10	DOM (in rainwater boundary solution)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
11	DOM (in rainwater boundary solution)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
12	Exchange capacity of HA and FA (SOM top 30 cm)	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
13	Exchange capacity of HA and FA (SOM top 30 cm)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
14	Exchange capacity of thiols (SOM top 30 cm)	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
15	Exchange capacity of thiols (SOM top 30 cm)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
16	Exchange capacity of HA, FA, thiols (SOM top 30 cm)	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
17	Exchange capacity of HA, FA, thiols (SOM top 30 cm)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
18	log k complexation Hg-DOM (HA and FA)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
19	log k complexation Hg-DOM (HA and FA)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
20	log k complexation Hg-DOM (thiols)	÷2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
21	log k complexation Hg-DOM (thiols)	×2	0.0	0.0	0.0	0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
22	log k complexation Hg-DOM (HA, FA, thiols)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
23	log k complexation Hg-DOM (HA, FA, thiols)	high	0.0	0.0	0.0	0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
24	log k sorption Hg-SOM (HA and FA)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
25	log k sorption Hg-SOM (HA and FA)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
26	log k sorption Hg-SOM (thiols)	÷2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
27	log k sorption Hg-SOM (thiols)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
28	log k sorption Hg-SOM (HA, FA, thiols)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
29	log k sorption Hg-SOM (HA, FA, thiols)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
30	K <sub>L</sub> sorption DOM to soil minerals	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
31	$K_L$ sorption DOM to soil minerals	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
32	S $_{\rm max}$ max. adsorption capacity of DOM to minerals	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
33	S $_{\rm max}$ max. adsorption capacity of DOM to minerals	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
34	NAPL and cinnabar dissolution rates	low										0.0	0.0	0.0							0.0	0.0	0.0			
35	NAPL and cinnabar dissolution rates	high										0.0	0.0	0.0							0.0	0.0	0.0			
36	Initial Hg conc.	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			

3	Hg top 10 cm (% of initial contamination)			Α			В			С			D			E			F			G				
Species :	Hg(g)		1	1 - 0 - 0			0 - 1 - 0			0 - 0 - 1		0.5	5 - 0.5 -	0	0 -	0.5 - 0.5	5	0.	5-0-0.	5	0.33	0.33-0	0.33	(HgS - NAPL - HgCl <sub>2</sub> )		
Simulation	SA parameter		5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	years		
1	Base case	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
2	Initial Hg conc.	×10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1		Color	legend
3	Initial Hg conc.	×100	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1			>2 ×base case
4	NAPL dissolution rate	÷10				0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0				0.0	0.0	0.0			>1.1×base case
5	NAPL dissolution rate	×10				0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0				0.0	0.0	0.0			<.9 × base case
6	Cinnabar dissolution rate	low	0.0	0.0	0.0							0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0			<0.5×base case
7	Cinnabar dissolution rate	high	0.0	0.0	0.0							0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0			
8	Hg <sup>II</sup> reduction rate	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
9	Hg <sup>II</sup> reduction rate	×10	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.1	0.1			
10	DOM (in rainwater boundary solution)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
11	DOM (in rainwater boundary solution)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
12	Exchange capacity of HA and FA (SOM top 30 cm)	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
13	Exchange capacity of HA and FA (SOM top 30 cm)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
14	Exchange capacity of thiols (SOM top 30 cm)	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
15	Exchange capacity of thiols (SOM top 30 cm)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
16	Exchange capacity of HA, FA, thiols (SOM top 30 cm)	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
17	Exchange capacity of HA, FA, thiols (SOM top 30 cm)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
18	log k complexation Hg-DOM (HA and FA)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
19	log k complexation Hg-DOM (HA and FA)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
20	log k complexation Hg-DOM (thiols)	÷2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
21	log k complexation Hg-DOM (thiols)	×2	0.0	0.0	0.0	0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
22	log k complexation Hg-DOM (HA, FA, thiols)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
23	log k complexation Hg-DOM (HA, FA, thiols)	high	0.0	0.0	0.0	0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
24	log k sorption Hg-SOM (HA and FA)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
25	log k sorption Hg-SOM (HA and FA)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
26	log k sorption Hg-SOM (thiols)	÷2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
27	log k sorption Hg-SOM (thiols)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
28	log k sorption Hg-SOM (HA, FA, thiols)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
29	log k sorption Hg-SOM (HA, FA, thiols)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
30	K <sub>L</sub> sorption DOM to soil minerals	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
31	K <sub>L</sub> sorption DOM to soil minerals	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
32	S <sub>max</sub> max. adsorption capacity of DOM to minerals	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
33	S <sub>max</sub> max. adsorption capacity of DOM to minerals	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
34	NAPL and cinnabar dissolution rates	low										0.0	0.0	0.0							0.0	0.0	0.0			
35	NAPL and cinnabar dissolution rates	high										0.0	0.0	0.0							0.0	0.1	0.1			
36	Initial Hg conc.	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			

### Table 16 – Gaseous mercury in the top 10 cm of the soil profile (in % of initial contamination), after 5, 25 and 50 years.

Figure 33 shows profiles of Hg concentrations at discrete times for simulation B04 (Hg NAPL as pollution source, slow dissolution rate).



### Figure 33 – Depth distribution of Hg (a) in NAPL and (b) sorbed to SOM at t = 0, 5, 10, 25 and 50 years for simulation B04. Note that for clarity the y-axis stops at 50 cm depth.

Figures 34 and 35 present Hg distribution over time when the three pollution types are combined (simulation G04) with slow NAPL dissolution rate. Figure 34a shows that, consistently with the dissolution rate chosen for the base case, half of the initial cinnabar is still present in the top 10 cm after 50 years. About one fifth of the initial NAPL is still present after 50 years (Figure 34b). As opposite to what was simulated in base case C01, not all sorption sites are immediately occupied after the initial input of  $HgCl_2(aq)$  (Figures 34c and 35b). Moreover, Figures 34c and 35b show that after 50 years, about the same quantity of Hg-SOM is present in the top 10 cm, but its vertical distribution has changed (leaching and accumulation at the bottom of the horizon).



Figure 34 – Cumulative depth distribution over time of (a) cinnabar, (b) NAPL and (c) other Hg species (in % of total initial Hg) for simulation G04.



Figure 35 – Depth distribution of Hg (a) in cinnabar and NAPL, and (b) sorbed to SOM at t = 0, 5, 10, 25 and 50 years for simulation G04. Note that for clarity the y-axis stops at 50 cm depth.

### 7.1.2.4 • Hg still present in the soil profile below the horizon originally contaminated (11-100 cm)

Tables 17 to 20 give the amount of mercury present between 11 and 100 cm after 5, 25 and 50 years for different (groups of) Hg phases and species : cinnabar (HgS), NAPL, Hg sorbed to SOM, Hg complexed with organic and inorganic ligands, and gaseous Hg. Most of the mercury present in the soil below the top horizon is Hg sorbed to SOM (SOM is uniformly distributed in the top 30 cm; see section 5.1).

### It is important to notice that the sensitivity of Hg-SOM below the top horizon is sometimes opposite to the sensitivity of Hg-SOM in the top horizon (see

**Table 13).** For example, a lower log k for Hg-DOM complexation reactions (simulation runs A20, B20, ..., to G20) results in more Hg sorbed to SOM in the top 10 cm but less Hg sorbed to SOM below. This is partly due to mass balance conservation : mercury stays longer sorbed to SOM in the top horizon because Hg-DOM complexation is less favoured, and therefore there is less mercury available below the top horizon for Hg-SOM sorption. It is therefore suggested that the geometry of (i) horizon contaminated with Hg, and (ii) SOM distribution in soil profile is critical for Hg fate though not directly included in the present SA.

# Table 17 – Mercury sorbed to SOM (thiol and humic and fulvic acid sites) below the top 10 cm of the soil profile (in % of initial contamination), after 5, 25 and 50 years.

4	Hg 11-100 cm (% of initial contamination)			Α			В			С			D			E			F			G				
Species :	Hg-SOM			1-0-0			0 - 1 - 0			0-0-1		0.	5 - 0.5 -	- 0	0 -	0.5-0.5	5	0.	5-0-0.	5	0.33	- 0.33 -	0.33	(HgS - NAPL - HgCl <sub>2</sub> )		
Simulation	SAparameter		5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	years		
1	Base case	-	2.0	11.0	20.7	4.7	20.3	34.4	56.4	62.4	66.0	4.1	16.6	28.4	15.1	28.8	41.1	14.7	25.2	35.3	4.9	18.4	31.0			
2	Initial Hg conc.	×10	0.4	3.4	9.0	18.2	24.9	30.8	11.2	11.2	11.1	3.1	9.4	16.3	13.8	17.6	21.5	9.8	10.8	13.3	10.6	14.4	19.0		Color	legend
3	Initial Hg conc.	×100	0.2	2.4	5.6	8.9	10.2	9.4	2.5	2.5	2.5	6.9	8.0	9.0	7.0	7.6	7.3	1.9	3.0	4.7	6.0	6.9	7.7			>2 × base case
4	NAPL dissolution rate	÷10				2.7	14.1	26.3				2.4	12.9	24.0	14.7	25.9	37.2				4.7	16.7	28.6			>1.1×base case
5	NAPL dissolution rate	×10				7.9	22.9	36.3				4.7	17.2	28.9	16.9	30.2	42.3				5.2	18.8	31.2			<.9 × base case
6	Cinnabar dissolution rate	low	0.2	0.3	0.3							4.0	16.0	26.0				14.6	24.6	29.6	4.9	17.9	29.4			<0.5×base case
7	Cinnabar dissolution rate	high	2.6	13.6	25.3							4.1	17.1	29.9				14.7	25.8	36.8	4.9	18.8	32.1			
8	Hg <sup>II</sup> reduction rate	÷10	2.0	11.0	20.7	4.7	20.3	34.4	56.4	62.4	66.0	4.1	16.6	28.4	15.1	28.8	41.1	14.7	25.2	35.3	4.9	18.4	31.0			
9	Hg <sup>II</sup> reduction rate	×10	2.0	11.0	20.7	4.7	20.3	34.4	56.4	62.4	66.0	4.1	16.6	28.4	15.1	28.8	41.1	14.7	25.2	35.3	4.9	18.4	31.0			
10	DOM (in rainwater boundary solution)	low	0.1	1.0	3.0	1.2	6.2	12.1	54.1	57.0	59.8	0.8	4.7	9.3	11.6	16.1	21.4	11.4	14.7	18.8	1.1	5.4	10.4			
11	DOM (in rainwater boundary solution)	high	3.7	16.7	22.3	6.8	27.1	43.5	57.5	64.5	33.9	6.0	22.3	34.8	17.2	34.8	46.7	16.5	30.3	32.7	7.1	24.7	38.5			
12	Exchange capacity of HA and FA (SOM top 30 cm)	÷10	2.0	11.0	20.8	9.0	56.7	72.3	61.9	67.3	62.6	4.2	28.0	43.2	22.5	61.1	72.4	17.0	32.0	43.7	7.9	39.5	53.7			
13	Exchange capacity of HA and FA (SOM top 30 cm)	×2	2.0	11.0	20.7	4.5	17.9	29.7	53.9	60.4	64.9	4.1	16.0	26.6	14.0	25.9	36.4	13.7	24.0	33.4	4.8	17.2	28.2			
14	Exchange capacity of thiols (SOM top 30 cm)	÷10	2.1	6.6	9.6	3.5	14.6	23.3	30.0	30.1	12.6	2.9	10.3	16.3	21.6	26.0	30.4	21.1	22.1	22.8	15.5	19.5	24.1			
15	Exchange capacity of thiols (SOM top 30 cm)	×2	1.7	10.8	20.9	4.4	19.9	34.1	29.5	41.6	52.7	3.7	16.8	29.1	5.1	20.6	34.6	4.6	17.6	29.7	4.7	18.6	31.5			
16	Exchange capacity of HA, FA, thiols (SOM top 30 cm)	÷10	2.2	10.6	10.5	13.0	67.1	23.3	21.4	6.4	0.0	7.7	41.1	11.3	23.3	47.6	0.9	17.6	16.7	0.2	19.4	39.3	3.4			
17	Exchange capacity of HA, FA, thiols (SOM top 30 cm)	×2	1.7	10.8	20.9	4.4	19.3	32.7	28.6	40.7	51.7	3.7	16.8	29.1	5.0	19.8	33.1	4.6	17.6	29.7	4.7	18.6	31.4			
18	log k complexation Hg-DOM (HA and FA)	low	2.0	11.0	20.7	4.7	20.3	34.4	56.4	62.4	66.0	4.1	16.6	28.4	15.1	28.8	41.1	14.7	25.2	35.3	4.9	18.4	31.0			
19	log k complexation Hg-DOM (HA and FA)	high	2.0	11.0	20.7	4.7	20.3	34.4	56.4	62.4	66.0	4.1	16.6	28.4	15.1	28.8	41.1	14.7	25.2	35.3	4.9	18.4	31.0			
20	log k complexation Hg-DOM (thiols)	÷2	0.0	0.0	4.2	2.2	17.4	34.7	54.5	59.0	63.5	0.3	9.0	21.3	13.4	26.6	42.2	11.4	17.1	26.9	2.1	13.3	27.5			
21	log k complexation Hg-DOM (thiols)	×2	0.0	0.0	0.1	0.4	5.6	10.7				0.0	1.6	4.6	11.2	15.1	19.0	10.7	11.5	13.2	0.3	3.2	6.8			
22	log k complexation Hg-DOM (HA, FA, thiols)	low	0.0	0.0	4.2	2.2	17.4	34.7	54.5	59.0	63.5	0.3	9.0	21.3	13.4	26.6	42.2	11.4	17.1	26.9	2.1	13.3	27.5			
23	log k complexation Hg-DOM (HA, FA, thiols)	high	0.0	0.0	0.1	0.4	5.6	10.7				0.0	1.6	4.6	11.2	15.1	19.0	10.7	11.5	13.2	0.3	3.2	6.8			
24	log k sorption Hg-SOM (HA and FA)	low	2.0	11.0	20.8	43.1	64.9	65.0	65.3	66.5	58.1	8.9	33.8	44.0	53.7	65.2	64.0	20.5	35.4	44.4	26.9	45.7	53.1			
25	log k sorption Hg-SOM (HA and FA)	high	1.5	10.3	20.0	4.0	19.4	33.3	5.1	20.3	34.1	3.4	15.7	27.5	4.7	20.0	33.8	4.2	16.3	28.0	4.2	17.6	30.6			
26	log k sorption Hg-SOM (thiols)	÷2	0.0	0.2	1.1	0.4	6.2	11.8	45.3	46.1	41.2	0.1	2.6	6.1	18.9	22.6	26.4	18.5	19.5	21.3	7.8	10.5	13.9			
27	log k sorption Hg-SOM (thiols)	×2	0.0	0.0	14.6	4.5	26.8	53.8	58.0	64.4	64.4	2.0	21.6	39.5	15.6	37.2	62.7	15.2	29.2	39.5	5.6	25.8	48.2			
28	log k sorption Hg-SOM (HA, FA, thiols)	low	0.0	0.5	2.9	39.4	60.3	51.9	48.1	51.3	36.5	5.9	23.4	27.6	50.8	61.8	49.4	21.4	27.5	30.1	24.0	37.2	39.2			
29	log k sorption Hg-SOM (HA, FA, thiols)	high	0.0	0.0	9.3	3.3	21.4	43.4	5.7	23.6	45.5	0.8	14.7	32.4	5.0	23.0	44.9	4.0	17.3	34.7	3.8	18.8	37.8			
30	K <sub>L</sub> sorption DOM to soil minerals	÷10	2.0	11.0	20.7	4.7	20.3	34.4	56.4	62.4	66.0	4.1	16.6	28.4	15.1	28.8	41.1	14.7	25.2	35.3	4.9	18.4	31.0			
31	K <sub>L</sub> sorption DOM to soil minerals	×2	2.0	11.0	20.7	4.7	20.3	34.4	56.4	62.4	66.0	4.1	16.6	28.4	15.1	28.8	41.1	14.7	25.2	35.3	4.9	18.4	31.0			
32	S max max. adsorption capacity of DOM to minerals	low	2.0	11.0	20.7	4.7	20.3	34.4	56.4	62.4	66.0	4.1	16.6	28.4	15.1	28.8	41.1	14.7	25.2	35.3	4.9	18.4	31.0			
33	S <sub>max</sub> max. adsorption capacity of DOM to minerals	high	2.0	11.0	20.7	4.7	20.3	34.4	56.4	62.4	66.0	4.1	16.6	28.4	15.1	28.8	41.1	14.7	25.2	35.3	4.9	18.4	31.0			
34	NAPL and cinnabar dissolution rates	low										2.1	11.2	19.7							4.6	16.3	27.0			
35	NAPL and cinnabar dissolution rates	high										4.8	17.7	30.4							5.3	19.2	32.4			
36	Initial Hg conc.	÷10	4.0	3.9	2.4	24.0	31.3	0.0	31.7	27.6	0.0	18.4	2.2	1.1	28.9	28.5	0.0	25.2	1.7	1.1	25.2	6.5	0.7			

4	Hg 11-100 cm (% of initial contamination)			Α			В			С			D			E			F			G				
Species :	Hg-DOM		:	1-0-0			0 - 1 - 0			0-0-1		0.5	5-0.5	- 0	0 -	0.5 - 0.	5	0.5	5-0-0.	5	0.33	- 0.33 - 0	0.33	(HgS - NAPL - HgCl <sub>2</sub> )		
Simulation	SA parameter		5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	years		
1	Base case	-	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.0	0.1			
2	Initial Hg conc.	×10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0		Color	legend
3	Initial Hg conc.	×100	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			>2×base case
4	NAPL dissolution rate	÷10				0.0	0.0	0.1				0.0	0.0	0.1	0.0	0.1	0.1				0.0	0.0	0.1			>1.1×base case
5	NAPL dissolution rate	×10				0.0	0.0	0.1				0.0	0.0	0.1	0.0	0.1	0.1				0.0	0.0	0.1			<.9×base case
6	Cinnabar dissolution rate	low	0.0	0.0	0.0							0.0	0.0	0.1				0.0	0.1	0.1	0.0	0.0	0.1			<0.5×base case
7	Cinnabar dissolution rate	high	0.0	0.0	0.1							0.0	0.0	0.1				0.0	0.1	0.1	0.0	0.0	0.1			
8	Hg <sup>II</sup> reduction rate	÷10	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.0	0.1			
9	Hg <sup>II</sup> reduction rate	×10	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.0	0.1			
10	DOM (in rainwater boundary solution)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
11	DOM (in rainwater boundary solution)	high	0.1	0.1	0.2	0.1	0.1	0.2	0.1	0.2	0.2	0.1	0.1	0.2	0.1	0.1	0.2	0.1	0.1	0.2	0.1	0.1	0.2			
12	Exchange capacity of HA and FA (SOM top 30 cm)	÷10	0.0	0.0	0.1	0.0	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.1	0.1			
13	Exchange capacity of HA and FA (SOM top 30 cm)	×2	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.0	0.1			
14	Exchange capacity of thiols (SOM top 30 cm)	÷10	0.0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1			
15	Exchange capacity of thiols (SOM top 30 cm)	×2	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.1			
16	Exchange capacity of HA, FA, thiols (SOM top 30 cm)	÷10	0.0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.1	0.1			
17	Exchange capacity of HA, FA, thiols (SOM top 30 cm)	×2	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.1			
18	log k complexation Hg-DOM (HA and FA)	low	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.0	0.1			
19	log k complexation Hg-DOM (HA and FA)	high	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.0	0.1			
20	log k complexation Hg-DOM (thiols)	÷2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
21	log k complexation Hg-DOM (thiols)	×2	0.1	0.1	0.1	0.1	0.1	0.1				0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1			
22	log k complexation Hg-DOM (HA, FA, thiols)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
23	log k complexation Hg-DOM (HA, FA, thiols)	high	0.1	0.1	0.1	0.1	0.1	0.1				0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1			
24	log k sorption Hg-SOM (HA and FA)	low	0.0	0.0	0.1	0.0	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.1	0.1			
25	log k sorption Hg-SOM (HA and FA)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
26	log k sorption Hg-SOM (thiols)	÷2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1			
27	log k sorption Hg-SOM (thiols)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
28	log k sorption Hg-SOM (HA, FA, thiols)	low	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1			
29	log k sorption Hg-SOM (HA, FA, thiols)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
30	K <sub>L</sub> sorption DOM to soil minerals	÷10	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.0	0.1			
31	K L sorption DOM to soil minerals	×2	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.0	0.1			
32	$S_{\rm max}$ max. adsorption capacity of DOM to minerals	low	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.0	0.1			
33	$S_{\max}\max$ . adsorption capacity of DOM to minerals	high	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.0	0.1			
34	NAPL and cinnabar dissolution rates	low										0.0	0.0	0.1							0.0	0.0	0.1			
35	NAPL and cinnabar dissolution rates	high										0.0	0.0	0.1							0.0	0.0	0.1			
36	Initial Hg conc.	÷10	0.0	0.1	0.1	0.1	0.4	0.0	0.1	0.4	0.0	0.1	0.1	0.0	0.1	0.4	0.0	0.1	0.0	0.0	0.1	0.3	0.0			

### Table 18 – Aqueous complex Hg-DOM below the top 10 cm of the soil profile (in % of initial contamination), after 5, 25 and 50 years.

### Table 19 – Aqueous complexes of Hg with inorganic ligands below the top 10 cm of the soil profile (in % of initial contamination), after 5, 25 and 50

years.

4	Hg 11-100 cm (% of initial contamination)			А			В			С			D			E			F			G				
Species	Hg-inorg		1	1 - 0 - 0			0-1-0			0-0-1		0.5	5 - 0.5 -	0	0 -	0.5 - 0.5	5	0.5	5-0-0.	5	0.33	- 0.33 -	0.33	(HgS - NAPL - HgCl <sub>2</sub> )		
Simulation	SA parameter		5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	years		
1	Base case	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
2	Initial Hg conc.	×10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0		Color	legend
3	Initial Hg conc.	×100	0.0	0.0	0.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0		1	>2×base case
4	NAPL dissolution rate	÷10				0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0				0.0	0.0	0.0			>1.1×base case
5	NAPL dissolution rate	×10				0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0				0.0	0.0	0.0			<.9×base case
6	Cinnabar dissolution rate	low	0.0	0.0	0.0							0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0			<0.5×base case
7	Cinnabar dissolution rate	high	0.0	0.0	0.0							0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0			
8	Hg <sup>II</sup> reduction rate	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
9	Hg <sup>II</sup> reduction rate	×10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
10	DOM (in rainwater boundary solution)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
11	DOM (in rainwater boundary solution)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
12	Exchange capacity of HA and FA (SOM top 30 cm)	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
13	Exchange capacity of HA and FA (SOM top 30 cm)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
14	Exchange capacity of thiols (SOM top 30 cm)	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
15	Exchange capacity of thiols (SOM top 30 cm)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
16	Exchange capacity of HA, FA, thiols (SOM top 30 cm)	÷10	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
17	Exchange capacity of HA, FA, thiols (SOM top 30 cm)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
18	log k complexation Hg-DOM (HA and FA)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
19	log k complexation Hg-DOM (HA and FA)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
20	log k complexation Hg-DOM (thiols)	÷2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
21	log k complexation Hg-DOM (thiols)	×2	0.0	0.0	0.0	0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
22	log k complexation Hg-DOM (HA, FA, thiols)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
23	log k complexation Hg-DOM (HA, FA, thiols)	high	0.0	0.0	0.0	0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
24	log k sorption Hg-SOM (HA and FA)	low	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
25	log k sorption Hg-SOM (HA and FA)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
26	log k sorption Hg-SOM (thiols)	÷2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
27	log k sorption Hg-SOM (thiols)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
28	log k sorption Hg-SOM (HA, FA, thiols)	low	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
29	log k sorption Hg-SOM (HA, FA, thiols)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
30	K <sub>1</sub> sorption DOM to soil minerals	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
31	K <sub>1</sub> sorption DOM to soil minerals	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
32	S <sub>max</sub> max. adsorption capacity of DOM to minerals	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
33	S <sub>max</sub> max. adsorption capacity of DOM to minerals	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
34	NAPL and cinnabar dissolution rates	low										0.0	0.0	0.0							0.0	0.0	0.0			
35	NAPL and cinnabar dissolution rates	high										0.0	0.0	0.0							0.0	0.0	0.0			
36	Initial Hg conc.	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			

4	Hg 11-100 cm (% of initial contamination)			Α			В			С			D			E			F			G				
Species :	Hg(g)		1	1-0-0		(	0-1-0			0-0-1		0.5	5 - 0.5 -	0	0 -	0.5 - 0.5	5	0.5	5-0-0.5	5	0.33	0.33-0	0.33	(HgS - NAPL - HgCl <sub>2</sub> )		
Simulation	SA parameter		5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	5	25	50	years		
1	Base case	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
2	Initial Hg conc.	×10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.8	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.2	0.1		Color	legend
3	Initial Hg conc.	×100	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.0			>2×base case
4	NAPL dissolution rate	÷10				0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0				0.0	0.0	0.0			>1.1×base case
5	NAPL dissolution rate	×10				0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0				0.1	0.1	0.1			<.9 × base case
6	Cinnabar dissolution rate	low	0.0	0.0	0.0							0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0			<0.5×base case
7	Cinnabar dissolution rate	high	0.0	0.0	0.0							0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0			
8	Hg <sup>II</sup> reduction rate	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
9	Hg <sup>II</sup> reduction rate	×10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
10	DOM (in rainwater boundary solution)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
11	DOM (in rainwater boundary solution)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
12	Exchange capacity of HA and FA (SOM top 30 cm)	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
13	Exchange capacity of HA and FA (SOM top 30 cm)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
14	Exchange capacity of thiols (SOM top 30 cm)	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
15	Exchange capacity of thiols (SOM top 30 cm)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
16	Exchange capacity of HA, FA, thiols (SOM top 30 cm)	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
17	Exchange capacity of HA, FA, thiols (SOM top 30 cm)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
18	log k complexation Hg-DOM (HA and FA)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
19	log k complexation Hg-DOM (HA and FA)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
20	log k complexation Hg-DOM (thiols)	÷2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
21	log k complexation Hg-DOM (thiols)	×2	0.0	0.0	0.0	0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
22	log k complexation Hg-DOM (HA, FA, thiols)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
23	log k complexation Hg-DOM (HA, FA, thiols)	high	0.0	0.0	0.0	0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
24	log k sorption Hg-SOM (HA and FA)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
25	log k sorption Hg-SOM (HA and FA)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
26	log k sorption Hg-SOM (thiols)	÷2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
27	log k sorption Hg-SOM (thiols)	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
28	log k sorption Hg-SOM (HA, FA, thiols)	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
29	log k sorption Hg-SOM (HA, FA, thiols)	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
30	K <sub>L</sub> sorption DOM to soil minerals	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
31	K <sub>L</sub> sorption DOM to soil minerals	×2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
32	S $_{\rm max}$ max. adsorption capacity of DOM to minerals	low	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
33	S $_{\rm max}$ max. adsorption capacity of DOM to minerals	high	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
34	NAPL and cinnabar dissolution rates	low										0.0	0.0	0.0							0.0	0.0	0.0			
35	NAPL and cinnabar dissolution rates	high										0.0	0.0	0.0							0.1	0.1	0.1			
36	Initial Hg conc.	÷10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			

### Table 20 – Gaseous mercury below the top 10 cm of the soil profile (in % of initial contamination), after 5, 25 and 50 years.

### 7.2 Elementary effects (Morris)

### 7.2.1 Method

This method provides insights into which input factors may be considered to have a negligible sensitivity, or having a linear and additive effect, or non-linear and/or interacting with other factors (Campolongo et al., 2007). Sampling trajectories are randomly designed across the parameter space (each parameter range being divided into *p* levels), and successive deviations in the trajectories result in the quantification of elementary effects. The calculation of elementary effects is described in detail in Morris (1991) and Campolongo et al. (2007). One computes then  $\mu$ , which assesses the overall influence of the factor on the output, and  $\sigma$ , which estimates the ensemble of the factor's higher order effects, i.e. non-linear and/or due to interactions with other factors (Campolongo et al., 2007). Campolongo et al. (2007) further proposed to use  $\mu^*$  (= mean of the distribution of the absolute value of elementary effects) as an indicator of parameter sensitivity to identify model non-monoticity (i.e. when for a given factor elementary effects of opposite signs cancel each other out in the measure of  $\mu$ ).

For a design of *r* trajectories of *k*+1 points (where *k* is the number of input factors varied) the computational cost of the experiment is thus r(k+1). However, in the present case, repeating the analysis with seven different initial pollution types increases the potential number of simulations to  $7 \times r(k+1)$ . Using the same 13 parameters of section 5.3 and 6 levels it was decided to take 5 trajectories. Some parameters are not relevant for a given Hg source (e.g. cinnabar dissolution rate in the case no cinnabar is present) and therefore the number of simulations equals 460. Typically between 10 and 50 trajectories are used (Campolongo et al., 2007). Using only 5 trajectories poses a risk of non-optimal coverage of the input parameter space. However, repeating the analysis with 7 different pollution types provides complementary coverage of input parameter space even if the 5×7 trajectories cannot strictly be considered as an ensemble of 35 trajectories because they do not use the same set of factors.

Sampling strategy was performed in Matlab ® according to Campolongo et al. (2007), who refined the original sampling strategy of Morris (1991) by maximising the distance between trajectories in the parameter space. The method was tested on the three cases where the initial contamination is of one type (A, B and C), and on one case combining two different Hg sources (NAPL and mercuric chloride; code E). The one-at-a-time analysis and the results presented hereafter show that the combined effect (different sources) always gives intermediate results compared to the single source cases.

The matrices of input parameter values for the different trajectories are provided in Annex (section 9.3).

Factor		Unit
<b>X</b> 1	Initial Hg concentration	mg kg⁻¹
X <sub>2</sub>	Cinnabar dissolution rate	$day^{-1} g_{OC}^{-1}$
<b>X</b> <sub>3</sub>	Hg <sup>II</sup> reduction rate	day <sup>-1</sup>
<b>X</b> 4	DOM (in rainwater boundary solution)	mg $L^{-1}$
<b>X</b> 5	Exchange capacity of HA and FA (SOM top 30 cm)	$meq dm^{-3}$
X <sub>6</sub>	Exchange capacity of thiols (SOM top 30 cm)	$meq dm^{-3}$
<b>X</b> <sub>7</sub>	log k complexation Hg-DOM (HA and FA)	-
<b>X</b> 8	log k complexation Hg-DOM (thiols)	-
X9	log k sorption Hg-SOM (HA and FA)	-
<b>X</b> 10	log k sorption Hg-SOM (thiols)	
<b>X</b> 11	$K_L$ sorption DOM to soil minerals	-
<b>X</b> <sub>12</sub>	$S_{\rm max}$ max. adsorption capacity of DOM to minerals	mg kg <sup>-1</sup>
<b>X</b> <sub>13</sub>	NAPL dissolution rate	day <sup>-1</sup>

Table 21 – List of factors included in the design of trajectories.

### 7.2.2 Results

7.2.2.1 Group A (cinnabar)

Tables 22 to 24 present the results of the SA using Morris trajectories for indicators **2** to **4**. Figures 36 to 38 show the corresponding plots of  $\mu$  (and  $\mu^*$ ) vs.  $\sigma$  for interpretation of factor sensitivity. No results are shown for the indicator **1** (% of mercury volatilized). This indicator was never above 0.0001% of the initial mercury after 50 years.

It can be seen from these tables and figures that factor sensitivity varies with the indicator assessed (2, 3 or 4) but also over time (after 5, 25 or 50 years). These results are discussed further below.

Factor	After 5 years				After 25 years		After 50 years			
	μ	μ*	σ	μ	μ*	σ	μ	μ*	σ	
X <sub>1</sub> : Hg initial conc.	-0.2639	0.2639	0.5901	-1.3367	1.3367	2.9889	-2.7107	2.7107	6.0612	
X <sub>2</sub> : HgS degradation rate	0.0023	0.0023	0.0052	0.0033	0.0033	0.0074	1.1533	1.1533	2.5789	
X <sub>3</sub> : Hg(II) reduction rate	0	0	0	0.0003	0.0003 0.0003		0	0	0	
X₄: DOM in rain	0.1423	0.1423	0.2041	1.0770	1.0770	1.5117	6.9937	6.9937	9.8479	
X₅: meq SOM (HA, FA)	0	0	0	0	0	0	-0.0003	0.0003	0.0007	
X <sub>6</sub> : meq SOM (thiols)	-0.0005	0.0005	0.0010	-0.0013	0.0013	0.0030	-0.0034	0.0034	0.0074	
X <sub>7</sub> : log k Hg-DOM (HA, FA)	0	0	0	0	0	0	0	0	0	
X₅: log k Hg-DOM (thiols)	0.2226	0.2226	0.3438	1.1177	1.1177	1.7215	2.2495	2.2495	3.4633	
X₃: log k Hg-SOM (HA,FA)	0	0	0	-0.0033	0.0033	0.0075	-1.1423	1.1423	2.5478	
X <sub>10</sub> : log k Hg-SOM (thiols)	-0.0497	0.0497	0.0944	-0.2510	0.2510	0.4901	-0.4928	0.4928	0.9946	
X <sub>11</sub> : log k DOM sorption	0	0	0	0	0	0	0	0	0	
X <sub>12</sub> : S <sub>max</sub> (DOM sorption)	0	0	0	0	0	0	0	0	0	

Table 22 – Elementary effects for Group A, indicator **2** (% of Hg leached at the bottom of the soil profile) after 5, 25 and 50 years.

Factor	After 5 years				After 25 years			After 50 years			
	μ	μ*	σ	μ	μ*	σ	μ	μ*	σ		
X <sub>1</sub> : Hg initial conc.	0.2794	0.2794	0.6249	1.3661	1.3661	3.0548	2.7346	2.8039	6.2027		
X <sub>2</sub> : HgS degradation rate	-0.0891	0.1615	0.2243	-2.4687	2.4687	4.7649	-6.3832	6.3832	13.1981		
X <sub>3</sub> : Hg(II) reduction rate	0	0	0	0	0	0	0	0	0		
X₄: DOM in rain	-0.2295	0.2749	0.2754	-10.6679	10.6679	20.6261	-14.6503	14.6503	26.6931		
X₅: meq SOM (HA, FA)	0	0	0	0.1018	0.1018	0.2185	5.3993	5.3993	11.9802		
X <sub>6</sub> : meq SOM (thiols)	0	0	0	0	0	0	0.0666	0.0666	0.1490		
X <sub>7</sub> : log k Hg-DOM (HA, FA)	0	0	0	0	0	0	0	0	0		
X <sub>8</sub> : log k Hg-DOM (thiols)	-0.2562	0.2562	0.3381	-1.2665	1.2665	1.7093	-2.5332	2.5332	3.3429		
X <sub>9</sub> : log k Hg-SOM (HA,FA)	0.0897	0.0897	0.2007	2.5462	2.5462	5.6934	12.8546	12.8546	14.2769		
X <sub>10</sub> : log k Hg-SOM (thiols)	0.0471	0.0478	0.1017	0.2742	0.2742	0.4985	0.3850	0.3850	0.5621		
X <sub>11</sub> : log k DOM sorption	-0.0104	0.0171	0.0246	0.0460	0.0660	0.0902	-0.0673	0.0673	0.0711		
X <sub>12</sub> : S <sub>max</sub> (DOM sorption)	0.0257	0.0396	0.0782	-0.0157	0.0823	0.1444	-0.0603	0.0603	0.1276		

 Table 23 – Elementary effects for Group A, indicator ③ (% Hg still in horizon initially polluted) after 5, 25 and 50 years.

Factor	After 5 years				fter 25 years		After 50 years			
	μ	μ*	σ	μ	μ*	σ	μ	μ*	σ	
X <sub>1</sub> : Hg initial conc.	-0.0118	0.0119	0.0266	-0.0230	0.0289	0.0598	-0.0280	0.0497	0.0943	
X <sub>2</sub> : HgS degradation rate	0.1378	0.1378	0.2009	2.4550	2.4550	4.7371	5.2073	5.2073	10.6446	
X <sub>3</sub> : Hg(II) reduction rate	0	0	0	0	0	0	0	0	0	
X <sub>4</sub> : DOM in rain	0.1091	0.1091	0.1491	9.5238	9.5238	21.1941	7.7270	7.8764	17.2608	
X₅: meq SOM (HA, FA)	0	0	0	-0.1065	0.1066	0.2254	-5.4230	5.4230	12.0498	
X <sub>6</sub> : meq SOM (thiols)	0.0006	0.0006	0.0014	-0.0101	0.0137	0.0273	-0.0677	0.0734	0.1581	
X <sub>7</sub> : log k Hg-DOM (HA, FA)	0	0	0	0	0	0	0	0	0	
X₀: log k Hg-DOM (thiols)	0.0324	0.0614	0.1078	0.1545	0.3117	0.5861	0.2910	0.6353	1.1851	
X <sub>9</sub> : log k Hg-SOM (HA,FA)	-0.0911	0.0911	0.2037	-2.5359	2.5359	5.6705	-11.6869	11.6869	12.1539	
X <sub>10</sub> : log k Hg-SOM (thiols)	0.0026	0.0107	0.0179	-0.0287	0.0632	0.1058	0.0986	0.3675	0.6095	
X <sub>11</sub> : log k DOM sorption	0	0	0	0	0.0001	0.0003	-0.0003	0.0005	0.0009	
X <sub>12</sub> : S <sub>max</sub> (DOM sorption)	0	0	0.0001	0.0449	0.0485	0.1054	0.0251	0.0417	0.0813	

Table 24 – Elementary effects for Group A, indicator ④ (% Hg still present in the soil profile below the horizon initially polluted) after 5, 25 and 50 years.



Figure 36 – Plots of  $\mu$  vs.  $\sigma$  and  $\mu^*$  vs.  $\sigma$  for elementary effects of Group A, indicator **2** (% Hg leached out of soil profile) after (a) 5, (b) 25 and (c) 50 years.



Figure 37 – Plots of  $\mu$  vs.  $\sigma$  and  $\mu^*$  vs.  $\sigma$  for elementary effects of Group A, indicator 3 (% Hg still in horizon initially polluted) after (a) 5, (b) 25 and (c) 50 years.



Figure 38 – Plots of  $\mu$  vs.  $\sigma$  and  $\mu^*$  vs.  $\sigma$  for elementary effects of Group A, indicator ④ (% Hg still present in the soil profile below the horizon initially polluted) after (a) 5, (b) 25 and (c) 50 years.

Table 25 shows the Hg (percentage of total initial amount) in the different phases/compartments after 50 years. Average absolute value of Hg mass balance error after 50 years was 0.005%.

					Top 10 cm						11-100 cm	1			
		Time (yr)	Hg atm	Hg leached	HgS	Hg NAPL	Hg SOM	Hg DOM	Hg inorg	Hg(g)	Hg SOM	Hg DOM	Hg inorg	Hg(g)	TOTAL
					_						_				
٣	-	<b>"</b> T	<b>T</b>	-	-		<b>•</b>	<b>_</b>	<b>•</b>	<b>•</b>	Ψ.	•	<b>T</b>	<b></b>	-
A	01	50	7.66E-06	8.75E+00	8.75E+01	0.00E+00	1.09E+00	1.49E-03	9.46E-05	3.55E-08	2.70E+00	2.37E-02	2.23E-04	2.35E-06	100.0
A	02	50	7.66E-06	8.64E+00	8.75E+01	0.00E+00	1.09E+00	1.49E-03	9.46E-05	3.55E-08	2.78E+00	2.35E-02	2.26E-04	2.31E-06	100.0
A	03	50	7.62E-06	8.64E+00	8.76E+01	0.00E+00	8.17E-01	1.49E-03	6.47E-05	3.56E-08	2.88E+00	2.35E-02	3.15E-04	2.32E-06	100.0
A	04	50	7.66E-06	1.21E+01	6.24E+01	0.00E+00	8.03E+00	2.40E-03	1.37E-03	1.83E-07	1.74E+01	2.37E-02	1.65E-02	4.57E-06	100.0
A	05	50	7.62E-06	8.68E+00	6.24E+01	0.00E+00	2.88E+01	2.40E-03	6.79E-12	1.52E-07	1.01E-01	2.35E-02	-4.58E-19	3.67E-06	100.0
A	06	50	7.62E-06	8.68E+00	6.24E+01	0.00E+00	2.88E+01	2.40E-03	6.79E-12	1.52E-07	1.01E-01	2.35E-02	-2.26E-35	3.67E-06	100.0
A	07	50	4.81E-07	5.48E-01	6.24E+01	0.00E+00	3.71E+01	1.65E-04	3.77E-11	1.20E-08	6.40E-03	1.48E-03	-3.21E-21	2.51E-07	100.0
A	08	50	4.81E-07	5.38E-01	6.24E+01	0.00E+00	3.71E+01	1.65E-04	3.66E-11	1.20E-08	1.50E-02	1.47E-03	-6.42E-21	2.51E-07	100.0
A	09	50	4.81E-07	5.38E-01	6.24E+01	0.00E+00	3.71E+01	1.65E-04	3.66E-11	8.34E-10	1.50E-02	1.47E-03	-2.73E-20	1.86E-08	100.0
A	10	50	4.81E-07	5.38E-01	6.24E+01	0.00E+00	3.70E+01	1.65E-04	5.97E-11	8.34E-10	1.50E-02	1.47E-03	1.61E-21	1.86E-08	100.0
A	11	50	4.81E-07	5.39E-01	6.24E+01	0.00E+00	2.09E+01	1.65E-04	2.18E-03	5.25E-09	1.62E+01	1.47E-03	1.85E-03	5.62E-07	100.0
A	12	50	4.81E-07	5.92E-04	6.24E+01	0.00E+00	2.09E+01	1.65E-04	2.18E-03	5.25E-09	1.67E+01	1.51E-04	2.17E-03	5.62E-07	100.0
A	13	50	4.81E-07	1.43E+01	2.51E+01	0.00E+00	2.09E+01	4.83E-04	2.31E-03	6.56E-09	3.98E+01	4.42E-03	5.81E-02	6.68E-07	100.0
A	14	50	1.92E-05	3.79E-03	3.38E+01	0.00E+00	5.65E+01	2.41E-03	1.6/E-04	1.00E-07	9.68E+00	2.39E-04	1.45E-05	7.34E-06	100.0
A	15	50	1.915-05	6.44E-05	3.36E+U1	0.00E+00	0.02E+01	8.00E-00	4.55E-07	3.72E-09	3.64E-03	1.046-10	1.205.25	1.20E-07	100.0
A	10	50	1.916-05	1.89E-04	3.36E+01	0.00E+00	6.00E+01	0.21E-05	4.39E-00	9.156-09	2.10E-01	1.516-17	1.205-25	2.34E-07	100.0
	18	50	1.910-05	2.00E-04	6.82E±01	0.000000	3 18E±01	4 30E-06	5 16E-07	3.50E-00	7 15 5-03	9 10F-10	4.26E-27	1.22E-07	100.0
Δ	19	50	1.92E-05	8 24E-05	6.82E+01	0.00E+00	3 18F+01	1.46E-08	1 72E-09	3 19F-09	3 20E-05	2 11E-23	3 96E-35	1.22E 07	100.0
Δ	20	50	1.92E-05	8 24F-05	6.82E+01	0.00E+00	3 18F+01	1.46E-08	1.72E-09	3 19F-09	3 20E-05	2.11E-23	3 96E-35	1.10E 07	100.0
A	21	50	1.21F-06	5.34F-06	6.82F+01	0.00F+00	3.18F+01	9.73F-07	1.19F-07	2.06F-10	3.88F-03	2.02F-19	3.54E-27	7.41F-09	100.0
A	22	50	1.21E-06	5.33E-06	6.98E+01	0.00E+00	3.02E+01	8.77E-07	1.15E-07	2.05E-10	2.77E-03	1.72E-19	1.40E-27	7.40E-09	100.0
Α	23	50	1.21E-06	4.38E-05	6.98E+01	0.00E+00	2.88E+01	4.14E-04	1.07E-07	2.10E-09	1.39E+00	5.04E-04	2.61E-13	4.67E-08	100.0
Α	24	50	1.21E-06	4.38E-05	6.98E+01	0.00E+00	2.88E+01	4.14E-04	1.07E-07	2.10E-09	1.39E+00	5.04E-04	2.61E-13	4.67E-08	100.0
Α	25	50	1.21E-06	1.94E-05	9.81E+01	0.00E+00	1.23E+00	2.13E-04	1.77E-11	5.26E-10	6.45E-01	2.21E-04	4.73E-15	3.01E-08	100.0
Α	26	50	1.21E-06	1.36E+00	9.81E+01	0.00E+00	4.87E-01	2.14E-04	2.17E-11	5.27E-10	2.23E-02	3.71E-03	1.53E-13	2.96E-08	100.0
А	27	50	1.21E-06	2.28E+00	4.61E+01	0.00E+00	5.16E+01	6.81E-04	6.64E-11	3.31E-09	8.17E-04	6.17E-03	1.62E-17	7.21E-08	100.0
А	28	50	1.21E-06	4.95E+00	1.85E+01	0.00E+00	7.65E+01	1.48E-03	1.74E-10	6.97E-09	1.30E-03	1.34E-02	4.35E-17	1.48E-07	100.0
A	29	50	1.21E-06	4.95E+00	1.84E+01	0.00E+00	7.66E+01	1.48E-03	9.77E-11	6.97E-09	9.79E-04	1.34E-02	2.67E-17	1.48E-07	100.0
A	30	50	1.21E-06	4.95E+00	1.80E+01	0.00E+00	7.70E+01	1.48E-03	9.57E-11	6.97E-09	8.30E-04	1.34E-02	1.33E-17	1.48E-07	100.0
A	31	50	1.21E-06	5.76E-06	1.80E+01	0.00E+00	8.19E+01	6.94E-06	1.06E-10	2.31E-10	2.24E-02	3.73E-12	4.99E-17	7.95E-09	100.0
A	32	50	1.21E-06	1.39E-05	1.80E+01	0.00E+00	8.19E+01	6.94E-06	1.06E-10	6.68E-10	2.24E-02	3.73E-12	4.99E-17	1.72E-08	100.0
A	33	50	1.21E-06	1.42E-05	1.80E+01	0.00E+00	8.19E+01	7.13E-06	1.09E-10	6.84E-10	2.38E-02	3.93E-12	5.28E-17	1.75E-08	100.0
A	34	50	1.21E-06	1.42E-05	1.80E+01	0.00E+00	8.19E+01	7.13E-06	1.09E-10	6.84E-10	2.38E-02	3.92E-12	5.28E-17	1.75E-08	100.0
A	35	50	1.21E-06	1.37E-05	1.80E+01	0.00E+00	8.19E+01	7.07E-06	1.08E-10	6.81E-10	2.39E-02	1.26E-18	4.49E-24	1.73E-08	100.0
A	36	50	1.91E-05	8.24E-05	1.81E+01	0.00E+00	8.19E+01	1.14E-08	1.72E-13	3.19E-09	2.20E-05	4.06E-24	1.00E-34	1.16E-07	100.0
A	37	50	1.91E-05	8.24E-05	6.19E+01	0.00E+00	3.81E+01	1.11E-09	1.67E-14	3.19E-09	8.72E-07	8.10E-25	3.87E-36	1.16E-07	100.0
A	38	50	1.91E-05	8.24E-05	6.19E+01	0.00E+00	3.81E+01	4.43E-09	6.66E-14	3.19E-09	3.33E-06	1.58E-24	1.50E-35	1.16E-07	100.0
A	39	50	1.92E-05	3.30E-03	6.19E+01	0.00E+00	3.00E+01	2.24E-03	4.16E-08	8.30E-08	8.07E+00	4.67E-04	7.86E-09	8.03E-06	100.0
A	40	50	7.62E-06	4.02E+00	9.58E+01	0.00E+00	4.63E-02	5.11E-04	5.98E-13	2.14E-08	1./1E-01	8.18E-03	1.58E-10	4.97E-07	100.0
A	41	50	7.02E-00	0.46E-05	9.93E+01	0.00E+00	2.59E-01	0.445.21	3.43E-13	3.57E-09	4.03E-01	2.39E-04	3.52E-12	1.40E-07	100.0
	42	50	7.62E-06	3.28E-05	9.935+01	0.000	6 71E-01	1.01E-21	1.55E-25 3 10E-31	1.275-09	0.011-10	0.00E±00	0.00E+00	4.02E-08	100.0
Δ	43	50	7.62E-06	3.28E-05	9.93E+01	0.00E+00	6 71E-01	1.01E-21	3 10E-31	1.27E-09	0.00E+00	0.00E+00	0.00E+00	4.02E-08	100.0
Δ	45	50	7.66E-06	3 28E-05	9 93E+01	0.00E+00	6 79E-01	8 80F-22	2 45F-31	1.27E-09	0.00E+00	0.00E+00	0.00E+00	4.62E-08	100.0
A	46	50	7.66F-06	3.28F-05	9.93F+01	0.00F+00	7.41F-01	9.19F-22	2.72F-31	1.27F-09	0.00F+00	0.00F+00	0.00F+00	4.62F-08	100.0
A	47	50	7.66E-06	3.28E-05	9.93E+01	0.00E+00	7.41E-01	1.78E-22	2.72E-31	1.27E-09	0.00E+00	0.00E+00	0.00E+00	4.62E-08	100.0
А	48	50	7.66E-06	3.28E-05	9.93E+01	0.00E+00	7.41E-01	1.78E-22	2.72E-31	1.27E-09	0.00E+00	0.00E+00	0.00E+00	4.62E-08	100.0
A	49	50	7.66E-06	3.29E-05	9.93E+01	0.00E+00	7.39E-01	5.81E-07	-6.21E-24	1.27E-09	1.71E-03	1.24E-09	-2.42E-26	4.62E-08	100.0
А	50	50	4.83E-07	2.26E-06	9.93E+01	0.00E+00	7.35E-01	4.36E-06	0.00E+00	9.94E-11	6.52E-03	5.22E-09	-7.18E-29	3.32E-09	100.0
А	51	50	4.81E-07	2.12E-05	8.68E+01	0.00E+00	1.28E+01	5.89E-05	3.18E-05	5.02E-10	3.37E-01	1.05E-05	3.40E-08	1.29E-08	100.0
A	52	50	4.81E-07	1.26E-05	8.68E+01	0.00E+00	1.29E+01	5.89E-05	1.18E-05	4.06E-10	2.62E-01	9.84E-06	1.45E-09	1.02E-08	100.0
A	53	50	4.81E-07	1.26E+00	3.36E+01	0.00E+00	6.51E+01	3.77E-04	4.35E-10	2.74E-08	1.69E-04	3.42E-03	9.38E-18	5.71E-07	100.0
A	54	50	4.81E-07	1.26E+00	3.36E+01	0.00E+00	6.51E+01	3.77E-04	8.17E-11	2.74E-08	2.46E-04	3.42E-03	4.28E-18	5.71E-07	100.0
A	55	50	4.81E-07	1.26E+00	3.36E+01	0.00E+00	6.51E+01	3.77E-04	8.13E-11	2.74E-08	2.46E-04	3.42E-03	4.35E-18	5.71E-07	100.0
A	56	50	4.81E-07	6.54E-06	3.36E+01	0.00E+00	6.64E+01	4.17E-06	8.42E-11	3.45E-10	1.30E-02	1.52E-12	2.52E-17	8.63E-09	100.0
A	57	50	4.81E-07	3.22E-06	7.37E+01	0.00E+00	2.63E+01	1.38E-06	2.73E-11	1.69E-10	3.40E-03	3.53E-13	5.79E-18	4.79E-09	100.0
A	58	50	4.81E-07	2.08E-06	9.54E+01	0.00E+00	4.64E+00	8.07E-09	1.08E-12	8.06E-11	1.62E-05	1.20E-16	8.16E-21	2.92E-09	100.0
A	59 66	50	4.81E-07	2.07E-06	9.54E+01	0.00E+00	4.60E+00	6.70E-09	1.21E-12	8.06E-11	1.03E-05	5.98E-17	8.08E-21	2.92E-09	100.0
A	60	50	7.62E-06	3.28E-05	9.54E+01	0.00E+00	4.59E+00	1.95E-11	3.50E-15	1.27E-09	4.76E-08	5.00E-18	3.48E-23	4.62E-08	100.0
A	61	50	7.62E-06	3.28E-05	9.54E+01	0.00E+00	4.59E+00	1.3/E-11	5.00E-15	1.27E-09	3.12E-08	5.//E-18	4.33E-23	4.62E-08	100.0
A	62	50	7.02E-06	3.28E-05	9.54E+01	0.00E+00	4.59E+00	3.80E-17	4.60E-22	1.27E-09	1.49E-13	2.83E-24	1.05E-35	4.02E-08	100.0
	64	50	7.02E-00	3.200-05	9.546+01	0.000000	4.595+00	5 205 10	4.000-22	1.275-09	1.945-14	1 155 25	1 225 26	4.020-08	100.0
	65	50	7.62E-06	3 285-05	9.54E+01	0.00E+00	4.59E+00	5 38F-19	4.00E-22	1 27F-09	1.94E-14	1 15F-25	1 32E-30	4.62E-08	100.0
- ^^	55	50		3.202.03	2.246.01	0.002.00		2.205 10	2.002 22		1.746 14		1.526.50		100.0

Table 25 – Percentage of Hg in the different phases after 50 years for group A.

### 2 Leaching

For indicator 2, factor X<sub>1</sub> (cinnabar concentration in the polluted horizon) is the most influential factor in the beginning of the simulation and remains the second most sensitive factor after 50 years. It is important to note that its value of  $\mu$  is negative, i.e. a higher cinnabar initial concentration results in less leaching. As already mentioned in section 6.3, this is partly a consequence of indicators being expressed in a relative way (% of initial Hg) combined to incomplete cinnabar dissolution over the simulation time.

Apart from  $X_1$ , the most sensitive factors for indicator **2** are  $X_4$  (DOM concentration in infiltrating rainwater) and  $X_8$  (log k Hg-DOM (thiols)); with  $X_4$  being by far the most important after 50 years. The high sensitivity of  $X_4$  is due to Hg transport occuring mainly via Hg-DOM complexes and to cinnabar dissolution rate being dependent on DOM in soil water (see section 4.4).

Interestingly, the simulations show that Hg leaching occurs through complexation with thiols (high and positive  $\mu$  for X<sub>8</sub>), while complexation with humic and fulvic acids (X<sub>7</sub>) does not seem to play a role. Concerning sorption, the relative importance of thiol and HA-FA binding forces change over time. After 5 and 25 years, log k of Hg-SOM sorption is a sensitive factor only for thiols (X<sub>10</sub>). After 50 years however, log k of exchange reactions for HA and FA (X<sub>9</sub>) was found slightly more influential than for thiols (X<sub>10</sub>).

As already suggested in the one-at-a time SA (section 7.1), SOM exchange capacity ( $X_5$  and  $X_6$ ) is not a sensitive parameter for Hg leaching in this group. It can be due to SOM exchange sites being in excess compared to available Hg (in most simulations), resulting in little effect on leaching when the sorption capacity is increased or decreased.

Other factors having a negligible sensitivity are  $Hg^{II}$  reduction rate (X<sub>3</sub>), and factors related to DOM sorption (X<sub>11</sub> and X<sub>12</sub>). Cinnabar degradation rate (X<sub>2</sub>) is a sensitive factor after 50 years, but not after 5 and 25 years.

For all factors,  $\mu^* = |\mu|$ . This means that model behavior is monotonic for this indicator and for these factors.

Maximum Hg leaching after 50 years was 14% of initial mercury in simulation run A13. Some parameter values (given in Annex, section 9.3) are those associated with higher leaching: high DOM concentration in the soil solution, high cinnabar degradation rate, and strong binding between Hg<sup>II</sup> and thiol groups. Figure 39a,b show the depth-cumulative distribution over time of cinnabar and all other Hg species, respectively. The leached fraction at the end of A13 simulation can be deduced as follows from Figure 39 : 100 - (25.1 + 60.7) = 14.2 (% of total initial Hg).



Figure 39 – Cumulative depth distribution over time of (a) cinnabar and (b) other Hg species (in % of total initial Hg) for simulation A13.



Figure 40 – Hg(II) flux at the bottom of the soil profile for the last 25 years of the simulation A13. Grey dots are daily simulated fluxes at the bottom of the soil profile. Red line is the result of a moving average (window 31 days) on the daily data. Grey bars show the surface precipitation input (averaged every two months for clarity). Note that the y-scale is logarithmic for the solute flux.



### Figure 41 – Cumulative depth distribution over time of (a) cinnabar and (b) other Hg species (in % of total initial Hg) for simulation A12.

Figure 40 shows Hg<sup>II</sup> flux at the bottom of the soil profile for simulation A13 (last 25 years). One can see that leaching at 1 m depth starts after ~32 years. Afterwards, the breakthrough curve is similar to what was already observed in previous simulations (one-at-a time SA; Figure 16 in section 7.1).

Among the 65 simulation runs of group A, 44 had a leaching fraction <0.1% after 50 years. This happened either because cinnabar dissolution rate was very low, and/or because Hg sorption to SOM was very strong. This is for example the case in simulation A12 (Figure 41a and b), which combines a low cinnabar degradation rate (62.4% of initial cinnabar still present after 50 years) with high Hg sorption. As a result, all Hg released from cinnabar dissolution has been retained in the top 30 cm of the soil profile (37.6% after 50 years).

#### **3** Hg still present in the soil horizon originally contaminated (top 10 cm)

For indicator ③, factor X<sub>1</sub> (cinnabar concentration in the polluted horizon), X<sub>4</sub> (DOM in rain) and X<sub>8</sub> (log k Hg-DOM (thiols)) are the most influential factors in the beginning of the simulation (Table 23 and Figure 37). After 25 and 50 years, X<sub>4</sub> becomes the most sensitive factor and factors X<sub>2</sub> (cinnabar degradation rate), X<sub>5</sub> (SOM (HA and FA) exchange capacity) and X<sub>9</sub> (log k Hg-SOM (HA and FA)) become important as well. Values of  $\mu$  for X<sub>4</sub> are logically negative, i.e. higher concentrations of DOM in infiltrating water remove more Hg from the topsoil and increases cinnabar degradation rate (DOM-dependent).

As far as log k for binding Hg-SOM are concerned, one can see that values for humic and fulvic acids  $(X_9)$  are much more sensitive than for thiols  $(X_{10})$ . This can be explained as follows: on the one hand Hg binding to thiol groups is so strong compared to other speciation reactions that in the range of  $X_{10}$  variability indicator 3 is not much affected. On the other hand, the amount of Hg staying in the top horizon (0-10 cm) depends heavily on the comparatively weaker Hg binding to HA and FA sites, which can be more easily competed by other speciation reactions if log k values decrease.

Model behavior is monotonic for this indicator ( $\mu^* = |\mu|$  except very small difference for X<sub>1</sub>; see Table 23).

Factors  $X_3$  (Hg<sup>II</sup> reduction rate),  $X_6$  (SOM (thiols) exchange capacity),  $X_7$  (log k Hg-DOM (HA and FA)),  $X_{11}$  and  $X_{12}$  (related to DOM sorption to mineral surfaces) have a negligible sensitivity for indicator (3) (except some influence for the last two after 5 years).

Mercury still present in the horizon initially polluted is mainly in the forms of cinnabar (depending on degradation rate) and Hg sorbed to SOM. For example in simulation A13, one can visualize cinnabar dissolution over time in Figure 42a (still about 1000 mg[Hg]/kg[soil] after 50 years). Figure 42 (b) shows that SOM sorption sites in the top 10 cm are filled after 10 years. At the depth of 30 cm, saturation of SOM sorption sites is achieved after 50 years.



Figure 42 – Depth distribution of Hg (a) in solid phase (HgS) and (b) sorbed to SOM at t = 0, 5, 10, 25 and 50 years for simulation A13. Note that for clarity the y-axis stops at 50 cm depth.

#### 4 Hg still present in the soil profile below the horizon originally contaminated (11-100 cm)

For indicator (4), all 12 factors are characterized by small  $\mu^*$  values after 5 years, because there has been hardly any Hg leaching and Hg concentrations below the contaminated top horizon remain low. Still, the  $\sigma$  values indicate that X<sub>2</sub> (cinnabar degradation rate), X<sub>4</sub> (DOM in rain), X<sub>8</sub> (log k Hg-DOM (thiols)) and X<sub>9</sub> (log k Hg-SOM (HA and FA)) have some effect.

After 25 years, factors  $X_2$ ,  $X_4$  and  $X_9$  have the highest  $\mu^*$  values, with  $X_4$  being by far the most sensitive.

After 50 years,  $X_5$  (exchange capacity SOM (HA and FA)) can be considered as a sensitive factor, too. Factor  $X_9$  has a higher  $\mu^*$  value (= higher overall influence) than  $X_4$ , but the latter shows has a higher  $\sigma$  values (= more non-linear effects and/or interactions with other factors). This can probably be explained by the influence that DOM concentration has on cinnabar dissolution rate.

For this indicator, non-monotonic behavior is revealed by  $\mu^* > |\mu|$  for several factors (see Table 24, e.g. parameters related to the strength of Hg binding to thiol groups, X<sub>8</sub> and X<sub>10</sub>). The explanation is that to increase the value of indicator **(4)**, at the same time (i) more leaching from the top 10 cm is "needed" to bring Hg from the topsoil to the horizons below ; and/or (ii) more sorption is "needed" between 10-30 cm to retain Hg in the soil below the horizon originally polluted. These effects cancel each other (to some extent) and are responsible for  $|\mu|$  lower than  $\mu^*$ .

Figure 43 shows concentration profiles over time for a simulation (A53) in which the fraction of Hg species in the 11-100 cm interval remains negligible, even after 50 years. However, there has been some Hg leaching (~1.6 % of initial Hg; Table 25). The results are similar for simulations A54 and A55. Checking the most sensitive parameters as indicated in Table 24 and Figure 38, these three SA runs are characterized by a combination of high cinnabar dissolution rate ( $X_2$ ), intermediate DOM concentration in rain ( $X_4$ ), and strong Hg sorption to HA and FA sites ( $X_9$ ). The values for ( $X_5$ ) are either high (A54 and A55) or low (A53) and seem thus not sensitive in this particular case. It is therefore the strong sorption ( $X_9$ ) which appears to determine the particular pattern of these three simulations.

Closer inspection of the results reveals that the combination of both strong sorption of Hg to SOM HA and FA sites, and high log k for Hg-DOM (thiols) complexes seems decisive to explain the profile of Hg concentrations observed in Figure 43b. Sorting log k values gives (Table 6): Hg-DOM(thiols) >> Hg-SOM(thiols) >> Hg-SOM(thiols) >> Hg-DOM(HA,FA). As thiol groups are limited in quantity in infiltrating water (see rain water composition in section 4.7) the inferred process functions as follows: (i) Hg is strongly sorbed to SOM(HA,FA) in the top soil; (ii) only DOM thiol groups can desorb and transport Hg (in limited quantity); (iii) Hg is not resorbed because binding to DOM thiol groups is stronger than sorption to SOM thiol, HA and FA groups.



Figure 43 – Depth distribution of Hg (a) in solid phase (HgS) and (b) sorbed to SOM at t = 0, 5, 10, 25 and 50 years for simulation A53. Note that for clarity the y-axis stops at 50 cm depth.

#### 7.2.2.2 Group B (NAPL)

In the SA simulations, five runs (B38, B47, B48, B63 and B64) failed due to convergence problems in PHREEQC with the parameter values given in Annex (section 9.3.2). Closer inspection suggested that this was mainly caused by a too high  $X_8$  value (even though this alone does not lead to the convergence problem; but rather the particular combination of all factor values and the type of Hg pollution sources). It was decided to decrease  $X_8$  (log k Hg-DOM (thiols) = 33 instead of 44). With this modification, convergence problems were solved without affecting the results, because (i) Morris trajectories are modified but the calculation of elementary effects is adapted accordingly, and (ii) Hg-DOM (thiols) remains by far the most favoured Hg aqueous complexation.

Tables 26 to 28 present the results of the SA using Morris trajectories for indicators **2** to **4**. Figures 44 to 46 show the corresponding plots of  $\mu$  (and  $\mu^*$ ) vs.  $\sigma$  for interpretation of factor sensitivity. No results are shown for the indicator **1** (% of mercury volatilized). This indicator was never above 0.001% of the initial mercury after 50 years.

It can be seen from these tables and figures that factor sensitivity varies with the indicator assessed (2, 3 or 4) but also over time (after 5, 25 or 50 years). These results are discussed further below.
Factor		After 5 years			After 25 years			After 50 years           μ         μ*           16.9484         27.7816           0.0301         0.0301           0         0           0         0           4.4763         8.4429	
	μ	μ*	σ	μ	μ*	σ	μ	μ*	σ
X <sub>1</sub> : Hg initial conc.	14.7434	15.7139	33.1583	15.2108	20.0292	40.8036	16.9484	27.7816	43.6745
X <sub>13</sub> : NAPL dissolution rate	0.0035	0.0035	0.0074	0	0	0	0.0301	0.0301	0.0670
X <sub>3</sub> : Hg(II) reduction rate	0	0	0	0	0	0	0	0	0
X₄: DOM in rain	-4.5637	5.3563	11.3192	-0.9876	8.0190	12.5911	4.4763	8.4429	10.2541
X₅: meq SOM (HA, FA)	-0.1800	0.1800	0.4025	-2.1734	2.1734	3.5129	-3.7179	3.7179	6.7474
X <sub>6</sub> : meq SOM (thiols)	-0.0157	0.0157	0.0350	-0.4100	0.4100	0.9168	-6.3800	6.3800	14.2661
X <sub>7</sub> : log k Hg-DOM (HA, FA)	0	0	0	0	0	0	0	0	0
X₅: log k Hg-DOM (thiols)	0.4320	0.4320	0.5209	2.4238	2.4238	2.9118	4.9880	5.0680	6.0832
X <sub>9</sub> : log k Hg-SOM (HA,FA)	-14.1685	14.1685	22.2630	-34.5990	34.5990	32.4317	-58.8406	58.8406	47.8521
X₁₀: log k Hg-SOM (thiols)	-0.1257	0.1257	0.2086	-0.4360	0.4360	0.6108	-1.0920	1.0920	0.8771
X <sub>11</sub> : log k DOM sorption	0	0	0	0	0	0	-0.0001	0.0001	0.0002
X <sub>12</sub> : S <sub>max</sub> (DOM sorption)	0	0	0	0.7333	0.7333	1.6398	1.3700	1.3700	3.0634

Table 26 – Elementary effects for Group B, indicator **2** (% of Hg leached at the bottom of the soil profile) after 5, 25 and 50 years.

Factor		After 5 years			After 25 years			After 50 years	
	μ	μ*	σ	μ	μ*	σ	μ	μ*	σ
X <sub>1</sub> : Hg initial conc.	-5.8932	14.6252	23.7415	-2.4246	33.4046	47.4842	-3.0805	29.3708	38.7204
X <sub>13</sub> : NAPL dissolution rate	-12.3119	12.3148	24.9606	-8.8911	8.8911	17.3642	-6.0169	6.0169	11.0265
X <sub>3</sub> : Hg(II) reduction rate	0	0	0	0	0	0	0	0	0
X₄: DOM in rain	4.4713	5.5892	11.5671	1.6045	7.0499	11.2902	-5.4614	5.4614	3.9821
X₅: meq SOM (HA, FA)	0.5727	0.5727	0.7165	1.9233	1.9233	2.9290	2.4651	2.6018	5.5944
X <sub>6</sub> : meq SOM (thiols)	1.0366	1.0366	2.2436	9.8569	9.8569	21.9569	8.7118	8.7118	19.4056
X <sub>7</sub> : log k Hg-DOM (HA, FA)	0	0	0	-0.0033	0.0033	0.0075	-0.0033	0.0033	0.0075
X₀: log k Hg-DOM (thiols)	-0.5822	0.5822	0.6865	-2.8522	2.8590	3.4681	-3.9756	4.0156	5.5745
X <sub>9</sub> : log k Hg-SOM (HA,FA)	18.1112	18.1112	18.9442	52.0492	52.0492	23.7438	88.5050	88.5050	32.8412
X <sub>10</sub> : log k Hg-SOM (thiols)	-0.0133	0.0133	0.0139	-0.0366	0.0366	0.0463	0.0889	0.1756	0.2551
X <sub>11</sub> : log k DOM sorption	-0.5750	0.6217	1.3518	-1.2767	1.3700	2.9859	-1.5637	1.6971	3.6110
X <sub>12</sub> : S <sub>max</sub> (DOM sorption)	-0.4304	0.4304	0.7764	-1.0599	1.0666	1.7770	-1.4000	1.4000	2.1892

 Table 27 – Elementary effects for Group B, indicator (3)(% Hg still in horizon initially polluted) after 5, 25 and 50 years.

Factor	ļ	After 5 years	_	Af	iter 25 years		Af	ter 50 years	
	μ	μ*	σ	μ	μ*	σ	μ	μ*	σ
X₁: Hg initial conc.	-8.8523	12.0655	16.0585	-12.7197	27.2722	37.9191	-13.7985	23.0584	30.8437
X <sub>13</sub> : NAPL dissolution rate	12.3063	12.3063	24.9495	8.8720	8.8720	17.3163	5.9708	5.9708	10.9365
X <sub>3</sub> : Hg(II) reduction rate	0	0	0	0	0	0	0	0	0
X₄: DOM in rain	0.0914	0.2382	0.3560	-0.6274	1.7538	3.0849	0.9200	4.8135	7.2066
X₅: meq SOM (HA, FA)	-0.3880	0.3882	0.5708	0.2435	0.3088	0.6258	1.3971	1.4520	1.9940
X₅: meq SOM (thiols)	-1.0213	1.0213	2.2094	-9.4266	9.4266	21.0030	-2.3316	2.3316	5.1409
X <sub>7</sub> : log k Hg-DOM (HA, FA)	0.0003	0.0003	0.0007	0.0033	0.0033	0.0075	0.0033	0.0033	0.0075
X₀: log k Hg-DOM (thiols)	0.1533	0.1567	0.2233	0.4404	0.4404	0.6967	-1.0095	2.1111	3.9592
X₀: log k Hg-SOM (HA,FA)	-3.9402	5.9300	7.0412	-17.4495	17.7555	12.9436	-29.5728	31.4823	27.9422
X <sub>10</sub> : log k Hg-SOM (thiols)	0.1312	0.1379	0.2193	0.4708	0.4708	0.6610	0.8335	0.9781	1.1923
X <sub>11</sub> : log k DOM sorption	0.5720	0.6230	1.3512	1.2754	1.3671	2.9791	1.5554	1.6856	3.5879
X <sub>12</sub> : S <sub>max</sub> (DOM sorption)	0.4292	0.4339	0.7850	0.3185	1.3310	2.3800	0.0235	1.9941	3.5068

Table 28 – Elementary effects for Group B, indicator (% Hg still present in the soil profile below the horizon initially polluted) after 5, 25 and 50 years.



Figure 44 – Plots of  $\mu$  vs.  $\sigma$  and  $\mu^*$  vs.  $\sigma$  for elementary effects of Group B, indicator **2** (% Hg leached out of soil profile) after (a) 5, (b) 25 and (c) 50 years.



Figure 45 – Plots of  $\mu$  vs.  $\sigma$  and  $\mu^*$  vs.  $\sigma$  for elementary effects of Group B, indicator  $\bigcirc$  (% Hg still in horizon initially polluted) after (a) 5, (b) 25 and (c) 50 years.



Figure 46 – Plots of  $\mu$  vs.  $\sigma$  and  $\mu^*$  vs.  $\sigma$  for elementary effects of Group B, indicator ④ (% Hg still present in the soil profile below the horizon initially polluted) after (a) 5, (b) 25 and (c) 50 years.

Table 29 shows the Hg (percentage of total initial amount) in the different phases/compartments after 50 years. Average absolute value of Hg mass balance error after 50 years was 0.024%.

					Top 10 cm						11-100 cn	ı			
		Tim	Hg atm	Hg leache	HgS	Hg NAPL	Hg SOM	Hg DOM	Hg inorg	Hg(g)	Hg SOM	Hg DOM	Hg inorg	Hg(g)	TOTAL
L															
1	· 🔻	T	<b>Y</b>	<b>Y</b>	<b>Y</b>	<b>_</b>	<b></b>	<b>Y</b>	<b>_</b>	<b>T</b>	<b>T</b>	<b>Y</b>	<b></b>	<b>Y</b>	-
Ľ	B 01	50	1.40E-03	1.84E+01	0.00E+00	1.94E+01	5.50E+01	2.33E-05	3.02E-03	6.22E-09	7.21E+00	2.03E-04	1.93E-02	3.77E-08	100.0
4	B 02	50	2.17E-05	7.03E-08	0.00E+00	1.94E+01	8.02E+01	7.46E-07	4.00E-07	4.59E-12	4.13E-01	1.65E-09	8.77E-10	3.46E-11	100.0
4	B 03	50	2.17E-05	7.03E-08	0.00E+00	1.94E+01	8.02E+01	7.47E-07	4.00E-07	4.59E-12	4.13E-01	1.65E-09	8.77E-10	3.46E-11	100.0
4	B 04	50	1.52E-05	5.08E-08	0.00E+00	1.94E+01	8.04E+01	4.50E-07	6.99E-07	4.54E-12	2.56E-01	3.10E-10	9.76E-10	3.44E-11	100.0
4	B 05	50	1.52E-05	5.05E-08	0.00E+00	1.94E+01	8.04E+01	4.50E-07	6.99E-07	4.55E-12	2.55E-01	3.08E-10	9.66E-10	3.44E-11	100.0
H	B 06	50	4.74E-07	6.27E-09	0.00E+00	1.94E+01	8.04E+01	4.50E-07	6.99E-07	3.22E-12	2.55E-01	3.08E-10	9.66E-10	2.80E-11	100.0
H	B 07	50	4.88E-07	6.33E-09	0.00E+00	1.94E+01	8.04E+01	4.54E-07	7.05E-07	3.22E-12	2.64E-01	4.32E-10	1.36E-09	2.80E-11	100.0
H	8 08	50	3.97E-06	3.55E-08	0.00E+00	5.09E-10	9.79E+01	4.96E-07	8.10E-07	3.24E-12	2.07E+00	3.26E-09	1.16E-08	2.81E-11	100.0
H	B 09	50	2.66E-07	6.28E-08	0.00E+00	5.09E-10	1.00E+02	2.24E-07	3.55E-07	4.97E-11	2.74E-02	4.81E-13	5.00E-13	4.38E-10	100.0
H	B 10	50	-1.36E-05	1.22E+00	0.00E+00	5.09E-10	9.87E+01	3.72E-04	3.49E-07	8.19E-11	3.77E-02	3.32E-03	1.44E-12	5.87E-10	100.0
H	3 11	50	-1.42E-05	1.22E+00	0.00E+00	5.09E-10	9.87E+01	3.72E-04	1.40E-06	8.20E-11	8.80E-02	3.33E-03	9.89E-12	5.8/E-10	100.0
H	3 12	50	-1.99E-05	7.92E+00	0.00E+00	5.09E-10	9.19E+01	2.30E-03	4.39E-06	3.03E-10	1.26E-01	2.15E-02	1.34E-10	1.84E-09	100.0
H	3 13	50	-1.99E-05	7.92E+00	0.00E+00	5.09E-10	9.20E+01	2.30E-03	2.35E-06	3.03E-10	9.97E-02	2.15E-02	3.44E-11	1.84E-09	100.0
H	5 14	50	5.27E-05	1.07E-06	0.00E+00	1.62E+00	5.74E+01	1.12E-03	4.15E-04	3.39E-10	4.09E+01	1.33E-03	1.51E-03	2.91E-09	100.0
Н	5 15	50	1.68E-03	1.43E-05	0.00E+00	1.62E+00	5.74E+01	1.12E-03	4.15E-04	8.25E-10	4.09E+01	1.33E-03	1.51E-03	6.78E-09	100.0
H	5 10	50	5.91E-00	3.95E-07	0.000000	1.02E+00	9.846+01	1.35E-07	3.09E-11	3.13E-10	2.585-04	1.55E-19	4.31E-27	2.70E-09	100.0
H	5 17	50	5.91E-00	3.95E-07	0.000000	1.02E+00	9.846+01	1.35E-07	3.09E-11	3.13E-10	2.586-04	2.50E-20	4.30E-27	2.70E-09	100.0
H	D 10	50	0.255.05	5.93E-07	0.000000	1.625:00	9.04E+01	2.275.02	1 075 11	4 715 00	1 565:00	1.30E-20	2 205 20	2.702-09	100.0
H	3 20	50	-9.33E-03	7.85E+00	0.0000000	1.02E+00	9.04E+01	2.27E-03	9.93E-11	4.71E-09	2 525-03	2 12E-02	2.04E-17	2.03E-00	100.0
H	B 20	50	-9.37E-05	7.85E+00	0.00E+00	1.02E+00	9.03E+01	2.27E-03	8 88F-11	4.71E-09	2.52E-03	2.12E-02	2.04E-17	2.03E-00	100.0
H	2 2 2 2	50	-9.37E-05	7.855+00	0.000100	1.62E+00	9.05E+01	2.27E-03	5.54E-12	4.71E-09	2.52L-03	2.12L-02	2.05L-17	2.83E-08	100.0
H	2 22	50	-9.37E-05	7.855+00	0.000100	1.62E+00	9.05E+01	2.27E-03	5.54E-12	4.71E-09	3.77E-03	2.12L-02	3 19F-18	2.83E-08	100.0
H	3 2 3	50	-9.37E-05	/ 05E-01	0.000100	1.62E+00	0 70F±01	1.48E-04	3 08F-11	3 10E-10	1.64E-04	1 34E-02	1 08E-10	1 81 E-00	100.0
H	B 25	50	-8.45E-06	4.95E-01	0.00E+00	1 73F-18	9.95E+01	1.48E-04	3.98E-11	3.10E-10	2 28F-04	1.34E-03	1.00L-19	1.81E-09	100.0
H	B 26	50	3.46E-06	3 17F+00	0.00E+00	1.73E-18	9.68E+01	9.47E-04	8 60F-11	1 98F-09	6 31E-04	8 58E-03	2 23E-18	1 15E-08	100.0
H	B 27	50	3.04E-06	2 21F-07	0.00E+00	6.89F-19	9.85E+01	1 48F-04	1.06E-06	1.30E 03	1 47F+00	2 49F-05	1.83E-09	7 36F-10	100.0
H	3 28	50	8 33E-06	7 98F-07	0.00E+00	6.89E-19	9.60E+01	9.46E-04	2.83E-06	7 90F-10	4.04E+00	6 38F-04	2 31F-09	4.61E-09	100.0
H	B 29	50	9 17E-06	7.94E-05	0.00E+00	6.89F-19	9 59E+01	9 46F-04	2.03E-06	7 90E-10	4.08E+00	1 27E-03	1 55E-08	4.61E-09	100.0
H	B 30	50	7.68E-06	3 98F-04	0.00E+00	6.89E-19	9 59E+01	9 46F-04	1 91F-06	7 90E-10	4.12F+00	1 44F-03	6 55E-09	4.61E-09	100.0
h	B 31	50	-7 56E-06	3 98F-04	0.00E+00	6.89E-19	9 59E+01	9 46F-04	1 91F-06	5 25E-11	4 12E+00	1 44F-03	6 55E-09	3 26F-10	100.0
H	3 32	50	-7 56E-06	4 38F-04	0.00E+00	6.89E-19	9 59E+01	9 46F-04	1.90E-06	5 25E-11	4.12E+00	1 44F-03	6 57E-09	3 26E-10	100.0
H	3 33	50	-8 27E-06	8 58F-05	0.00E+00	3 19F-03	9.66F+01	9 46F-04	1.93E-06	5 25E-11	3 38F+00	1 33E-03	1.66E-10	3 26E-10	100.0
H	B 34	50	-8 27E-06	8 57F-01	0.00E+00	3 19F-03	9.66E+01	9 46F-04	1.93E-06	5 25E-11	2 51E+00	4 73E-03	1.00E 10	3 26E-10	100.0
h	B 35	50	-8.27E-06	8.57E-01	0.00F+00	3.19F-03	9.66F+01	9.46F-04	1.93E-06	5.25E-11	2.51E+00	4.73E-03	1.07E-10	3.26F-10	100.0
h	B 36	50	-8.39F-06	8.33F-01	0.00F+00	3.19F-03	9.67F+01	9.46F-04	4.48F-07	5.25F-11	2.48F+00	4.57E-03	4.11F-11	3.26F-10	100.0
h	B 37	50	7.56F-05	4.17F+01	0.00F+00	3.19F-03	3.20F+01	8.05F-04	6.86F-03	2.05F-10	2.63F+01	8.59F-03	7.83F-02	1.76F-09	100.0
h	B 38	50	5.30F-05	4.16F+01	0.00F+00	3.19F-03	3.21F+01	7.65F-04	6.88F-03	1.05F-10	2.63F+01	8.57F-03	7.82F-02	1.00F-09	100.0
h	B 39	50	4.57F-05	5.05F+01	0.00F+00	3.19F-03	7.91F-18	7.84F-05	1.25F-22	3.13F-10	4.94F+01	1.34F-01	1.99F-05	2.76F-09	100.0
h	B 40	50	-8.16F-06	3.17F+00	0.00F+00	5.09F-10	9.66F+01	9.47F-04	3.13F-06	5.26F-11	1.78F-01	8.58F-03	4.50F-10	3.26F-10	100.0
h	B 41	50	-2.35F-06	3.17F+00	0.00F+00	5.09F-10	9.66F+01	9.47F-04	3.13F-06	7.91F-10	1.78F-01	8.58F-03	4.50F-10	4.61F-09	100.0
h	B 42	50	-2.95E-06	3.17E+00	0.00E+00	5.09E-10	9.67E+01	9.47E-04	2.98E-06	7.91E-10	1.48E-01	8.58E-03	1.75E-10	4.61E-09	100.0
h	B 43	50	-4.83E-06	3.17E+00	0.00E+00	1.94E+01	7.74E+01	9.47E-04	2.44E-06	7.90E-10	3.56E-02	8.58E-03	3.33E-11	4.61E-09	100.0
h	B 44	50	5.55E-04	4.39E+01	0.00E+00	1.94E+01	1.67E+01	9.48E-04	6.13E-03	1.92E-09	1.99E+01	8.60E-03	1.28E-01	1.40E-08	100.0
	B 45	50	5.51E-04	3.98E+01	0.00E+00	1.94E+01	1.79E+01	9.47E-04	6.23E-03	2.07E-09	2.29E+01	8.59E-03	9.82E-02	1.52E-08	100.0
	B 46	50	5.51E-04	3.98E+01	0.00E+00	1.94E+01	1.79E+01	9.47E-04	6.23E-03	2.07E-09	2.28E+01	8.58E-03	9.82E-02	1.52E-08	100.0
Γ	B 47	50	4.20E-04	2.98E+01	0.00E+00	1.94E+01	2.21E+01	1.48E-04	7.85E-03	1.19E-09	2.87E+01	1.34E-03	9.57E-02	1.03E-08	100.0
[	B 48	50	4.13E-04	2.04E+01	0.00E+00	1.94E+01	2.95E+01	1.48E-04	8.16E-03	1.68E-09	3.06E+01	1.34E-03	6.89E-02	1.49E-08	100.0
[	B 49	50	4.83E-04	7.85E+00	0.00E+00	1.94E+01	5.39E+01	2.27E-03	1.77E-03	2.73E-09	1.88E+01	2.12E-02	7.07E-04	1.83E-08	100.0
	B 50	50	4.61E-04	7.85E+00	0.00E+00	1.94E+01	5.40E+01	2.27E-03	2.10E-03	2.85E-09	1.87E+01	2.12E-02	9.45E-04	1.93E-08	100.0
[	B 51	50	4.55E-04	7.43E+00	0.00E+00	1.94E+01	5.41E+01	2.27E-03	2.04E-03	2.78E-09	1.90E+01	2.04E-02	9.39E-04	1.89E-08	100.0
	B 52	50	2.35E-04	2.86E-06	0.00E+00	1.94E+01	5.69E+01	2.02E-03	1.72E-03	2.25E-09	2.37E+01	9.02E-04	1.16E-03	1.65E-08	100.0
	B 53	50	1.62E-03	5.44E+01	0.00E+00	1.62E+00	4.82E+00	3.77E-03	9.84E-05	5.14E-10	3.90E+01	9.77E-02	2.62E-02	3.99E-09	100.0
	B 54	50	8.18E-04	3.53E+01	0.00E+00	1.62E+00	3.09E+01	7.69E-03	4.80E-04	6.00E-09	3.22E+01	9.61E-02	1.14E-03	4.64E-08	100.0
	B 55	50	1.07E-03	3.54E+01	0.00E+00	2.74E-17	1.71E+01	4.59E-03	1.52E-04	5.85E-10	4.74E+01	9.65E-02	1.29E-03	4.59E-09	100.0
	B 56	50	1.03E-03	3.54E+01	0.00E+00	2.74E-17	2.19E+01	5.60E-03	5.58E-05	1.52E-09	4.26E+01	9.64E-02	2.68E-04	1.27E-08	100.0
1	B 57	50	9.81E-04	3.54E+01	0.00E+00	2.74E-17	2.49E+01	5.60E-03	5.12E-05	1.53E-09	3.96E+01	9.63E-02	1.02E-04	1.27E-08	100.0
	B 58	50	9.81E-04	3.54E+01	0.00E+00	2.74E-17	2.49E+01	5.60E-03	5.12E-05	1.53E-09	3.96E+01	9.63E-02	1.02E-04	1.27E-08	100.0
	B 59	50	2.32E-03	8.99E+01	0.00E+00	1.73E-18	2.68E+00	5.46E-04	1.29E-05	4.39E-10	7.54E+00	6.17E-03	6.70E-04	3.08E-09	100.1
	B 60	50	2.36E-03	8.39E+01	0.00E+00	1.73E-18	2.44E+00	9.09E-04	6.12E-04	6.37E-10	1.34E+01	1.34E-02	1.03E-01	5.59E-09	99.9
[	B 61	50	1.44E-04	8.39E+01	0.00E+00	1.73E-18	2.44E+00	9.09E-04	6.12E-04	4.59E-11	1.34E+01	1.34E-02	1.03E-01	3.73E-10	99.9
1	B 62	50	1.45E-04	8.21E+01	0.00E+00	1.73E-18	2.23E+00	9.09E-04	5.40E-04	4.58E-11	1.58E+01	1.34E-02	9.26E-02	3.73E-10	100.3
	B 63	50	1.45E-04	8.21E+01	0.00E+00	1.73E-18	2.23E+00	9.09E-04	5.40E-04	4.59E-11	1.58E+01	1.34E-02	9.26E-02	3.73E-10	100.3
	B 64	50	1.46E-04	8.16E+01	0.00E+00	1.73E-18	2.51E+00	9.09E-04	3.91E-04	4.58E-11	1.56E+01	1.34E-02	9.57E-02	3.73E-10	99.7
	B 65	50	2.70E-05	4.95E+00	0.00E+00	1.73E-18	7.65E+01	1.48E-03	2.28E-04	9.08E-11	1.85E+01	1.34E-02	3.89E-05	5.46E-10	100.0

Table 29 – Percentage of Hg in the different phases after 50 years for group B.

# 2 Leaching

For indicator 2, factors X<sub>9</sub> (log k Hg-SOM (HA, FA)) and X<sub>1</sub> (Hg initial concentration in the polluted horizon) are the most influential factors at all stages of the simulation, with X<sub>9</sub> becoming dominant over time. While X<sub>1</sub> shows some non-monotonic features at stages 25 and 50 years ( $\mu^* > |\mu|$ ), this is not the case for X<sub>9</sub>. Fulvic and humic acids are more numerous than thiol groups in SOM ; therefore X<sub>9</sub> is more sensitive than X<sub>10</sub> (log k Hg-SOM (thiols)) to prevent Hg from leaching out of the profile.

Other factors having a non-negligible impact are those directly involved in the leaching process (X<sub>4</sub> DOM in rain, and X<sub>8</sub> log k Hg-DOM(thiols)) and those related to the amount of sorption sites (X<sub>5</sub> and  $X_6$ : SOM exchange capacity). For these factors,  $|\mu| = \mu^*$  except for  $X_4$ , which has a negative  $\mu$  value after 5 years, close to zero after 25 years and positive after 50 years (cf. Table 26). Looking in details to the elementary effects, it appears that the negative value of  $\mu$  after 5 years and the value close to zero after 25 years are due to one trajectory (simulation B59 vs. B60), while the elementary effects of the other four trajectories were positive. Simulations B59 and B60 are characterized by weak sorption to HA and FA (X<sub>9</sub>) compared to the other trajectories (see Annex 9.3). Figure 47 shows the cumulative depth distribution over time of Hg-SOM for these two simulations. Interestingly, it can be seen that after 50 years, in simulation B60 (higher DOM in rain than in B59) more Hg has left the horizon originally polluted, but that more sorption (or retardation) occurred in the soil horizon between 11 and 30 cm. This can be explained by the fact that Hg sorption to HA and FA occurs through the sorption of  $Hg^{2+}$  ions but also of  $Hg(OH)^+$  (section 4.3). If sorption strength is very low (X<sub>9</sub>), then the leaching of inorganic Hg complexes becomes more important than that of Hg-DOM species. When this is the case, higher DOM in rain appears to decrease slightly the formation and leaching of inorganic Hg complexes.

Factors  $X_2$  (NAPL dissolution rate),  $X_3$  (Hg<sup>II</sup> reduction rate),  $X_7$  (log k Hg-DOM (HA, FA)),  $X_{11}$  and  $X_{12}$  (related to DOM sorption) have no influence on the percentage of Hg leaching.

Maximum values for indicator **2** after 50 years is 89.9% for simulation B59.



Figure 47 – Cumulative depth distribution over time of sorbed Hg (in % of total initial Hg) for simulations (a) B59 and (b) B60.



Figure 48 - Depth distribution over time of sorbed Hg at t = 0, 5, 10, 25 and 50 years for simulations (a) B59 and (b) B60.

Figure 49 presents  $Hg^{II}$  leaching at the bottom of the soil profile over time (case B59). This simulation is characterized by respectively low and high values of the most sensitive factors X<sub>9</sub> and X<sub>1</sub>. Relatively high initial leaching peak is probably caused by the high NAPL degradation rate but after 5, 25 or 50 years this factor is not showing significant sensitivity.



Figure 49 – Hg(II) flux at the bottom of the soil profile in simulation B59. Grey dots are daily simulated fluxes at the bottom of the soil profile. Red line is the result of a moving average (window 31 days) on the daily data. Grey bars show the surface precipitation input (averaged every two months for clarity). Note that the y-scale is logarithmic for solute flux.

### **3** Hg still present in the soil horizon originally contaminated (top 10 cm)

For indicator 3, factor X<sub>9</sub> (log k Hg-SOM (HA, FA)) is the most influential factor over the whole simulation period (after 5, 25 and 50 years). This factor determines how long Hg will be retained in the top soil due to sorption processes. Factor X<sub>10</sub> (log k Hg-SOM (thiols)) shows no sensitivity due to the high proportion of HA and FA sites compared to thiols. Factor X<sub>1</sub> (Hg initial concentration in the polluted horizon) is the second most important factor and is characterized by  $\mu$  values indicating non monotonic behaviour of the model. NAPL degradation rate (X<sub>13</sub>) is also important especially in the early times of the simulation. It should be noted that the sensitivity of this factor over time likely depends on the input range of NAPL degradation rate, which was set arbitrarily (cf.

Table 6).

Other factors having an non negligible impact are those directly involved in the leaching process ( $X_4$  DOM in rain, and  $X_8$  log k Hg-DOM(thiols)) and those related to the amount of sorption sites ( $X_5$  and  $X_6$ : SOM exchange capacity). Factors related to DOM sorption ( $X_{11}$  and  $X_{12}$ ) show some interactions with other factors (cf.  $\sigma$  values in Table 27 and Figure 45).

In group B, most of the mercury present in the top 10 cm is in the form of NAPL not yet dissolved or Hg sorbed to SOM. After 50 years, the percentage of Hg still in the horizon originally contaminated varies between 0 (B39) and 100% (B16 to B18).

Figure 50a shows the profile of Hg NAPL at different times for simulation B39. One can see that fast NAPL dissolution occurs and no more NAPL is still present in the top horizon after 25 years. For Hg sorbed to SOM, Figure 50b shows that leaching of Hg acts in two ways on the concentration profiles in the top 10 cm. On the one hand, maximum sorbed Hg concentration decreases and stabilizes to ~40 mg[Hg]/kg[soil] after 25 years. Simultaneously on the other hand, leaching progressively removes all sorbed Hg from the soil and no more Hg is present in the top horizon after 50 years. Particularities of the parameter set that are relevant for explaining this behaviour are a very low  $X_9$  (log k Hg-SOM (HA, FA); by far the most sensitive parameter), and a low initial concentration (the sensitivity of this parameter can impact indicator 3 in both directions, but in the present case it explains the difference with simulation B38 which has a higher initial concentration and hence still ~32% of Hg in the top 10 cm after 50 years).



Figure 50 – Depth distribution over time of (a) Hg NAPL and (b) Hg sorbed to SOM at t = 0, 5, 10, 25 and 50 years for simulation B39.

Figure 51 illustrates an example with an intermediate value for indicator () (case B54) : 32.5% of the initial Hg is still present in the top horizon after 50 years. Figure 51a shows that after 50 years almost all NAPL has dissolved. Concentration of Hg sorbed to SOM progressively increases up to a maximum of ~85 mg[Hg]/kg[soil] after 25 years, and then decreases to ~75 mg[Hg]/kg[soil] after 50 years while leaching has removed Hg only from the first few centimeters of the soil profile. Remarkably, simulation B54 has a very low value of factor X<sub>9</sub> (cf. Annex, section 9.3.2), but the value of indicator () is relatively high compared to other simulations with the same value for factor X<sub>9</sub> (B53 and B55 to B64; cf. Table 29). This results from the other parameter values and interactions between parameters (low X<sub>1</sub> and high X<sub>6</sub>, among others).



Figure 51 – Depth distribution over time of (a) Hg NAPL and (b) Hg sorbed to SOM at t = 0, 5, 10, 25 and 50 years for simulation B54.

### 4 Hg still present in the soil profile below the horizon originally contaminated (11-100 cm)

For this indicator (Table 28 and Figure 46),  $X_9$  (log k Hg-SOM (HA, FA)) and  $X_1$  (initial concentration) remain the two most sensitive factors after 50 years. NAPL degradation rate is a sensitive factor, but its importance decreases over time.

Factor  $X_6$  (exchange capacity of SOM (thiols) has a relatively high sensitivity after 25 years, but lower impact after 5 and 50 years. The high sensitivity at stage 25 years comes mainly from the elementary effect calculated between simulations B53 and B54. In the former, 48% of the initial mercury is present between 11 and 100 cm after 25 years, while for the latter it is only 20%. Results of simulation B54 are displayed in Figure 51. Figure 52 shows NAPL and Hg-SOM concentration profiles for simulation B53. One can see in Figure 52b that the effect of a lower  $X_6$  value in simulation B53 leads to a decrease of the maximum concentration of Hg that can sorb to SOM in the soil profile and as a consequence after 25 years more Hg has already been transported below the horizon originally polluted. After 50 years, the difference between these two simulations is less important: values of indicator **4** are 39.2% for B53 and 32.2% for B54.

(a)

(b)



Figure 52 – Depth distribution over time of (a) Hg NAPL and (b) Hg sorbed to SOM at t = 0, 5, 10, 25 and 50 years for simulation B53.

Factors  $X_3$  (Hg<sup>II</sup> reduction rate) and  $X_7$  (log k Hg-DOM (HA, FA)) have a negligible sensitivity. Comparing the values of  $\mu$  and  $\mu^*$  indicates that the model is non-monotonic for many of the factors :  $X_1$ ,  $X_4$ ,  $X_5$ ,  $X_8$ ,  $X_9$ ,  $X_{10}$ ,  $X_{11}$  and  $X_{12}$ .

After 50 years, values of indicator **4** vary between <0.01% (B16 to B18, B24 to B26) and 49.5% (B39). In simulation case B26, after 50 years 3.2% of the initial mercury has leached out of the soil profile (with leachate concentrations of inorganic Hg complexes about ten times higher than Hg-DOM complexes) and 96.8% is still in the top horizon (Figure 53). The small amount of leaching is due to higher DOM concentration in rain (X<sub>4</sub>) than in B16 to B18, B24 and B25; and the high persistence of Hg in the top horizon is due to high parameter values for X<sub>9</sub> (log k Hg-SOM (HA, FA) and X<sub>1</sub> (initial Hg concentration).



Figure 53 – (a) Cumulative depth distribution over time (in % of total initial Hg) and (b) depth distribution at t = 0, 5, 10, 25 and 50 years of Hg sorbed to SOM for simulation B26.

### 7.2.2.3 Group C (HgCl<sub>2</sub>(aq))

Tables 30 to 33 present the results of the SA using Morris trajectories for indicators **1** to **4**. Figures 54 to 57 show the corresponding plots of  $\mu$  (and  $\mu^*$ ) vs.  $\sigma$  for interpretation of factor sensitivity.

As already found previously, factor sensitivity varies with the indicator assessed (1) to 4) but also over time (after 5, 25 or 50 years).

Factor		After 5 years			After 25 years			After 50 years	
	μ	μ*	σ	μ	μ*	σ	μ	μ*	σ
X <sub>1</sub> : Hg initial conc.	0.0080	0.0080	0.0096	-0.0070	0.0156	0.0286	-0.0073	0.0154	0.0285
X <sub>3</sub> : Hg(II) reduction rate	0.0273	0.0273	0.0131	0.0282	0.0282	0.0134	0.0303	0.0303	0.0148
X <sub>4</sub> : DOM in rain	0.0010	0.0010	0.0022	0.0120	0.0120	0.0264	0.0021	0.0021	0.0034
X₅: meq SOM (HA, FA)	-0.0017	0.0018	0.0026	-0.0027	0.0029	0.0051	0.0003	0.0013	0.0022
X₅: meq SOM (thiols)	-0.0008	0.0008	0.0009	-0.0011	0.0011	0.0014	-0.0012	0.0012	0.0018
X <sub>7</sub> : log k Hg-DOM (HA, FA)	0	0	0	0	0	0	0	0	0
X₅: log k Hg-DOM (thiols)	0.0001	0.0001	0.0002	0.0003	0.0003	0.0003	0.0006	0.0006	0.0009
X₀: log k Hg-SOM (HA,FA)	-0.0142	0.0142	0.0173	-0.0153	0.0153	0.0185	-0.0166	0.0168	0.0209
X <sub>10</sub> : log k Hg-SOM (thiols)	0	0	0	0	0	0	0	0	0
X <sub>11</sub> : log k DOM sorption	0	0	0	0	0	0.0001	0.0001	0.0001	0.0001
X <sub>12</sub> : S <sub>max</sub> (DOM sorption)	0	0	0	0	0	0	0	0	0

Table 30 – Elementary effects for Group C, indicator ① (% Hg volatilized to atmosphere) after 5, 25 and 50 years.

Factor		After 5 years			After 25 years			After 50 years	
	μ	μ*	σ	μ	μ*	σ	μ	μ*	σ
X <sub>1</sub> : Hg initial conc.	61.9973	61.9973	55.4294	49.7567	49.7567	49.0835	36.2800	36.2800	51.5386
X <sub>3</sub> : Hg(II) reduction rate	0	0	0	0	0	0	0	0	0
X₄: DOM in rain	1.9115	1.9115	3.0830	8.9013	8.9013	14.9987	17.7280	17.7280	30.0563
X₅: meq SOM (HA, FA)	-3.2533	3.2533	5.4609	-2.9333	2.9333	5.5096	-2.7667	2.7667	5.6441
X <sub>6</sub> : meq SOM (thiols)	-7.6167	7.6167	10.5517	-7.6000	7.6000	10.0427	-6.2667	6.2667	7.1924
X <sub>7</sub> : log k Hg-DOM (HA, FA)	0	0	0	0	0	0	0	0	0
$X_8$ : log k Hg-DOM (thiols)	0.4293	0.4293	0.7292	2.4367	2.4367	3.5188	4.8533	4.8533	7.1037
X <sub>9</sub> : log k Hg-SOM (HA,FA)	-93.1503	93.1503	56.6084	-95.3180	95.3180	59.3941	-96.2683	96.2683	62.7079
X₁₀: log k Hg-SOM (thiols)	-1.2610	1.2610	2.6503	-1.3167	1.3167	2.6236	-1.1633	1.1633	2.1612
X <sub>11</sub> : log k DOM sorption	0.0033	0.0033	0.0075	0	0	0	0	0	0
X <sub>12</sub> : S <sub>max</sub> (DOM sorption)	0.0001	0.0001	0.0001	0.0667	0.0667	0.1491	0.0003	0.0003	0.0007

 Table 31 – Elementary effects for Group C, indicator **2** (% Hg in original polluted horizon) after 5, 25 and 50 years.

Factor		After 5 years			After 25 years			After 50 years	
	μ	μ*	σ	μ	μ*	σ	μ	μ*	σ
X <sub>1</sub> : Hg initial conc.	-44.9514	44.9514	37.9815	-33.7226	33.7226	34.7286	-25.8732	29.9406	38.1414
X <sub>3</sub> : Hg(II) reduction rate	-0.0010	0.0010	0.0022	-0.0433	0.0433	0.0723	-0.0400	0.0400	0.0723
X₄: DOM in rain	-1.9766	1.9766	3.3876	-8.9418	8.9418	15.3702	-11.7009	11.7009	17.2320
X₅: meq SOM (HA, FA)	6.8235	6.8235	7.7656	6.5402	6.5402	8.2077	6.5640	6.5640	8.3949
X₅: meq SOM (thiols)	3.7479	3.7479	4.0959	3.0776	3.0776	3.0641	2.7267	2.7267	2.8188
X <sub>7</sub> : log k Hg-DOM (HA, FA)	0	0	0	0	0	0	0	0	0
X₅: log k Hg-DOM (thiols)	-0.5223	0.5223	0.6867	-2.4857	2.4857	3.5754	-4.9552	4.9552	7.1391
X₃: log k Hg-SOM (HA,FA)	81.7732	81.7732	65.1838	82.8104	82.8104	68.0476	82.7555	82.7555	70.0401
X <sub>10</sub> : log k Hg-SOM (thiols)	0.2000	0.2000	0.3613	0.1933	0.1933	0.4323	0.1966	0.1966	0.4397
X <sub>11</sub> : log k DOM sorption	0	0	0	0	0	0	-0.0333	0.0333	0.0745
X <sub>12</sub> : S <sub>max</sub> (DOM sorption)	-0.0033	0.0033	0.0074	-0.0067	0.0067	0.0149	-0.0067	0.0067	0.0149

## Table 32 – Elementary effects for Group C, indicator (3) (% Hg still in horizon initially polluted) after 5, 25 and 50 years.

Factor		After 5 years		Af	ter 25 years		Af	After 50 years $\mu$ $\mu^*$ $\sigma$ -10.3869         26.3481         38           0         0         0           -6.0390         6.1432         13           -3.8260         4.0873         4           3.6193         4.7179         6           0         0         0           13.7125         19.1707         18           1 0771         1 0957         2		
	μ	μ*	σ	μ	μ*	σ	μ	μ*	σ	
X <sub>1</sub> : Hg initial conc.	-16.7454	32.8846	39.4312	-16.0242	32.0732	40.3678	-10.3869	26.3481	38.5033	
X <sub>3</sub> : Hg(II) reduction rate	-0.0003	0.0003	0.0007	-0.0001	0.0001	0.0002	0	0	0	
X <sub>4</sub> : DOM in rain	0.0531	0.2323	0.3849	-0.0246	0.2883	0.4676	-6.0390	6.1432	13.1175	
X₅: meq SOM (HA, FA)	-3.5463	4.1565	4.3378	-3.5860	4.1888	4.3675	-3.8260	4.0873	4.1964	
X <sub>6</sub> : meq SOM (thiols)	4.0217	5.1204	7.6347	4.5195	5.6188	8.6754	3.6193	4.7179	6.8164	
X <sub>7</sub> : log k Hg-DOM (HA, FA)	0	0	0	0	0	0	0	0	0	
X₅: log k Hg-DOM (thiols)	0.0341	0.0341	0.0502	0.0405	0.1131	0.1858	0.0882	0.1549	0.2737	
X <sub>9</sub> : log k Hg-SOM (HA,FA)	11.5719	20.9900	22.3272	12.5125	20.1883	20.6559	13.7125	19.1707	18.7301	
X₁₀: log k Hg-SOM (thiols)	0.9703	0.9903	2.0680	1.0270	1.0464	2.0406	1.0771	1.0957	2.0227	
X <sub>11</sub> : log k DOM sorption	-0.0003	0.0003	0.0008	-0.0010	0.0010	0.0022	-0.0013	0.0013	0.0030	
X <sub>12</sub> : S <sub>max</sub> (DOM sorption)	-0.0202	0.0202	0.0452	-0.0207	0.0207	0.0444	-0.0277	0.0277	0.0591	

Table 33 – Elementary effects for Group C, indicator ④ (% Hg still present in the soil profile below the horizon initially polluted) after 5, 25 and 50 years.



Figure 54 – Plots of  $\mu$  vs.  $\sigma$  and  $\mu^*$  vs.  $\sigma$  for elementary effects of Group C, indicator **①** (% Hg volatilized to the atmosphere) after (a) 5, (b) 25 and (c) 50 years.



Figure 55 – Plots of  $\mu$  vs.  $\sigma$  and  $\mu^*$  vs.  $\sigma$  for elementary effects of Group C, indicator **2** (% Hg leached out of soil profile) after (a) 5, (b) 25 and (c) 50 years.



Figure 56 – Plots of  $\mu$  vs.  $\sigma$  and  $\mu^*$  vs.  $\sigma$  for elementary effects of Group C, indicator 3 (% Hg still in horizon initially polluted) after (a) 5, (b) 25 and (c) 50 years.



Figure 57 – Plots of  $\mu$  vs.  $\sigma$  and  $\mu^*$  vs.  $\sigma$  for elementary effects of Group C, indicator ④ (% Hg still present in the soil profile below the horizon initially polluted) after (a) 5, (b) 25 and (c) 50 years.

Table 34 shows the Hg (percentage of total initial amount) in the different phases/compartments after 50 years. Average absolute value of Hg mass balance error after 50 years was 0.054%.

					Top 10 cm						11-100 cm	1			
		Time (yr)	Hg atm	Hg leached	HgS	Hg NAPL	Hg SOM	Hg DOM	Hg inorg	Hg(g)	Hg SOM	Hg DOM	Hg inorg	Hg(g)	TOTAL
			-												
-	-	ΙΨ	*	*	*	<b>T</b>	<b>v</b>	*	*	*	-	*	*	<b>v</b>	*
С	01	50	5.80E-02	4.83E+01	0.00E+00	0.00E+00	8.59E+00	3.56E-03	1.24E-05	9.24E-09	4.30E+01	9.77E-02	1.08E-04	7.80E-08	100.0
С	02	50	5.80E-02	4.83E+01	0.00E+00	0.00E+00	8.59E+00	3.56E-03	1.24E-05	9.24E-09	4.30E+01	9.77E-02	1.08E-04	7.80E-08	100.0
С	03	50	6.01E-02	4.06E+01	0.00E+00	0.00E+00	2.07E+01	5.60E-03	8.34E-06	7.98E-08	3.86E+01	9.77E-02	2.61E-05	6.86E-07	100.0
С	04	50	5.91E-02	3.79E+01	0.00E+00	0.00E+00	2.49E+01	5.60E-03	5.45E-06	7.98E-08	3.70E+01	9.77E-02	9.43E-06	6.86E-07	100.0
С	05	50	5.89E-02	3.79E+01	0.00E+00	0.00E+00	2.49E+01	5.60E-03	5.30E-06	7.98E-08	3.70E+01	9.77E-02	6.89E-06	6.86E-07	100.0
с	06	50	6.38E-02	8.05E+01	0.00E+00	0.00E+00	2.77E-24	1.36E-05	-7.33E-24	3.17E-10	1.92E+01	2.04E-01	1.16E-05	2.78E-09	100.0
С	07	50	6.38E-02	8.05E+01	0.00F+00	0.00E+00	2.78E-24	1.36E-05	4.88E-25	3.17E-10	1.92E+01	2.04E-01	1.16E-05	2.78E-09	99.9
C	08	50	6 38F-02	8 03F+01	0.00F+00	0.00F+00	1 96F-08	1 35F-05	4 17F-15	3 17F-10	1 93F+01	2 04F-01	1 31F-05	2 78F-09	99.9
c	09	50	2 98F-02	8 10F+01	0.00F+00	0.00F+00	6 10F+00	1.05F-03	6 68F-06	4 50F-08	1 27F+01	1 34F-02	2 18F-05	3 45F-07	99.8
c	10	50	1 87E-03	8 10F+01	0.00E+00	0.00E+00	6 12E+00	1.05E-03	6 73E-06	2 84F-09	1 27E+01	1 34F-02	2 18F-05	2 18F-08	99.8
c	11	50	1 93F-03	7 80F±01	0.002+00	0.0000000	6 71 F±00	9 16F-04	4 60E-06	2.04E-09	1.55F±01	1 3/F-02	2.102.05	1 935-08	100.2
c	12	50	1.550-05	0.055+01	0.000100	0.000100	2 14 E+00	2 475 05	9.425.15	5 90E 11	6 205+00	5.975.04	1 025 12	2 01E 10	00.0
c	12	50	1.03E-03	9.03E+01	0.000000	0.0000000	3.140	2.476-03	1 705 05	5.696-11	0.292+00	3.67E-04	1.926-15	3.916-10	100.0
c	13	50	1.065-03	1.346+01	0.0000000	0.0000000	3.00E+01	1.926-03	1.702-05	5.552-09	4.05E+01	1.156-02	1.65E-05	3.425-00	100.0
C	14	50	1.06E-03	1.34E+01	0.00E+00	0.00E+00	3.81E+01	1.93E-03	1.68E-05	5.56E-09	4.85E+01	1.15E-02	7.66E-06	3.43E-08	100.0
C	15	50	1.88E-02	1.34E+01	0.00E+00	0.00E+00	3.80E+01	1.92E-03	1.67E-05	8./8E-08	4.85E+01	1.15E-02	7.66E-06	5.40E-07	100.0
C	16	50	2.93E-02	8.81E+01	0.00E+00	0.00E+00	4.11E+00	1.40E-04	6.60E-05	8.58E-09	7.88E+00	1.31E-03	1.93E-04	5.58E-08	100.1
С	17	50	2.92E-02	8.81E+01	0.00E+00	0.00E+00	4.11E+00	1.43E-04	6.79E-05	8.90E-09	7.88E+00	1.34E-03	1.83E-04	5.72E-08	100.1
С	18	50	3.17E-02	9.29E+01	0.00E+00	0.00E+00	2.32E+00	1.32E-04	1.05E-04	9.48E-09	4.67E+00	1.34E-03	4.07E-04	6.64E-08	99.9
С	19	50	3.17E-02	9.29E+01	0.00E+00	0.00E+00	2.32E+00	1.32E-04	1.05E-04	9.48E-09	4.67E+00	1.34E-03	4.07E-04	6.64E-08	99.9
С	20	50	2.49E-03	4.95E-01	0.00E+00	0.00E+00	8.84E+01	1.48E-04	2.75E-11	6.89E-09	1.11E+01	1.34E-03	1.98E-12	3.93E-08	100.0
С	21	50	2.49E-03	4.96E-01	0.00E+00	0.00E+00	8.84E+01	1.48E-04	2.87E-11	6.89E-09	1.11E+01	1.34E-03	2.50E-12	3.93E-08	100.0
С	22	50	3.08E-03	3.17E+00	0.00E+00	0.00E+00	8.57E+01	9.47E-04	6.56E-11	4.41E-08	1.11E+01	8.58E-03	7.98E-12	2.51E-07	100.0
С	23	50	3.07E-03	3.17E+00	0.00E+00	0.00E+00	8.57E+01	9.47E-04	6.47E-11	4.41E-08	1.11E+01	8.58E-03	7.65E-12	2.51E-07	100.0
С	24	50	4.63E-03	3.17E+00	0.00E+00	0.00E+00	8.05E+01	9.47E-04	1.57E-10	4.41E-08	1.63E+01	8.58E-03	3.21E-11	2.51E-07	100.0
С	25	50	3.23E-04	1.00E+02	0.00E+00	0.00E+00	1.15E-05	9.81E-09	4.21E-13	3.13E-12	1.05E-03	9.21E-06	6.16E-09	2.76E-11	100.0
с	26	50	5.13E-03	1.00E+02	0.00E+00	0.00E+00	1.14E-05	9.75E-09	4.18E-13	3.14E-12	1.05E-03	9.17E-06	6.13E-09	2.77E-11	100.0
С	27	50	4.83E-03	1.00F+02	0.00F+00	0.00E+00	7.84E-05	6.70E-08	2.89F-12	4.97E-11	9.25E-03	8.38F-05	5.59E-08	4.38E-10	100.0
c	28	50	4 65F-03	8 93F+01	0.00F+00	0.00F+00	1 99F+00	2 59F-04	1 26F-08	1 21F-09	8 79F+00	1 53E-02	5 89F-05	8 75F-09	100 1
c	29	50	4 65E-03	8 93E+01	0.00E+00	0.00E+00	1 99E+00	2.59E-04	1 26E-08	1 21E-09	8 79E+00	1 53E-02	5.89E-05	8 75E-09	100.1
c	30	50	1 99F-03	8 87E+01	0.005+00	0.005+00	2.07E+00	2.76F-04	1 38F-08	1 205-00	9 18E+00	1 72F-02	9.84E-05	9 28F-09	99.9
c	21	50	5 96E 06	1 165 07	0.000100	0.000100	0.00E+01	4 255 06	1.365 10	7 295 11	1.01E+00	0.246.11	5.042-05	5.46E 10	100.0
c	22	50	7.245.04	1.025.01	0.000	0.000	9.90L+01	4.33L-00	1.201-10	2 1 5 5 0 9	1.011+00	3.341-11	5.651-15	1 265 07	100.0
c	22	50	7.246-04	1.020+01	0.000000	0.0000000	0.0000101	2.956-05	1.105-10	2.156-00	1.000000	2.705-02	5.556-15	1.202-07	100.0
C	33	50	7.13E-04	9.81E+00	0.00E+00	0.00E+00	8.88E+U1	2.95E-03	1.01E-10	2.15E-08	1.30E+00	2.08E-02	5.05E-10	1.20E-07	100.0
C	34	50	7.13E-04	9.81E+00	0.00E+00	0.00E+00	8.88E+U1	2.95E-03	2.13E-10	2.15E-08	1.30E+00	2.08E-02	1.29E-15	1.266-07	100.0
C	35	50	7.13E-04	9.81E+00	0.00E+00	0.00E+00	8.88E+01	2.95E-03	1.14E-10	2.15E-08	1.36E+00	2.68E-02	6.11E-16	1.26E-07	100.0
C	36	50	1.14E-04	3.20E+00	0.00E+00	0.00E+00	9.56E+01	1.04E-03	6.15E-11	7.68E-09	1.23E+00	8.87E-03	2.95E-16	4.38E-08	100.0
С	37	50	1.75E-03	7.57E+01	0.00E+00	0.00E+00	1.29E+01	1.46E-06	1.57E-07	6.83E-12	1.15E+01	9.54E-07	1.31E-06	4.43E-11	100.1
С	38	50	1.75E-03	7.63E+01	0.00E+00	0.00E+00	1.28E+01	1.50E-06	1.61E-07	6.96E-12	1.10E+01	9.81E-07	1.34E-06	4.49E-11	100.0
С	39	50	1.75E-03	7.64E+01	0.00E+00	0.00E+00	1.28E+01	1.51E-06	1.61E-07	6.97E-12	1.09E+01	9.12E-07	1.22E-06	4.50E-11	100.0
С	40	50	1.75E-03	7.64E+01	0.00E+00	0.00E+00	1.28E+01	8.71E-07	3.22E-07	6.05E-12	1.09E+01	4.29E-07	2.58E-06	4.05E-11	100.0
С	41	50	1.97E-03	9.90E+01	0.00E+00	0.00E+00	2.72E-01	6.00E-07	3.89E-07	4.40E-12	5.17E-01	4.25E-06	3.06E-05	3.37E-11	99.8
С	42	50	1.62E-03	8.75E+01	0.00E+00	0.00E+00	4.30E+00	9.40E-06	6.09E-06	6.95E-11	8.19E+00	6.66E-05	4.79E-04	5.34E-10	100.0
С	43	50	1.63E-03	8.75E+01	0.00E+00	0.00E+00	4.30E+00	9.46E-06	6.13E-06	6.96E-11	8.19E+00	6.70E-05	4.83E-04	5.34E-10	100.0
С	44	50	1.63E-03	8.75E+01	0.00E+00	0.00E+00	4.30E+00	9.45E-06	6.13E-06	6.96E-11	8.19E+00	6.65E-05	4.83E-04	5.34E-10	100.0
С	45	50	1.63E-03	8.66E+01	0.00E+00	0.00E+00	4.60E+00	2.06E-06	3.94E-06	5.70E-11	8.77E+00	1.53E-05	1.80E-04	4.74E-10	99.9
С	46	50	2.60E-02	8.66E+01	0.00E+00	0.00E+00	4.60E+00	2.05E-06	3.92E-06	2.03E-10	8.77E+00	1.52E-05	1.80E-04	1.40E-09	100.0
С	47	50	2.60E-02	8.66E+01	0.00E+00	0.00E+00	4.62E+00	2.96E-06	2.11E-06	1.91E-10	8.85E+00	3.45E-05	1.36E-04	1.27E-09	100.1
с	48	50	2.71E-02	8.76E+01	0.00E+00	0.00E+00	3.45E+00	2.98E-04	1.37E-06	1.32E-08	8.86E+00	3.37E-03	1.43E-04	9.06E-08	99.9
С	49	50	1.63E-05	9.58E-08	0.00E+00	0.00E+00	9.67E+01	5.21E-06	1.98E-10	5.92E-11	3.27E+00	1.48E-07	3.95E-12	4.82E-10	100.0
C	50	50	2.53E-06	6.74F-08	0.00F+00	0.00E+00	9.90E+01	1.35E-06	5.08F-11	5.21F-11	1.00E+00	5.02E-11	1.35E-15	4,49F-10	100.0
c	51	50	2.53F-06	6.74F-08	0.00F+00	0.00F+00	9.90F+01	1.35F-06	5.08F-11	5.21F-11	1.00F+00	5.02F-11	1.35F-15	4.49F-10	100.0
c	52	50	3 02F-06	6 71 F-08	0.00F+00	0.00F+00	9 90F+01	1 25F-06	4 76F-11	5 19F-11	9 72F-01	1 33F-11	3.61F-16	4 48F-10	100.0
c	52	50	4 31F-06	6.67F-00	0.005+00	0.005+00	9 90 5+01	9 91 F-07	5 91F-11	5 17F-11	9 60F-01	6 90F-12	6.60F-16	4 47F-10	100.0
c	5/	50	2 15E-06	6 7/F-00	0.00L+00	0.0000+00	0 00F±01	1 26E-06	4 72F-11	5 10F-11	9.73E-01	1 35F-11	3 50F-16	4.47L-10	100.0
c	54	50	2.131-00	6 715 00	0.0001+00	0.0001+00	0.015:01	1 165 00	1 255 11	5.105.11	0.255.01	5 205 10	1 205 22	4.40L-10	100.0
c	55	50	2.205-00	2 165-00	0.000000	0.0000000	0.515+01	1.105-00	4.536-11	3.105-11	1.255-01	0 77E 02	5 5 75 20	4.40E-10	100.0
c	50	50	2.935-05	3.100+00	0.0000000	0.0000000	3.30E+01	1.046-03	4.030-11	1 02F 10	1.235+00	0.77E-03	-J.57E-20	1.105.00	100.0
C C	5/	50	1.U8E-U3	2.51E+U1	0.00E+00	0.00E+00	4.98E+U1	0.50E-05	3.53E-11	1.93E-10	2.52E+U1	5.95E-04	2.4/E-11	1.10E-09	100.2
L C	58	50	1.72E-U2	2.51E+U1	0.00E+00	0.00E+00	4.98E+U1	0.50E-U5	3.53E-11	3.00E-09	2.52E+U1	3.95E-04	2.4/E-11	1.74E-U8	100.2
C	59	50	1./3E-02	2.55E+01	U.UUE+00	0.00E+00	4.94E+01	1.92E-04	6.34E-11	8.95E-09	2.52E+01	1.74E-03	5.4/E-11	5.10E-08	100.1
C	60	50	3.30E-02	9.81F+01	U.UUE+00	U.UUE+00	2.42E-01	8.10E-05	1.5/E-06	4.80E-10	1.91E+00	1.74E-03	5.36E-04	4.11E-09	100.3

Table 34 – Percentage of Hg in the different phases after 50 years for group C.

### 1 Volatilization

For indicator ①, all  $\mu$  values are very close to zero, because the percentage of Hg volatilized is always very low (max. 0.06% after 50 years).

As could be expected from model conceptualization of Hg volatilization (sections 2.8 and 4.6),  $X_3$  (Hg<sup>II</sup> reduction rate) is amongst the most sensitive factors.  $X_1$  (initial Hg concentration) and  $X_9$  (log k Hg-SOM (Ha, FA)) are also important factors, and their relative sensitivity compared to  $X_3$  increases after 25 and 50 years. It should be noted that the model is non-monotonic for factor  $X_1$ .

Maximum volatilization after 50 years occurs in simulations C06 to C08 (see Annex, section 9.3.3 for input parameter values). Figure 58 shows the volatilization of Hg(0) over time. One can see that volatilization occurs mainly in the first half of the simulation period, and seems to be correlated to the amount of precipitation. This can be explained by the conditions required for significant Hg<sup>II</sup> reduction to take place close near the soil surface. Higher concentrations of Hg<sup>II</sup> in aqueous phase occur (i) at the beginning of the simulation, when much of the initial mercury is still present close to the surface, and (ii) when DOM brought by infiltrating rainwater helps to desorb Hg from SOM.



Figure 58 – Hg(0)(g) flux at the soil surface in simulation C06. Grey dots are daily simulated fluxes and the red line is the result of a moving average (window 31 days) on the daily data. Grey bars show the surface precipitation input (averaged every two months for clarity).

### 2 Leaching

For indicator 2, factor  $X_9$  (log k Hg-SOM (HA, FA)) is the most influential factor at all stages of the simulation. This is certainly related to the form of initial Hg pollution in group C (HgCl<sub>2</sub>(aq)); i.e. most of the initial Hg<sup>2+</sup> ions immediately sorb to SOM and actually Hg-SOM could be viewed as the initial Hg pool. Fulvic and humic acids are more numerous than thiol groups in SOM; therefore  $X_9$  is more sensitive than  $X_{10}$  to eventually determine how much Hg may leach out of the profile.

Factor  $X_1$  (Hg initial concentration in the polluted horizon) is the second most important factor. Other factors having an non negligible impact are those directly involved in the leaching process ( $X_4$  DOM in

rain, and  $X_8 \log k$  Hg-DOM(thiols)) and those related to the amount of sorption sites ( $X_5$  and  $X_6$ : SOM exchange capacity).

For all factors,  $|\mu| = \mu^*$ . This means that model behavior is monotonic for this indicator and these factors.

Factors  $X_3$  (Hg<sup>II</sup> reduction rate),  $X_7$  (log k Hg-DOM (HA, FA)),  $X_{11}$  and  $X_{12}$  (related to DOM sorption) have no influence on the percentage of Hg leaching.

Maximum values for indicator **2** is 100% for simulations C25 to C27. Compared to other simulations displaying high leaching, these simulations are in particular characterized by a very small amount of sorption sites (small  $X_5$  and  $X_6$ ; see Annex, section 9.3.3).

Figure 59 shows the cumulative depth distribution over time of Hg-SOM and aqueous species for simulation C06. At t = 0 about 72.5% of the initial Hg instantly sorbs to SOM and rapidly ~100% of the mercury is sorbed to SOM. The transition between 72.5 and 100% of the initial Hg is not visible in Figure 59a as it occurs in a few days (after that the Hg that remained in the aqueous phase has leached from the top soil and has sorbed to SOM in the underlying layer). Similarly in Figure 59b, there is initially 27.5% of Hg in soil solution (not visible with the color code), but this percentage rapidly decreases to ~0.2% for the rest of the simulation period. In this particular example, high leaching subsequently occurs. After 50 years, 71.6% of the initial Hg has leached.



Figure 59 – Cumulative depth distribution over time of (a) sorbed Hg and (b) aqueous Hg species (in % of total initial Hg) for simulation C06.

Figure 60 presents Hg<sup>II</sup> leaching at the bottom of the soil profile over time (case C06). It can be seen that leaching starts early and is sustained over the entire simulation period, as opposed to cases where Hg was introduced as solid (group A) or NAPL (group B; not shown) and dissolution was first required.



Figure 60 – Hg(II) flux at the bottom of the soil profile in simulation C06. Grey dots are daily simulated fluxes at the bottom of the soil profile. Red line is the result of a moving average (window 31 days) on the daily data. Grey bars show the surface precipitation input (averaged every two months for clarity). Note that the y-scale is logarithmic for solute flux.

Figures 61 and 62 present the results of a simulation for which relatively low leaching occurs (case C13; characterized by very low DOM in rain (X<sub>4</sub>), and low initial Hg concentration (X<sub>1</sub>)). The value of indicator **2** is 11.2 and 13.4% after 25 and 50 years, respectively. The rest of the mercury is mainly sorbed to SOM in the top 30 cm of the soil profile (86.6% after 50 years; Figure 61a). In Figure 62, the shape of Hg<sup>II</sup> breakthrough curve is the same as in Figure 60 (i.e. hydraulics determine the flux dynamics), but absolute values are much smaller.



Figure 61 – Cumulative depth distribution over time of (a) sorbed Hg and (b) aqueous Hg species (in % of total initial Hg) for simulation C13.



Figure 62 – Hg(II) flux at the bottom of the soil profile in simulation C13. Grey dots are daily simulated fluxes at the bottom of the soil profile. Red line is the result of a moving average (window 31 days) on the daily data. Grey bars show the surface precipitation input (averaged every two months for clarity). Note that the y-scale is logarithmic for solute flux.

### 3 Hg still present in the soil horizon originally contaminated (top 10 cm)

For indicator ③, the results of the SA using the elementary effects are very similar to what was found for indicator ② (see above). Factor  $X_9$  (log k Hg-SOM (HA, FA)) is the most influential factor. It determines how long Hg will be retained in the top soil due to sorption processes. It should be noted that factor  $X_{10}$  (log k Hg-SOM (thiols)) shows no sensitivity due to the high proportion of HA and FA sites compared to thiols. Factor  $X_1$  (Hg initial concentration in the polluted horizon) is the second most important factor. Other factors having an non negligible impact are those directly involved in the leaching process ( $X_4$  DOM in rain, and  $X_8$  log k Hg-DOM(thiols)) and those related to the amount of sorption sites ( $X_5$  and  $X_6$  : SOM exchange capacity).

In group C, most of the mercury present in the top 10 cm is in the form of Hg sorbed to SOM. After 50 years, the percentage of Hg still in the horizon originally contaminated varies between 0 (C06 to C08) and 99.1% (C55).

As shown in Figure 63a for simulation C06, Hg-SOM is still present in the top horizon after 25 years, but not after 50 years. In Figure 63b, the initial distribution of Hg species in solution shows that Hg rapidly migrates until 20 cm deep (and sorbs there too; cf. red curve in Figure 63a until 20 cm deep). Afterwards, Hg aqueous species represent a small fraction of total Hg (not visible in Figure 63b) but are important for Hg leaching.

Figure 64 illustrates an example with a middle value for indicator () (case C13): 38% of the initial Hg is still present in the top horizon after 50 years. Figure 64a shows that after the initial redistribution of Hg in horizons containing SOM, the concentration profile does not change between 5, 10, 25 and 50 years (this can also be oberved in Figure 61a). Figure 64b includes a zoom to visiualize the concentration profile of Hg aqueous species (essentially Hg-DOM and Hg hydroxides). It can be seen that in the top 30 cm, where most of the Hg is present, Hg concentrations in aqueous phase are higher than deeper in the soil profile. Below 30 cm, no retardation occurs in the absence of SOM and the concentration is constant with depth (but decreases over time as Hg is slowly leached out of the profile).



Figure 63 – Depth distribution over time of (a) sorbed Hg and (b) aqueous Hg species at t = 0, 5, 10, 25 and 50 years for simulation C06.



Figure 64 – Depth distribution over time of (a) sorbed Hg and (b) aqueous Hg species at t = 0, 5, 10, 25 and 50 years for simulation C13.

#### **4** Hg still present in the soil profile below the horizon originally contaminated (11-100 cm)

For this indicator (Table 33 and Figure 57), the three most sensitive factors after 50 years are the same as for indicator 3, but the most important one is X<sub>1</sub> (Hg initial concentration in the polluted horizon). It should be noted that factors X<sub>7</sub> and X<sub>8</sub> (log k Hg-DOM) have a negligible sensitivity.

Comparing the values of  $\mu$  and  $\mu^*$  indicates that the model is non-monotonic for several factors, notably X<sub>1</sub>, X<sub>5</sub>, X<sub>6</sub> and X<sub>9</sub>. For X<sub>1</sub>, elementary effect is generally negative (higher initial concentration gives smaller **4** value) due to the indicator being computed as a percentage of initial concentration. However, when sorption to SOM is so strong that most of Hg is retained in the top horizon (0-10 cm), then higher X<sub>1</sub> can eventually result in saturation of the sorption sites in the contaminated horizon and mobilization of Hg which then sorbs in the horizons below, thus giving higher value of **4** (simulation C57 compared to C56). Similarly, non-monotonic behaviour of factor X<sub>9</sub> (log k Hg-SOM (HA, FA))

occurs if initial Hg is relatively low and sorption becomes so strong that almost no Hg leaves the initially contaminated horizon (simulation C31 compared to C30).

After 50 years, values of indicator **4** vary between 0 (C25 to C27) and 48.5% (C13 to C15). In the former case, all Hg has leached; while an example of the latter case is shown in Figures 61 and 64 (simulation C13).

### 7.2.2.4 Group E (NAPL and HgCl<sub>2</sub>(aq))

In the SA simulations, one run (E06) failed due to convergence problems in PHREEQC with the parameter values given in Annex (section 9.3.4). Closer inspection suggested that this was caused by a too high  $X_8$  value (even though this alone does not lead to the convergence problem; but rather the particular combination of all factor values and the type of Hg pollution sources). It was decided to slightly decrease  $X_8$  (log k Hg-DOM (thiols) = 28 instead of 33.3). With this modification, convergence problem was solved without affecting the results, because (i) factor value stays in the same level of the elementary effects, and (ii) Hg-DOM (thiols) remains by far the most favoured Hg aqueous complexation.

Tables 35 to 38 present the results of the sensitivity analysis using Morris trajectories for indicators ① to ④. Figures 65 to 68 show the corresponding plots of  $\mu$  (and  $\mu^*$ ) vs.  $\sigma$  for interpretation of factor sensitivity. Factor sensitivity varies with the indicator assessed (① to ④) but also over time (after 5, 25 or 50 years).

Factor		After 5 years			After 25 years		-	After 50 years μ μ*		
	μ	μ*	σ	μ	μ*	σ	μ	μ*	σ	
X <sub>1</sub> : Hg initial conc.	0.0028	0.0028	0.0032	0.0009	0.0013	0.0019	0.0010	0.0014	0.0021	
X <sub>13</sub> : NAPL dissolution rate	0.0037	0.0037	0.0041	0.0035	0.0035	0.0030	0.0025	0.0025	0.0033	
X <sub>3</sub> : Hg(II) reduction rate	0.0305	0.0305	0.0578	0.0347	0.0347	0.0633	0.0406	0.0406	0.0761	
X₄: DOM in rain	0.0004	0.0004	0.0009	0.0007	0.0007	0.0009	0.0008	0.0009	0.0012	
X₅: meq SOM (HA, FA)	0.0007	0.0009	0.0018	0.0002	0.0012	0.0020	-0.0007	0.0019	0.0031	
X₅: meq SOM (thiols)	0	0	0.0001	-0.0001	0.0001	0.0001	-0.0001	0.0001	0.0001	
X <sub>7</sub> : log k Hg-DOM (HA, FA)	0	0	0	0	0	0	0	0	0	
X₅: log k Hg-DOM (thiols)	0	0	0	0.0001	0.0001	0.0001	0.0002	0.0002	0.0004	
X₀: log k Hg-SOM (HA,FA)	-0.0048	0.0048	0.0078	-0.0077	0.0077	0.0070	-0.0090	0.0090	0.0075	
X <sub>10</sub> : log k Hg-SOM (thiols)	0	0	0	0	0	0	0	0.0001	0.0001	
X <sub>11</sub> : log k DOM sorption	0	0.0001	0.0001	0	0.0001	0.0001	-0.0001	0.0002	0.0002	
X <sub>12</sub> : S <sub>max</sub> (DOM sorption)	0	0	0.0001	0	0	0	0	0	0.0001	

## Table 35 – Elementary effects for Group E, indicator ① (% Hg volatilized to atmosphere) after 5, 25 and 50 years.

Factor		After 5 years			After 25 years		-	After 50 years           μ         μ*           22.8067         35.0067		
	μ	μ*	σ	μ	μ*	σ	μ	μ*	σ	
X <sub>1</sub> : Hg initial conc.	46.6433	46.6433	38.1195	24.6633	39.1300	48.8374	22.8067	35.0067	43.2698	
X <sub>13</sub> : NAPL dissolution rate	4.7336	4.7336	7.1194	19.1667	19.1667	19.9381	11.2333	11.2333	10.5367	
X <sub>3</sub> : Hg(II) reduction rate	0	0	0	0	0	0	-0.2000	0.2000	0.4472	
X₄: DOM in rain	-1.7333	6.1333	10.7733	-1.4667	6.3333	11.0173	1.8027	9.0027	15.0401	
X₅: meq SOM (HA, FA)	-2.1224	2.1891	4.3578	-0.2133	0.2133	0.3906	-1.2460	1.2460	1.6648	
X <sub>6</sub> : meq SOM (thiols)	-15.6567	15.6567	33.9938	-15.6000	15.6000	34.0503	-15.6690	15.6690	34.0111	
X <sub>7</sub> : log k Hg-DOM (HA, FA)	0	0	0	0	0	0	0	0	0	
X₀: log k Hg-DOM (thiols)	1.0557	1.0557	1.5379	5.3733	5.3733	7.5964	11.0200	11.0200	15.1915	
X <sub>9</sub> : log k Hg-SOM (HA,FA)	-35.8840	35.8840	33.8770	-53.1233	53.1233	44.7827	-70.4797	70.4797	55.3291	
X₁₀: log k Hg-SOM (thiols)	0	0	0	-0.1667	0.1667	0.3727	-1.2867	1.2867	2.2085	
X <sub>11</sub> : log k DOM sorption	-1.5333	2.1333	3.2089	-1.3667	2.0334	2.8587	-2.1507	3.1507	3.2827	
X <sub>12</sub> : S <sub>max</sub> (DOM sorption)	-1.2667	1.8667	3.7279	-0.8667	1.6667	3.1763	-0.6000	1.6000	2.9453	

## Table 36 – Elementary effects for Group E, indicator **2** (% Hg in original polluted horizon) after 5, 25 and 50 years.

Factor		After 5 years			After 25 years			After 50 years μ μ*		
	μ	μ*	σ	μ	μ*	σ	μ	μ*	σ	
X <sub>1</sub> : Hg initial conc.	-39.8804	43.3430	43.9294	-19.5742	34.3637	39.4640	-17.1100	23.6829	27.9799	
X <sub>13</sub> : NAPL dissolution rate	-19.0869	19.0869	14.2878	-23.9703	23.9703	17.8805	-14.5555	14.5555	13.1539	
X <sub>3</sub> : Hg(II) reduction rate	0	0	0	0	0	0	-0.0133	0.0133	0.0298	
X <sub>4</sub> : DOM in rain	1.5521	5.8687	9.7368	-7.3175	14.0578	16.4791	-14.0076	18.9153	24.8886	
X₅: meq SOM (HA, FA)	11.1948	11.1948	7.4067	13.7636	13.7636	13.8448	25.1103	25.1103	28.8194	
X <sub>6</sub> : meq SOM (thiols)	6.9891	6.9891	11.1096	7.9828	7.9828	11.0441	8.9783	8.9783	11.0391	
X <sub>7</sub> : log k Hg-DOM (HA, FA)	0	0	0	0	0	0	0	0	0	
X₀: log k Hg-DOM (thiols)	-0.6654	0.6655	1.3101	-2.6321	2.6321	4.1840	-5.4983	5.4983	8.1397	
X9: log k Hg-SOM (HA,FA)	34.8969	34.8969	20.4202	65.2686	65.2686	27.2359	84.6356	84.6356	34.5185	
X <sub>10</sub> : log k Hg-SOM (thiols)	1.6991	1.6991	3.1883	2.3327	2.3328	3.8505	3.0654	3.0654	4.9610	
X <sub>11</sub> : log k DOM sorption	1.1661	1.4335	2.6409	1.7965	2.1365	2.5014	2.4873	2.7193	2.6439	
X <sub>12</sub> : S <sub>max</sub> (DOM sorption)	-0.1005	0.1671	0.3241	0.0199	0.5799	0.6897	0.1802	0.8196	1.0781	

able 37 – Elementary effects for Group E, ind	cator 🚯 (% Hg	still in horizon initially	polluted) after 5	5, 25 and 50 y	years.
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Factor	After 5 years			After 25 years			After 50 years		
	μ	μ*	σ	μ	μ*	σ	μ	μ*	σ
X <sub>1</sub> : Hg initial conc.	-6.6925	21.5051	25.2306	-5.0976	19.2692	22.2377	-5.6070	19.5958	23.0379
X <sub>13</sub> : NAPL dissolution rate	14.3395	14.3395	10.9640	4.7857	6.2213	8.6848	3.3104	5.0763	7.9663
X <sub>3</sub> : Hg(II) reduction rate	0	0	0	0	0	0	0	0	0.0001
X₄: DOM in rain	0.0704	2.8124	4.0639	8.7726	9.5451	12.3608	11.9938	19.6131	26.5346
X₅: meq SOM (HA, FA)	-9.0470	9.0470	4.8823	-13.5292	13.5292	13.9363	-23.8703	23.8703	27.7491
X <sub>6</sub> : meq SOM (thiols)	8.6224	11.9436	23.4855	7.7118	12.9215	24.2055	6.8104	13.8282	24.9193
X <sub>7</sub> : log k Hg-DOM (HA, FA)	0	0	0	0	0	0	0	0	0
X₅: log k Hg-DOM (thiols)	-0.3560	0.3560	0.4295	-2.7281	2.8648	3.6421	-5.5053	5.7770	7.4200
X₃: log k Hg-SOM (HA,FA)	0.9620	24.8097	33.4966	-12.0374	33.6477	42.4914	-14.0606	37.0766	45.6950
X <sub>10</sub> : log k Hg-SOM (thiols)	-1.6566	1.6566	3.1356	-2.1989	2.3310	3.9510	-1.7795	2.0455	3.0280
X <sub>11</sub> : log k DOM sorption	0.3950	2.3376	3.8112	-0.3603	2.7635	3.6008	-0.5036	2.6895	3.3350
X <sub>12</sub> : S <sub>max</sub> (DOM sorption)	1.3452	1.7877	3.6475	0.9399	1.9972	3.3701	0.3483	2.1875	3.0339

Table 38 – Elementary effects for Group E, indicator ④ (% Hg still present in the soil profile below the horizon initially polluted) after 5, 25 and 50 years.



Figure 65 – Plots of  $\mu$  vs.  $\sigma$  and  $\mu^*$  vs.  $\sigma$  for elementary effects of Group E, indicator **()** (% Hg volatilized to the atmosphere) after (a) 5, (b) 25 and (c) 50 years.



Figure 66 – Plots of  $\mu$  vs.  $\sigma$  and  $\mu^*$  vs.  $\sigma$  for elementary effects of Group E, indicator **Q** (% Hg leached out of soil profile) after (a) 5, (b) 25 and (c) 50 years.






Figure 68 – Plots of  $\mu$  vs.  $\sigma$  and  $\mu^*$  vs.  $\sigma$  for elementary effects of Group E, indicator ④ (% Hg still present in the soil profile below the horizon initially polluted) after (a) 5, (b) 25 and (c) 50 years.

Table 39 shows the Hg (percentage of total initial amount) in the different phases / compartments after 50 years. Average absolute value of Hg mass balance error after 50 years was 0.036%.

					Top 10 cm						11-100 cm				
		Tim	Hg atm	Hg leached	HgS	Hg NAPL	Hg SOM	Hg DOM	Hg inorg	Hg(g)	Hg SOM	Hg DOM	Hg inorg	Hg(g)	TOTAL
	-	T								0.0,					
-	-	<b>T</b>	1 265 02	0.405.04	0.005.00	2 5 5 5 4 0	2.005.04	4 355 04		0.405.42	4 405 04	2 425 02	5 205 02	7 5 5 5 4 4	100.0
E	01	50	1.26E-03	8.49E+01	0.00E+00	2.55E-10	2.06E-01	1.25E-04	1.41E-04	9.10E-12	1.49E+01	3.42E-03	5.29E-02	7.55E-11	100.0
E	02	50	1.27E-03	8.82E+01	0.00E+00	2.55E-10	2.15E-01	1.25E-04	1.63E-04	9.11E-12	1.1/E+01	3.42E-03	4.93E-02	7.56E-11	100.1
E	03	50	1.26E-03	8.51E+01	0.00E+00	2.55E-10	2.07E-01	1.25E-04	1.43E-04	9.10E-12	1.45E+01	3.42E-03	5.22E-02	7.55E-11	99.9
E	04	50	5.41E-04	9.76E+01	0.00E+00	2.55E-10	1.54E-23	6.47E-12	-1.06E-28	1.25E-10	2.13E+00	4.51E-02	2.36E-08	1.10E-09	99.8
E	05	50	4.32E-04	8.30E+01	0.00E+00	2.55E-10	4.15E+00	6.61E-04	7.99E-08	3.11E-10	1.27E+01	8.46E-03	6.15E-06	2.27E-09	99.8
E	06	50	3.66E-04	3./1E+01	0.00E+00	2.55E-10	2.00E+01	9.02E-04	4.14E-07	4.22E-10	4.29E+01	8.46E-03	1.39E-05	2.55E-09	100.0
E	07	50	3.79E-04	3.54E+01	0.00E+00	2.55E-10	2.21E+01	3.40E-05	4.62E-09	1.32E-10	4.25E+01	8.68E-04	2.71E-07	1.14E-09	100.0
E	08	50	3.79E-04	3.54E+01	0.00E+00	2.55E-10	2.21E+01	3.40E-05	4.62E-09	1.32E-10	4.25E+01	8.68E-04	2.71E-07	1.14E-09	100.0
E	10	50	3.70E-04	3.400+01	0.00E+00	2.55E-10	2.250+01	1.15E-10	1.456-14	1.25E-10	4.292+01	2.42E-09	5.94E-15	1.102-09	100.0
E	10	50	4.65E-04	3.40E+01	0.00E+00	2.55E-10	2.25E+01	1.15E-10	1.45E-14	1.25E-10	4.292+01	2.42E-09	5.94E-13	1.102-09	100.0
	11	50	7.000-00	3.400+01	0.00E+00	2.55E-10	2.250+01	1.13E-10	0.225.04	1.235-10	4.290+01	2.42E-09	0.225.02	1.10E-09	100.0
	12	50	2.265.05	2.44E+01	0.00E+00	9.092+00	2.200+01	0.20E-04	0.52E-04	0.92E-09	4.55E+01	0.34E-U3	9.222-03	1.205.00	100.0
E	14	50	3.68E-04	7.86F±00	0.000100	0.005+00	8 8/F±01	2 27E-03	1.13L-07	1.66E-08	3 73 5+00	2 13E-02	1.42E-07	0.71E-08	100.0
E	15	50	2 28F-04	1 73E-05	0.00E+00	0.00E+00	9.09F+01	1.46E-03	4.01E-00	1.00L-08	9 13E+00	2.13L-02	4 17E-07	6.46E-08	100.0
F	16	50	2.20E 04	1.67E-05	0.00E+00	8 11F-01	9.03E+01	1.46E-03	4.05E-06	1.12E-08	8 88F+00	2.25E-04	4.01F-07	6.45E-08	100.0
F	17	50	2 25E-04	1 72E-05	0.00E+00	8 11F-01	8 98F+01	1 58F-03	2 53E-06	1 16F-08	9 37F+00	3 36F-04	1 51E-07	6 72F-08	100.0
E	18	50	-1.03E-04	1.20F-06	0.00F+00	8.11F-01	8.98F+01	1.58E-03	2.53E-06	7.93F-10	9.37E+00	3.36E-04	1.51E-07	4.96F-09	100.0
Е	19	50	3.21E-04	3.08E-01	0.00E+00	8.11E-01	5.81E+01	8.50E-03	4.26E-06	3.66E-09	4.07E+01	1.79E-02	9.02E-06	2.71E-08	100.0
Е	20	50	3.45E-04	3.06E+00	0.00E+00	8.11E-01	5.59E+01	8.51E-03	3.37E-06	3.57E-09	4.02E+01	4.19E-02	1.15E-05	2.71E-08	100.0
Е	21	50	3.45E-04	3.06E+00	0.00E+00	8.11E-01	5.59E+01	8.51E-03	3.37E-06	3.57E-09	4.02E+01	4.19E-02	1.15E-05	2.71E-08	100.0
Е	22	50	2.33E-04	3.63E-06	0.00E+00	8.11E-01	6.29E+01	5.51E-03	1.18E-06	9.68E-10	3.63E+01	4.50E-03	6.31E-07	7.20E-09	100.0
Е	23	50	3.67E-04	2.07E-01	0.00E+00	8.11E-01	5.51E+01	8.47E-03	3.81E-06	3.48E-09	4.38E+01	3.11E-02	6.37E-06	2.69E-08	100.0
Е	24	50	-1.01E-05	1.90E-06	0.00E+00	8.11E-01	8.64E+01	3.77E-03	1.41E-07	1.56E-09	1.28E+01	3.66E-04	9.56E-09	1.07E-08	100.0
Е	25	50	7.56E-05	9.82E+00	0.00E+00	8.11E-01	6.80E+01	7.68E-04	4.32E-07	3.57E-10	2.14E+01	3.09E-03	1.00E-06	2.05E-09	100.0
Е	26	50	4.05E-04	8.87E+01	0.00E+00	8.11E-01	2.20E-01	2.85E-04	1.50E-05	6.44E-11	1.01E+01	8.57E-03	5.97E-02	5.29E-10	99.9
Е	27	50	1.80E-02	1.00E+02	0.00E+00	2.09E-27	3.17E-02	9.83E-07	4.00E-23	6.34E-12	6.32E-02	3.49E-05	-7.99E-23	4.29E-11	100.1
Е	28	50	1.80E-02	9.91E+01	0.00E+00	2.09E-27	4.20E-01	5.95E-06	-1.20E-22	3.08E-11	8.21E-01	2.03E-04	4.79E-22	2.12E-10	100.3
Е	29	50	1.97E-02	8.83E+01	0.00E+00	2.09E-27	7.78E+00	1.46E-04	1.31E-03	8.10E-09	3.86E+00	1.36E-03	2.23E-02	5.91E-08	100.0
E	30	50	2.15E-02	8.78E+01	0.00E+00	2.09E-27	8.82E+00	1.48E-04	1.65E-03	1.04E-08	3.30E+00	1.36E-03	2.15E-02	7.33E-08	100.0
E	31	50	2.18E-02	8.99E+01	0.00E+00	2.09E-27	5.51E+00	1.46E-04	1.41E-03	9.03E-09	4.56E+00	1.36E-03	2.23E-02	6.55E-08	100.0
E	32	50	9.91E-03	5.43E+01	0.00E+00	2.09E-27	2.75E+01	1.50E-04	9.55E-05	1.91E-09	1.81E+01	1.36E-03	3.83E-04	1.10E-08	100.0
E	33	50	9.91E-03	5.43E+01	0.00E+00	2.09E-27	2.75E+01	1.50E-04	9.55E-05	1.91E-09	1.81E+01	1.36E-03	3.83E-04	1.10E-08	100.0
E	34	50	5.06E-03	4.44E+01	0.00E+00	8.11E-01	4.67E+01	1.50E-04	1.77E-04	2.40E-09	8.07E+00	1.36E-03	6.72E-05	1.39E-08	100.0
E	35	50	3.18E-04	4.44E+01	0.00E+00	8.11E-01	4.6/E+01	1.50E-04	1.//E-04	1.52E-10	8.07E+00	1.36E-03	6.73E-05	8.81E-10	100.0
E	36	50	1.54E-04	1.99E+01	0.00E+00	8.11E-01	5.57E+01	2.30E-03	1.44E-04	1.12E-09	2.36E+01	2.16E-02	6.88E-05	6.59E-09	99.9
E	37	50	1.38E-04	1.99E+01	0.00E+00	8.11E-01	5.63E+01	2.30E-03	1.20E-04	1.11E-09	2.30E+01	2.16E-02	2.48E-05	6.57E-09	100.0
E	38	50	1.26E-04	1.99E+01	0.00E+00	8.11E-01	5.03E+01	2.30E-03	1.21E-04	1.11E-09	2.30E+01	2.16E-02	2.47E-05	6.57E-09	100.0
<u>с</u> г	39	50	1.410-04	2.405.00	0.00E+00	0.11E-01 1 E0E 02	3.04E+01	2.23E-03	2.045.10	2.505.00	2.4401	1.776-02	6.03E-03	0.45E-09	100.0
E	40	50	4.20E-03 8.43E-04	2.49E+00 1.34E-05	0.00E+00	1.59E-05	7.4/E±01	0.10E-03	2.94E-10	2.50E-09 3.13E-09	2.56E+01	5.68E-04	0.70E-10	2.07E-08	100.0
F	41	50	5.43L-04	8.82E-06	0.00E+00	1.59E-03	8 74F+01	2 28F-03	6.45E-12	5.07E-09	1 26E+01	2 32E-04	3 43F-13	3 94F-08	100.0
E	42	50	5 75E-04	1 16E-05	0.00E+00	1.59E-03	8 56F+01	3.02E-03	1 19F-11	8.03E-09	1.44F+01	3 23E-04	4 97E-13	5.67E-08	100.0
F	44	50	5 75E-04	1 16E-05	0.00E+00	1 59E-03	8 56F+01	3.02E-03	1 19E-11	8.03E-09	1 44F+01	3 23E-04	4 97F-13	5.67E-08	100.0
E	45	50	3.79F-04	1.00F-05	0.00F+00	1.59F-03	8.85F+01	2.45E-03	5.83F-12	6.51F-09	1.15F+01	1.79F-04	1.98F-13	4,46F-08	100.0
E	46	50	2.90E-04	9.13E-06	0.00E+00	1.59E-03	9.08E+01	2.23E-03	1.51E-11	6.44E-09	9.20E+00	1.02E-04	8.01E-13	4.22E-08	100.0
Е	47	50	3.33E-04	9.53E-06	0.00E+00	1.59E-03	8.98E+01	2.43E-03	7.68E-12	6.69E-09	1.02E+01	1.44E-04	3.23E-13	4.51E-08	100.0
Е	48	50	9.13E-04	2.20E+01	0.00E+00	1.59E-03	7.80E+01	5.84E-03	8.18E-12	1.67E-08	2.21E-03	5.95E-02	1.89E-17	1.05E-07	100.0
Е	49	50	5.90E-03	2.20E+01	0.00E+00	1.59E-03	4.24E+01	5.26E-03	1.39E-04	1.48E-08	3.55E+01	5.95E-02	5.40E-04	1.01E-07	100.0
Е	50	50	7.72E-03	2.20E+01	0.00E+00	0.00E+00	4.01E+01	5.26E-03	7.18E-05	1.48E-08	3.78E+01	5.95E-02	3.84E-04	1.01E-07	100.0
Е	51	50	7.14E-03	7.44E+01	0.00E+00	0.00E+00	6.32E+00	4.00E-04	6.27E-04	1.59E-09	1.95E+01	3.75E-03	1.30E-02	1.09E-08	100.3
Е	52	50	1.13E-01	7.38E+01	0.00E+00	0.00E+00	6.28E+00	4.00E-04	6.21E-04	2.51E-08	1.95E+01	3.75E-03	1.29E-02	1.71E-07	99.7
Е	53	50	5.98E-03	7.96E+01	0.00E+00	2.55E-10	1.44E+01	1.08E-04	2.07E-03	5.74E-09	5.99E+00	9.79E-04	2.15E-02	4.05E-08	100.0
E	54	50	5.98E-03	7.96E+01	0.00E+00	2.55E-10	1.44E+01	1.03E-04	2.08E-03	5.74E-09	6.00E+00	9.30E-04	2.15E-02	4.04E-08	100.0
E	55	50	5.97E-03	7.96E+01	0.00E+00	2.55E-10	1.44E+01	1.03E-04	2.08E-03	5.74E-09	6.00E+00	9.30E-04	2.15E-02	4.04E-08	100.0
E	56	50	3.29E-03	8.54E+01	0.00E+00	2.55E-10	4.75E+00	9.68E-05	1.27E-05	2.61E-10	9.93E+00	1.15E-03	2.04E-03	1.74E-09	100.1
E	57	50	3.36E-03	8.69E+01	0.00E+00	2.55E-10	4.40E+00	6.54E-05	3.83E-05	2.25E-10	8.66E+00	5.90E-04	3.94E-03	1.54E-09	99.9
E	58	50	3.29E-03	8.54E+01	0.00E+00	2.55E-10	4.74E+00	9.57E-05	1.30E-05	2.59E-10	9.89E+00	1.14E-03	2.10E-03	1.73E-09	100.0
E	59	50	2.92E-03	7.18E+01	0.00E+00	9.69E+00	6.40E+00	8.10E-04	4.04E-04	2.89E-09	1.21E+01	5.53E-03	1.90E-02	1.92E-08	100.0
E	60	50	2.92E-03	7.18E+01	0.00E+00	9.69E+00	6.40E+00	8.10E-04	4.04E-04	2.89E-09	1.21E+01	5.53E-03	1.90E-02	1.92E-08	100.0
E	61	50	2.89E-03	7.31E+01	0.00E+00	9.69E+00	5.86E+00	1.25E-03	2.52E-04	3.56E-09	1.12E+01	9.00E-03	1.99E-02	2.38E-08	99.9
<u>с</u> г	62	50	3.5UE-U4	3.41E-U1	0.00E+00	9.09E+00	0.00E+U1	2.42E-05	1.72E-Ub	1.U/E-10	2.10E+01	3.0/E-Ub	1.58E-06	0.90E-10	100.0
E	64	50	2.1/E-04	2.795-07	0.00E+00	9.03E+00	7.57E+01	7.24E-06	5.10E-07	6.67F-11	1.40E+01	4.00E-07	6 85F-00	5.13E-10	100.0
E	65	50	3.65E-03	3 48F-06	0.00E+00	9.69E+00	7.57E+01	7.43E-06	5.24L-07	4 28F-10	1.47E+01	4.20L-07	6.85F-08	2 47F-00	100.0
-		20	3.33L 0J	35L 00	0.001.00	5.052.00	,	,JL 00	5.LTL 07	0L 10	1		0.001 00		100.0

Table 39 – Percentage of Hg in the different phases after 50 years for group E.

### 1 Volatilization

For indicator ①, factor X<sub>3</sub> (Hg<sup>II</sup> reduction rate) is by far the most sensitive at all time steps presented in Table 35 and Figure 65. The second most sensitive factor is X<sub>9</sub> (log k Hg-SOM (HA,FA)).

The percentage of Hg volatilized is always very low (max. 0.11% after 50 years). Maximum volatilization after 50 years occurs in simulations E52, characterized by high Hg<sup>II</sup> reduction rate (X<sub>3</sub>), relatively low log k Hg-SOM (HA,FA) (X<sub>9</sub>), and relatively high NAPL dissolution rate (X<sub>13</sub>) and initial concentration (X<sub>1</sub>; see Annex, section 9.3.4 for input parameter values).

Figure 69 shows the volatilization flux of Hg(0) over time for simulation E52. Most of the volatilization occurs in the first year. Note that maximum volatilization flux is ~3 orders of magnitude higher than the maximum in simulation C06 (Figure 58). The presence of NAPL thus seems to increase volatilization.



Figure 69 – Hg(0)(g) flux at the soil surface in simulation E52. Grey dots are daily simulated fluxes and the red line is the result of a moving average (window 31 days) on the daily data. Grey bars show the surface precipitation input (averaged every two months for clarity).

### 2 Leaching

For indicator 2, factors X<sub>1</sub> (Hg initial concentration) and X<sub>9</sub> (log k Hg-SOM (HA, FA)) are the most influential factors, with the latter being the most sensitive after 25 and 50 years. Other factors having a relatively important impact are X<sub>13</sub> (NAPL dissolution rate), X<sub>4</sub> (DOM in rain), X<sub>6</sub> (SOM (thiols) exchange capacity) and X<sub>8</sub> (log k Hg-DOM(thiols)). Factor X<sub>11</sub> (log k DOM sorption) shows a non-negligible sensitivity. Factor X<sub>7</sub> (log k Hg-DOM (HA, FA)) has no influence on the percentage of Hg leaching.

The model is non-monotonic for factors  $X_1$  and  $X_4$  ( $|\mu| < \mu^*$ ). For the former, higher initial concentration giving less leaching happen when  $X_9$  was very low and  $X_8$  very high. Figure 70 shows Hg (as Hg-SOM complexes mainly) concentration profiles at different times for simulations E03 and E04. Simulation E03 has a much higher initial Hg concentration than E04, but in E04 sorption capacity and strength are insufficient to retain more than 20 mg[Hg]/kg[soil] after 10 years, and hence higher leaching (relative to initial concentration) follows. After 50 years, 97.6% of Hg has leached in simulation E04 (vs. 85.1% for E03). However, this non-monotonic effect is due to the indicator being calculated

relative to the initial concentration, because in absolute values more leaching has occurred in simulation E03 than in E04.

For  $X_4$ , non-monotonic behavior of the model occurred when very low DOM concentration in rain was combined with high DOM sorption and very low Hg sorption strength to humic and fulvic acids ( $X_9$ ). In these conditions, smaller  $X_4$  that resulted in higher leaching (simulation E28 compared to simulation E29) could be explained by inorganic ligands becoming efficient for Hg complexation and transport.



Figure 70 – Depth distribution of Hg-SOM and Hg aqueous species for simulations (a) E03 and (b) E04, at t = 0, 5, 10, 25 and 50 years.

Maximum values for indicator **2** is 100% for simulations E27. The conditions resulting in this extreme leaching are similar to those explained for simulation E04 above.



Figure 71 – Hg(II) flux at the bottom of the soil profile in simulation E34. Grey dots are daily simulated fluxes at the bottom of the soil profile. Red line is the result of a moving average (window 31 days) on the daily data. Grey bars show the surface precipitation input (averaged every two months for clarity). Note that the y-scale is logarithmic for solute flux.

Figure 71 presents  $Hg^{II}$  leaching at the bottom of the soil profile over time for simulation E34, which has a relatively low value for indicator (2) (4.4%). It is interesting to note that significant Hg leaching

occurs only at the beginning of the simulation period, when the initial amount  $HgCl_2(aq)$  cannot completely be retained by SOM. Afterwards, as shown in Figure 72, the sorption capacity is high enough to keep in the top horizon all Hg released by NAPL dissolution (characterized by a low rate in this case).



Figure 72 – Depth distribution of Hg sorbed to SOM for simulation E34 at t = 0, 5, 10, 25 and 50 years.

### **3** Hg still present in the soil horizon originally contaminated (top 10 cm)

For indicator ③, the results of the SA using the elementary effects (Table 37 and Figure 67) show that factors X<sub>1</sub> (Hg initial concentration) and X<sub>9</sub> (log k Hg-SOM (HA, FA)) are the most influential factors, with the latter being the most sensitive after 25 and 50 years. Factor X<sub>9</sub> determines how long initial Hg contamination is retained in the top soil. As already observed in other groups, factor X<sub>10</sub> (log k Hg-SOM (thiols)) shows no sensitivity due to the high proportion of HA and FA sites compared to thiols.

Other factors having an non negligible influence on indicator 3 are X<sub>13</sub> (NAPL dissolution rate), X<sub>4</sub> (DOM in rain), X<sub>6</sub> (SOM (thiols) exchange capacity) and X<sub>8</sub> (log k Hg-DOM(thiols)).

After 50 years, the percentage of Hg still in the horizon originally contaminated varies between 0 (simulations E04 and E27) and 97.9% (E13). Figures 73 and 74 present the results for simulation E13, which factors are characterized by a high  $X_9$ , and low  $X_{13}$  and  $X_4$ . New Hg available from (slow) NAPL dissolution is progressively accumulated (Hg-SOM) in the top horizon (Figure 74).

Figure 75 illustrates an example with a middle value for indicator 3 (case E12) : 32.3% of the initial Hg is still present in the top horizon after 50 years. The effect of the low value of X<sub>9</sub> (promoting Hg leaching) is in this case offset by low X<sub>13</sub> and X<sub>1</sub>, very low X<sub>4</sub> and very high X<sub>5</sub> (cf. Annex, section 9.3.4).



Figure 73 – Cumulative depth distribution over time of Hg (a) NAPL and (b) sorbed to SOM (in % of total initial Hg) for simulation E13.



Figure 74 – Depth distribution over time of Hg (a) as NAPL and (b) sorbed to SOM at t = 0, 5, 10, 25 and 50 years for simulation E13.



Figure 75 – Depth distribution over time of Hg sorbed to SOM at t = 0, 5, 10, 25 and 50 years for simulation E12.

#### **4** Hg still present in the soil profile below the horizon originally contaminated (11-100 cm)

For this indicator (Table 38 and Figure 68),  $X_5$  (SOM (HA, FA) exchange capacity) and  $X_9$  (log k Hg-SOM (HA, FA)) are the most sensitive factor after 50 years. The  $\sigma$  value of  $X_9$  is much higher than for  $X_5$ , denoting more non-linear and/or interaction effects for the former factor.

Other important factors are  $X_1$  (initial Hg concentration),  $X_{13}$  (NAPL dissolution rate),  $X_4$  (DOM in rain),  $X_6$  (SOM (thiols) exchange capacity) and  $X_8$  (log k Hg-DOM(thiols)). Factors  $X_{10}$  (log k Hg-SOM (thiols)),  $X_{11}$  and  $X_{12}$  (related to DOM sorption) have a non-negligible sensitivity, while  $X_3$  (HgII reduction rate) and  $X_7$  (log k Hg-DOM(HA, FA)) show no influence on indicator (4).

Comparing the values of  $\mu$  and  $\mu^*$  indicates that the model is non-monotonic for several factors. This effect is particularly important for factors X<sub>1</sub>, X<sub>4</sub>, X<sub>6</sub> and X<sub>9</sub>. The processes leading to non-monotonic behavior of the model were previously addressed (e.g. for group C, indicator **4**).

After 50 years, values of indicator **4** vary between 0 (E27 and E48) and 59.1% (E40). In the former case, all Hg has leached. The results of Hg concentration profiles for simulation E40 are shown in Figure 76a and 76b for NAPL and Hg sorbed to SOM, respectively.



Figure 76 – Depth distribution over time of Hg (a) as NAPL and (b) sorbed to SOM at t = 0, 5, 10, 25 and 50 years for simulation E40.

# 8 Conclusions and perspectives

Deliverable D.2.1 of the IMaHg project was to give "Mercury associated physical and chemical constants for a comprehensive mercury fate and transport understanding in the vadose zone". Because of the relevance for the numerical model, the main emphasis was on thermodynamic constants for inorganic and organic complexation and for mercury-containing solid phases. Inorganic complexation and solid phases were implemented in the THERMODDEM database as described in Chapter 3.

Deliverable D2.2 of the IMaHg project was to provide a "Numerical tool for mercury fate and transport in soils". A conceptual model was developed for mercury fate and transport in the vadose zone. This model was numerically implemented in HP1 and two sensitivity analyses were performed (one-at-a time using upper and lower limits of parameter ranges; and elementary effects using Morris trajectories).

The model includes the physical and chemical processes identified as relevant for modelling mercury fate and transport in the vadose zone, assuming anthropogenic sources of contamination. These processes included: Hg transport by advection-dispersion in the aqueous phase and diffusion in the gaseous phase under variable-saturated and transient water flow conditions, speciation in aqueous and gas phases (with transport of Hg-DOM complexes as a surrogate for colloid transport), Hg sorption to SOM, cinnabar and Hg NAPL dissolution, Hg<sup>II</sup> reduction and volatilization, DOM sorption to minerals. The model uses the themodynamic database IM003\_THERMODDEM (Blanc et al., 2012a), augmented with some data of Skyllberg (2012).

Initial mercury contamination was tested for Hg NAPL, solid phase (cinnabar), aqueous phase (HgCl<sub>2</sub>(aq)) and combinations of them. Simulations were performed using a time series of 50 years of daily meteorological data including precipitation and evapotranspiration (from Dessel, Belgium). DOM was introduced to the system in rainwater chemical composition. At the bottom of a sandy 1-m soil profile free drainage was assumed, thereby making oxidising conditions prevail.

Deliverable D2.3 of the IMaHg project was to define a "List of critical processes and parameters in simulating mercury fate and transport in soils". This was achieved first *via* a literature review (Leterme and Jacques, 2014) and second with a sensitivity analysis (Chapter 1) of the numerical model presented here.

Processes identified as important based on a literature review are: aqueous speciation and complexation, sorption/desorption, leaching, Hg<sup>II</sup> precipitation/dissolution, NAPL dissolution, Hg volatilization from soils, colloid transport, methylation/demethylation. Processes and parameters identified as critical based on the sensitivity analysis differed from one scenario to the other; depending on pollution type (cinnabar, NAPL, aqueous Hg), on the indicator assessed (leached Hg, Hg in soil horizon originally polluted...) and on time (after 5, 25 or 50 years). However, in general DOM in soil water was the most critical parameter. Other important parameters were those related to Hg sorption on SOM (thiols, and humic and fulvic acids), and to Hg complexation with DOM. Initial Hg concentration was also often identified as a sensitive parameter. The sensitivity analysis using the elementary effect method also revealed that the model is non-monotonic with respect to some parameters, but this could fluctuate with the type of contamination and over time (5, 25 or 50 years). Interactions between factors and nonlinear effects as measured by the elementary effect method were generally important, but again dependent on the type of contamination and on time (5, 25 or 50 years).

The sensitivity analysis using the elementary effect method was not performed for all combinations of Hg sources (groups D, F and G). However, conclusions drawn from the one-at-a time sensitivity

analysis and from Morris method for groups A, B, C and E brought sufficient information on parameter sensitivity.

Detailed modelling of Hg fate and transport in the soil can benefit ecological risk assessments and the design of soil remediation strategies, by:

- i. Defining probable transport pathways and quantifying Hg fluxes. This is notably useful for long term risk assessments. Numerical simulations showed that certain risks (e.g. Hg leaching to groundwater) may still be relevant after several tens of years, which could not in practice be predicted or captured by site monitoring;
- ii. Guiding Hg speciation analyses to perform in the field. Numerical simulations can help to predict which Hg species can be expected on a contaminated sites, at different depths in the unsaturated zone;
- iii. Designing and comparing different remediation techniques. The numerical simulations allow to assess the effectiveness of different remediation options regarding environmental objectives (e.g. limitation of volatilization, immobilization of Hg...).

These types of applications will generally require a good characterization of some important variables/parameters of the unsaturated zone. However, depending on the pathway in a risk assessment study or the option chosen for site remediation, the critical indicator might be different and thus the choice of important parameters or site characterization may differ. In general, the speciation of the initial contamination is a crucial factor. When leaching is an important factor, a Hg initial contamination under an aqueous form is the most sensitive to rapid leaching. On the other hand, when persistency of Hg in the top soil layer is of importance (e.g. for a soil dust intake pathway), Hg incorporated in a solid phase (or as NAPL) is the most sensitive initial speciation. As discussed, the critical parameters and processes strongly depend on indicator, time and initial contamination. But as a general rule:

- The sorption strength of the humic and fulvic acids on the SOM is quite sensitive because their sorption capacity is large. Increasing the sorption strength of HA and FA may have a large effect on the retardation of Hg in the contamination layer (and the underlying soil horizons). Hg typically sorbs strongly on the thiol sites on SOM. Because sorption is always very strong (and capacity relatively small), the actual value of the log\_k of the complexation constant is not critical;
- Dissolution kinetics of the solid phase is only important in relation to the sorption capacity of the initial contaminated soil layer (and thus to saturation of the sorption capacity). As such, underestimation of the dissolution rate is less critical when a soil pathway is considered compared to a leaching pathway;
- The dominant process for Hg leaching is complexation of aqueous Hg to DOM (thiols) and the transport of DOM is the soil system. Knowledge of DOM concentration is therefore crucial. In contrast to the SOM, the amount of thiols and their sorption strength (log\_k of thiols on DOM) are also sensitive parameters;
- It was also shown that transient flow conditions should be considered if one wants to estimate maximum fluxes (both solute fluxes to the ground water or volatilization);
- Based on the sensitivity studies in this report, and the aim of modelling in either risk assessment or site remediation, parameter values could be selected using the ranges studies in this report (e.g. selection as average parameters, or conservative estimates).

Given the current conceptualisation of the model, several recommendations can be made for developments of the numerical tool used in the present report.

First, it may be desirable to better characterize DOM input and cycle than introducing it through rainwater composition. Given the importance of DOM in the fate and transport of Hg, a submodel of DOM-SOM cycle in the soil could significantly improve model realism, and provide better insights in the processes related to Hg-OM interactions. Examples of a conceptual model of DOM/DOC in soils can be found in Kalbitz et al. (2000) or Neff and Asner (2001), among others.

Secondly, all simulations were done with 'standard' water composition. One should investigate the effect of water compositions more typical of contaminated sites (few data available).

Mercury methylation and demethylation was not implemented in the current version of the model, because it could be neglected in an oxidising environment. However, if the model is to be tested in more reducing conditions (e.g. shallow groundwater table), methyl- and dimethylmercury formation can be non-negligible.

Colloid transport was represented as simple Hg<sup>2+</sup> transport in aqueous phase. Other possibilities for modeling Hg–colloid interactions may exist in PHREEQC and can be explored. The colloid transport module in HYDRUS was not tested because it contains too many parameters that are currently unavailable for mercury modelling.

It should be noted that the HYDRUS component of HP1 assumed matrix flow only. However, preferential flow is known to occur in many situations and this can cause higher leaching of contaminants, especially shortly after soil contamination. The effect of preferential flow on Hg fate in the soil was not investigated.

Finally, no model calibration was performed until now. However, the numerical tool could greatly benefit from partial model calibration and/or validation. Ideally, detailed speciation data on a contaminated site would be required, together with a good characterization of the pollution source.

It is recognized that these types of model need a high level of expertise from the users. However, the current model is implemented with a Graphical User Interface. Nevertheless, further guidance could be developed as some straightforward selection of options for different parameters for different conditions and a detailed step-by-step instruction list on how to perform alterations for specific conditions.

# 9 Annexes

## 9.1 WHAM model

 $\Delta$ LK1 = 2.8 for HA and FA

<u>Hg</u>

Log Kd(A) = 3.0 for HA and 3.5 for FA (strong acids, e.g. carboxylic acid) Log Kd(B) =  $3.39 \times \text{Log Kd}(A)$ -1.15 = 9.02 for HA and 10.715 for FA  $\Delta \text{LK2} = 5.1$  for HA and FA MeHg Log Kd(A) = 3.0 for HA and FA Log Kd(B) = 9.02 for HA and FA

Note : WHAM Model VII is available (Tipping et al., 2011) + correction of coding error in Model VI

WHAM VII (and previous versions) has two main limitations: Oxidation-reduction equilibria are not simulated. To simulate systems with multiple oxidation states of the same element (e.g. Fe(II) and Fe(III)), concentrations of each must be input separately. The precipitation of solid phases is not simulated.

## 9.2 Visual Minteq

- Can simulate the presence of DOM: "If the water contains dissolved organic matter, there is a choice between three different models (Gaussian DOM, SHM and NICA-Donnan); you are advised to use SHM or NICA-Donnan because these are modern advanced models that are considered to be state-of-the-art"

SHM menu for problems in which solid-phase reactions are included :

Stockholm Humic Model menu	and the second			-	-	and some the same
	<b>mg / L DOC</b> 25.0		2 100	ameters for dissolve Ratio % of a		<i>l organic carbon</i> f active DOM to DOC tive DOM that is FA
	Fulvic acid 🛛 👻	Humic acid	•	Fulvic acid	-	Click to add
Solid / dissolved	Solid 🗸	Solid	-	Dissolved	-	
Total concentration (g / l)	25	25		.05		j
Site conc. (low aff.; mmol / l)	175.5	133.25		.351		
Site conc. (high aff.; mmol / I)	Click to add	Click to	add	Click to	add	
Acid-base parameters from	soilfa.mpf.txt	soilha.m	pf.txt	typicalfa.n	npf.txt	
Complexation database	risbergfa08.vdb risbergfa08.vdb		shmgeneric	10.vdb		
Counter-ion accumulation		<b>V</b>				
Counter-ion database	gthumic.cdb	gthumic.cdb		)		
Symbol	(6)	(7)		(8)		
Options   Image: Solid FA and sol	IA lissolved HA					
Save and back to main m	Quitas	d araea an	v modo	Inaramete		

The SHM uses a discrete-site approach, similar to that used by (Tipping, 1998), to describe the pH dependence of HS dissociation. There are 8 ROH sites of different acid strengths and so there are 8 Ki values. The 4 most strongly acid sites (i = 1-4) are referred to as type A sites, whereas sites 5-8 are type B sites.

*Note : Fulvic acids, and not humic acids, may be dissolved.* The user supplies a value for the concentration of dissolved fulvic acid (FA) that represents the concentration of 'active' dissolved organic matter in the system.

It cannot be expected that all solid-phase organic matter is 'active' with respect to proton and metal binding. Therefore, to make simulations of reactions in the presence of solid-phase HA and FA, an

optimization of the 'active' HA and FA may be required. See (Gustafsson et al., 2003; Gustafsson and Van Schaik, 2003) for further details.

Monodentate complexation:

$$Kd = \frac{[ROHg +][H+]}{[ROH][Hg2+]}e^{-g_f \frac{F(0.5\Psi_0 - 1.5\Psi_d)}{RT}}$$

*F* is Farday constant, *R* is gas constant, *T* absolute temp.,  $\Psi_0$  is potential in the 0-plane (i.e. at the surface),  $\Psi_d$  is potential in the outer d-plane (i.e. at the surface),  $g_f$  is the "gel-fraction" parameter (value between 0 and 1). Since the potential is not analytically available, a charge-potential relationship is needed to solve this equation. In SHM, the 1-pK Basic Stern Model (BSM) has been used, for details see Gustafsson (2001). The  $g_f$  value reflects the proportion of the humics that are aggregated in gel-like structures; electrostatic corrections are only made for this part.

To account for heterogeneity of site affinity for metal complexation the parameter  $\Delta$ LK2 is introduced :

 $Log Kx = Log K + x\Delta LK2; x = 0,1,2,3$ 

And similarly with bidentate complex formation:

$$Kd = \frac{[(RO)_{2}Hg][H+]^{2}}{[ROH]^{2}[Hg2+]}e^{-g_{f}\frac{F(0.75\Psi_{0}-0.75\Psi_{d})}{RT}} \times SA_{s}N_{s}$$

where S is the HS concentration (g L<sup>-1</sup>),  $A_s$  the specific surface area (m<sup>2</sup> g<sup>-1</sup>) and  $N_s$  is the site density (mol m<sup>-2</sup>). The extra term  $SA_sN_s$  is needed to correct the constant for the bidentate coordination.

 $Log Kx = Log K + 2x\Delta LK2; x = 0,1,2,3$ 

Database values for Hg2+

Solid FA, (and solid HA and dissolved FA ?):

 $2\text{ROH} + \text{Hg}^{2+} \leftrightarrow \text{Hg}(\text{RO})_2 + 2\text{H}^+$  log K = 6.7;  $\Delta$ LK2 = 3.1

This gives:

X	$Log \ K_{x,Hg2+}$
0 (default: 90.1% of sites)	6.7
1 (9% of sites)	12.9
2 (0.9% of sites)	19.1
3 (0% of sites <sup><math>\dagger</math></sup> )	25.3

<sup>†</sup> seems not possible to implement a value >0 for x=3 in present version of V Minteq

Note that highest Log K (19.1) is lower than for complexation of Cl<sup>-</sup> bound species; therefore complexation to humic acids will not be the dominant complex in solution (see Results).

#### Example Visual Minteq

Solution 0.1 M Hg<sup>2+</sup>, 0.2 M Cl<sup>-</sup>, HA and FA see screenshot above.

Species tableau:

	log K	delta Hr (kJ/mol)	CI-1	H+1	H2O	Hg(II)
Hg+2	6.164	-39.72	0	2	-2	1
Hg2OH+3	9.031	-65.39	0	3	-3	2
Hg3(OH)3+3	12.101	0	0	3	-3	3
HgCl+	13.49	-60.7	1	2	-2	1
HgCl2 (aq)	20.19	-91.1	2	2	-2	1
HgCl3-1	21.19	-90.7	3	2	-2	1
HgCl4-2	21.79	-99.1	4	2	-2	1
HgClOH (aq)	10.444	-42.72	1	1	-1	1
HgOH+	2.767	-18.89	0	1	-1	1
OH-	-13.997	55.81	0	-1	1	0

Note : log K HA < log K of CI-bound species (but x=2 max in def of Log K<sub>x,Hg2+</sub>)

#### Results:

Component	% of total concentration	Species name
Hg(OH)2	1.33	(6)Hg+2D(s)
	46.992	HgCl2 (aq)
	17.786	HgCl3-1
	3.761	HgCl4-2
	0.072	HgClOH (aq)
	30.026	/HA2Hg(s)
	0.029	/FA2Hg(aq)
Cl-1	18.771	CI-1
	46.992	HgCl2 (aq)
	26.679	HgCl3-1
	7.522	HgCl4-2
	0.036	HgClOH (aq)
HFA-dum(6)(s)	99.816	HFA-dum(s)
	0.178	/HA-H+1G(s)
HFA-dum(7)(ag)	99.906	HFA-dum(ag)
	0.091	/FA-H+1G(aq)
H+1D(s)(6)	96.941	(6)H+1D(s)
	3.058	(6)Hg+2D(s)
OH-D(s)(6)	100	(6)OH-D(s)
/HA(s)	52.315	/HFA(s)
	28.235	/HA-(s)
	19.45	/HA2Hg(s)
/FA(aq)	43.789	/HFA(aq)
	16.517	/FA2Hg(aq)
	39.694	/FA-(an)

#### <u>Cinnabar</u>

 $HgS + 2H_2O = Hg(OH)_2 + HS^- + H^+ (log_k - 45.1885)$ 

**Metacinnabar** 

 $HgS + 2H_2O = Hg(OH)_2 + HS^- + H^+ (log_k - 44.822)$ 

#### **Montroydite**

 $HgO + H_2O = Hg(OH)_2 (log_k - 3.6503)$ 

# 9.3 Elementary effects : trajectories

In this Annex, seven Tables give the factor values of the five trajectories for each group. Definitions and units of factors  $X_1$  to  $X_{13}$  are given in Table 21.

### 9.3.1 Group A

Simulation	X1	X2	X3	X4	X5	X6	X7	X8	X9	X10	X11	X12
	(log10)		(log10)				[0-1]	(log2)	[0-1]	(log2)		
A 01	2.53E+00	3.21E-03	-4.96E+00	2.52E+01	9.86E+01	7.00E-02	1.00E+00	5.46E+00	4.00E-01	3.34E+00	5.26E-03	1.09E+02
A 02	2.53E+00	3.21E-03	-4.96E+00	2.52E+01	9.86E+01	7.00E-02	1.00E+00	5.46E+00	4.00E-01	4.54E+00	5.26E-03	1.09E+02
A 03	2.53E+00	3.21E-03	-4.96E+00	2.52E+01	9.86E+01	7.00E-02	1.00E+00	5.46E+00	4.00E-01	4.54E+00	5.26E-03	4.04E+02
A 04	2.53E+00	1.15E-02	-4.96E+00	2.52E+01	9.86E+01	7.00E-02	1.00E+00	5.46E+00	4.00E-01	4.54E+00	5.26E-03	4.04E+02
A 05	2.53E+00	1.15E-02	-4.96E+00	2.52E+01	9.86E+01	7.00E-02	1.00E+00	5.46E+00	1.00E+00	4.54E+00	5.26E-03	4.04E+02
A 06	2.53E+00	1.15E-02	-4.96E+00	2.52E+01	9.86E+01	7.00E-02	4.00E-01	5.46E+00	1.00E+00	4.54E+00	5.26E-03	4.04E+02
A 07	3.73E+00	1.15E-02	-4.96E+00	2.52E+01	9.86E+01	7.00E-02	4.00E-01	5.46E+00	1.00E+00	4.54E+00	5.26E-03	4.04E+02
A 08	3.73E+00	1.15E-02	-4.96E+00	2.52E+01	9.86E+01	8.74E-01	4.00E-01	5.46E+00	1.00E+00	4.54E+00	5.26E-03	4.04E+02
A 09	3.73E+00	1.15E-02	-6.16E+00	2.52E+01	9.86E+01	8.74E-01	4.00E-01	5.46E+00	1.00E+00	4.54E+00	5.26E-03	4.04E+02
A 10	3./3E+00	1.15E-02	-6.16E+00	2.52E+01	9.86E+01	8.74E-01	4.00E-01	5.46E+00	1.00E+00	4.54E+00	1.23E-02	4.04E+02
A 11	3.73E+00	1.15E-02	-0.10E+00	2.52E+01	7.95E+00	8.74E-01	4.00E-01	5.46E+00	1.00E+00	4.54E+00	1.23E-02	4.04E+02
A 12	3.73E+00	1.15E-02	-0.10E+00	2.52E+01 7.29E+01	7.95E+00	0.74E-01	4.00E-01	4.200+00	1.00E+00	4.54E+00	1.235-02	4.04E+02
Δ 14	2 13E+00	8 70F-02	-0.10E100	7.38E+01	7.95E+00	1 14F+00	8.00E-01	3.46E+00	2 00E-01	4.94E+00	5.60E-04	5.03E+02
A 15	2.13E+00	8 70F-03	-4 96F+00	7 38F+01	7.95E+00	1 14F+00	8.00E-01	3.46F+00	8 00F-01	4.94E+00	5.60E-04	5.03E+02
A 16	2.13E+00	8.70E-03	-4.96F+00	7.38F+01	7.95E+00	3.38F-01	8.00E-01	3.46F+00	8.00E-01	4.94F+00	5.60E-04	5.03E+02
A 17	2.13E+00	8.70F-03	-4.96F+00	7.38F+01	7.95E+00	3.38F-01	8.00F-01	3.46F+00	8.00F-01	4.94F+00	5.60F-04	2.07F+02
A 18	2.13E+00	8.70E-03	-4.96E+00	2.52E+01	7.95E+00	3.38E-01	8.00E-01	3.46E+00	8.00E-01	4.94E+00	5.60E-04	2.07E+02
A 19	2.13E+00	8.70E-03	-4.96E+00	2.52E+01	9.86E+01	3.38E-01	8.00E-01	3.46E+00	8.00E-01	4.94E+00	5.60E-04	2.07E+02
A 20	2.13E+00	8.70E-03	-6.16E+00	2.52E+01	9.86E+01	3.38E-01	8.00E-01	3.46E+00	8.00E-01	4.94E+00	5.60E-04	2.07E+02
A 21	3.33E+00	8.70E-03	-6.16E+00	2.52E+01	9.86E+01	3.38E-01	8.00E-01	3.46E+00	8.00E-01	4.94E+00	5.60E-04	2.07E+02
A 22	3.33E+00	8.70E-03	-6.16E+00	2.52E+01	9.86E+01	3.38E-01	8.00E-01	3.46E+00	8.00E-01	4.94E+00	7.60E-03	2.07E+02
A 23	3.33E+00	8.70E-03	-6.16E+00	2.52E+01	9.86E+01	3.38E-01	8.00E-01	4.66E+00	8.00E-01	4.94E+00	7.60E-03	2.07E+02
A 24	3.33E+00	8.70E-03	-6.16E+00	2.52E+01	9.86E+01	3.38E-01	2.00E-01	4.66E+00	8.00E-01	4.94E+00	7.60E-03	2.07E+02
A 25	3.33E+00	4.59E-04	-6.16E+00	2.52E+01	9.86E+01	3.38E-01	2.00E-01	4.66E+00	8.00E-01	4.94E+00	7.60E-03	2.07E+02
A 26	3.33E+00	4.59E-04	-6.16E+00	2.52E+01	9.86E+01	3.38E-01	2.00E-01	4.66E+00	8.00E-01	3.74E+00	7.60E-03	2.07E+02
A 27	3.33E+00	1.15E-02	-6.16E+00	4.14E+01	1.29E+02	1.41E+00	6.00E-01	5.06E+00	1.00E+00	3.74E+00	9.95E-03	5.03E+02
A 28	3.33E+00	1.15E-02	-6.16E+00	9.00E+01	1.29E+02	1.41E+00	6.00E-01	5.06E+00	1.00E+00	3.74E+00	9.95E-03	5.03E+02
A 29	3.33E+00	1.15E-02	-6.16E+00	9.00E+01	1.29E+02	1.41E+00	6.00E-01	5.06E+00	1.00E+00	3.74E+00	2.91E-03	5.03E+02
A 30	3.33E+00	1.15E-02	-6.16E+00	9.00E+01	1.29E+02	1.41E+00	6.00E-01	5.06E+00	1.00E+00	3.74E+00	2.91E-03	2.07E+02
A 31	3.33E+00	1.15E-02	-6.16E+00	9.00E+01	1.29E+02	1.41E+00	6.00E-01	3.86E+00	1.00E+00	3.74E+00	2.91E-03	2.07E+02
A 32	3.33E+00	1.15E-02	-4.96E+00	9.00E+01	1.29E+02	1.41E+00	6.00E-01	3.86E+00	1.00E+00	3.74E+00	2.91E-03	2.07E+02
A 33	3.33E+00	1.15E-02	-4.96E+00	9.00E+01	1.29E+02	6.06E-01	0.00E-01	3.86E+00	1.00E+00	3.74E+00	2.91E-03	2.07E+02
A 34	3.33E+00	1.15E-02	-4.90E+00	9.00E+01	1.296+02	6.06E-01	0.00E+00	3.80E+00	1.00E+00	3.74E+00	2.91E-03	2.07E+02
A 36	2 13E+00	1.15E-02	-4.96E+00	9.00E+01	1.29E+02	6.06E-01	0.00E+00	3.86E+00	1.00E+00	4.94E+00	2.91E-03	2.07E+02
A 37	2.13E+00	3.21F-03	-4.96F+00	9.00F+01	1.29E+02	6.06F-01	0.00F+00	3.86F+00	1.00F+00	4.94F+00	2.91E-03	2.07F+02
A 38	2.13E+00	3.21E-03	-4.96E+00	9.00E+01	3.82E+01	6.06E-01	0.00E+00	3.86E+00	1.00E+00	4.94E+00	2.91E-03	2.07E+02
A 39	2.13E+00	3.21E-03	-4.96E+00	9.00E+01	3.82E+01	6.06E-01	0.00E+00	3.86E+00	4.00E-01	4.94E+00	2.91E-03	2.07E+02
A 40	2.53E+00	4.59E-04	-4.96E+00	5.76E+01	6.84E+01	7.00E-02	8.00E-01	4.26E+00	0.00E+00	3.74E+00	7.60E-03	4.04E+02
A 41	2.53E+00	4.59E-04	-4.96E+00	9.00E+00	6.84E+01	7.00E-02	8.00E-01	4.26E+00	0.00E+00	3.74E+00	7.60E-03	4.04E+02
A 42	2.53E+00	4.59E-04	-4.96E+00	9.00E+00	6.84E+01	7.00E-02	8.00E-01	4.26E+00	0.00E+00	4.94E+00	7.60E-03	4.04E+02
A 43	2.53E+00	4.59E-04	-4.96E+00	9.00E+00	6.84E+01	8.74E-01	8.00E-01	4.26E+00	0.00E+00	4.94E+00	7.60E-03	4.04E+02
A 44	2.53E+00	4.59E-04	-6.16E+00	9.00E+00	6.84E+01	8.74E-01	8.00E-01	4.26E+00	0.00E+00	4.94E+00	7.60E-03	4.04E+02
A 45	2.53E+00	4.59E-04	-6.16E+00	9.00E+00	6.84E+01	8.74E-01	8.00E-01	4.26E+00	0.00E+00	4.94E+00	7.60E-03	1.09E+02
A 46	2.53E+00	4.59E-04	-6.16E+00	9.00E+00	6.84E+01	8.74E-01	8.00E-01	4.26E+00	0.00E+00	4.94E+00	5.60E-04	1.09E+02
A 47	2.53E+00	4.59E-04	-6.16E+00	9.00E+00	6.84E+01	8.74E-01	2.00E-01	4.26E+00	0.00E+00	4.94E+00	5.60E-04	1.09E+02
A 48	2.53E+00	4.59E-04	-6.16E+00	9.00E+00	6.84E+01	8.74E-01	2.00E-01	4.26E+00	6.00E-01	4.94E+00	5.60E-04	1.09E+02
A 49	2.53E+00	4.59E-04	-6.16E+00	9.00E+00	6.84E+01	8.74E-01	2.00E-01	5.46E+00	6.00E-01	4.94E+00	5.60E-04	1.09E+02
A 50	3.73E+00	4.59E-04	-6.16E+00	9.00E+00	6.84E+01	8.74E-01	2.00E-01	5.46E+00	6.00E-01	4.94E+00	5.60E-04	1.09E+02
A 51	3.73E+00	8.70E-03	-6.16E+00	9.00E+00	6.84E+01	8.74E-01	2.00E-01	5.46E+00	6.00E-01	4.94E+00	5.60E-04	1.09E+02
A 52	3.73E+00	8.70E-03	-6.16E+00	9.00E+00	1.59E+02	8.74E-01	2.00E-01	5.46E+00	6.00E-01	4.94E+00	5.60E-04	1.09E+02
A 53	3./3E+00	1.15E-02	-4.96E+00	5.76E+01	3.82E+01	1.41E+00	8.00E-01	5.06E+00	1.00E+00	3.34E+00	2.91E-03	3.06E+02
A 54	3./3E+00	1.15E-02	-4.96E+00	5./0E+01	1.29E+02	1.41E+00	8.00E-01	5.06E+00	1.005+00	3.34E+00	2.91E-03	3.06E+02
A 55	3.735+00	1.150-02	-4.900+00	5 765-01	1.295+02	6.06E-01	8.00E-01	3.000+00	1.000+00	3.34E+00	2.915-03	3.000+02
A 50 A 57	3.73E+00	3 21 E-02	-4.50E+00	5.70E+01	1 295+02	6.06E-01	8.00E-01	3.80E+00	1.000+00	3.34E+00	2.715-03	3.000+02
A 58	3.73E+00	3 21F-03	-4 96F+00	9 00F+00	1 29F+02	6.06F-01	8 00F-01	3.86F+00	1.00E+00	3 34F+00	2.91E-03	3.00E+02
A 59	3.73F+00	3.21E-03	-4.96F+00	9.00F+00	1.29F+02	6.06F-01	8.00F-01	3.86F+00	1.00F+00	3.34F+00	9.95F-03	3.06F+02
A 60	2.53E+00	3.21E-03	-4.96E+00	9.00E+00	1.29E+02	6.06E-01	8.00E-01	3.86E+00	1.00E+00	3.34E+00	9.95E-03	3.06E+02
A 61	2.53E+00	3.21E-03	-4.96E+00	9.00E+00	1.29E+02	6.06E-01	8.00E-01	3.86E+00	1.00E+00	3.34E+00	9.95E-03	6.01E+02
A 62	2.53E+00	3.21E-03	-4.96E+00	9.00E+00	1.29E+02	6.06E-01	8.00E-01	3.86E+00	1.00E+00	4.54E+00	9.95E-03	6.01E+02
A 63	2.53E+00	3.21E-03	-4.96E+00	9.00E+00	1.29E+02	6.06E-01	2.00E-01	3.86E+00	1.00E+00	4.54E+00	9.95E-03	6.01E+02
A 64	2.53E+00	3.21E-03	-4.96E+00	9.00E+00	1.29E+02	6.06E-01	2.00E-01	3.86E+00	4.00E-01	4.54E+00	9.95E-03	6.01E+02
A 65	2.53E+00	3.21E-03	-6.16E+00	9.00E+00	1.29E+02	6.06E-01	2.00E-01	3.86E+00	4.00E-01	4.54E+00	9.95E-03	6.01E+02

### 9.3.2 Group B

Simulation	X1	X13	X3	X4	X5	X6	X7	X8	X9	X10	X11	X12
	(log10)	(log10)	(log10)				[0-1]	(log2)	[0-1]	(log2)		
B 01	4 13E+00	-4.06E+00	-4 56E+00	9 00F+00	1 29F+02	8 74F-01	2 00F-01	3 46E+00	2 00F-01	4 94F+00	5.26E-03	6 01F+02
B 02	4 13E+00	-4.06E+00	-4 56E+00	9.00E+00	1 29E+02	8 74F-01	2.00E-01	3.46E+00	8 00E-01	4 94E+00	5 26E-03	6.01E+02
B 03	4 13E+00	-4.06E+00	-4 56E+00	9.00E+00	1 20F+02	8 74E-01	8 00F-01	3 46E+00	8 00E-01	4 94E+00	5 26E-03	6.01E+02
B 04	4.13E+00	-4.06E+00	-4 56E+00	9.00E+00	1 20F+02	8 74E-01	8 00F-01	3.46E+00	8 00E-01	4.94E+00	1 23E-02	6.01E+02
B 05	4.13E+00	-4.06E+00	-4 56E+00	9.00E+00	1.20E+02	8 7/F-01	8 00F-01	3.46E+00	8 00F-01	3 7/F+00	1.23E-02	6.01E+02
B 06	4.13E+00	-4.06E+00	-5 76E+00	9.00E+00	1.20E+02	8 7/F-01	8 00F-01	3.46E+00	8 00F-01	3.74E+00	1.23E-02	6.01E+02
B 07	4.13E+00	-4.06E+00	-5 76E+00	9.00E+00	1.20E+02	7 00F-02	8 00F-01	3.46E+00	8 00F-01	3.74E+00	1.23E-02	6.01E+02
B 08	4.13E+00	-2.86E+00	-5 76E+00	9.00E+00	1.29E+02	7.00E-02	8 00F-01	3.46E+00	8 00F-01	3.74E+00	1.23E-02	6.01E+02
B 09	2 93E+00	-2.86E+00	-5 76E+00	9.00E+00	1 29E+02	7.00E-02	8 00F-01	3.46E+00	8 00F-01	3 74E+00	1.23E-02	6.01E+02
B 10	2 93E+00	-2.86F+00	-5 76E+00	9.00E+00	1 29E+02	7.00E-02	8 00F-01	4 66F+00	8 00F-01	3 74F+00	1 23E-02	6.01E+02
B 11	2 93E+00	-2.86F+00	-5 76E+00	9.00E+00	3.82F+01	7.00E-02	8 00F-01	4 66F+00	8 00F-01	3 74F+00	1 23E-02	6.01E+02
B 12	2.93E+00	-2.86E+00	-5.76E+00	5.76E+01	3.82E+01	7.00E-02	8.00E-01	4.66E+00	8.00E-01	3.74E+00	1.23E-02	6.01E+02
B 13	2.93E+00	-2.86E+00	-5.76E+00	5.76E+01	3.82E+01	7.00E-02	8.00E-01	4.66E+00	8.00E-01	3.74E+00	1.23E-02	3.06E+02
B 14	2.13E+00	-3.66E+00	-5.76E+00	9.00E+00	3.82E+01	1.14E+00	1.00E+00	3.86E+00	4.00E-01	4.54E+00	9.95E-03	4.04E+02
B 15	2.13E+00	-3.66E+00	-4.56E+00	9.00E+00	3.82E+01	1.14E+00	1.00E+00	3.86E+00	4.00E-01	4.54E+00	9.95E-03	4.04E+02
B 16	2.13E+00	-3.66E+00	-4.56E+00	9.00E+00	3.82E+01	1.14E+00	1.00E+00	3.86E+00	1.00E+00	4.54E+00	9.95E-03	4.04E+02
B 17	2.13E+00	-3.66E+00	-4.56E+00	9.00E+00	3.82E+01	1.14E+00	4.00E-01	3.86E+00	1.00E+00	4.54E+00	9.95E-03	4.04E+02
B 18	2.13E+00	-3.66E+00	-4.56E+00	9.00E+00	3.82E+01	1.14E+00	4.00E-01	3.86E+00	1.00E+00	4.54E+00	9.95E-03	1.09E+02
B 19	2.13E+00	-3.66E+00	-4.56E+00	9.00E+00	3.82E+01	1.14E+00	4.00E-01	5.06E+00	1.00E+00	4.54E+00	9.95E-03	1.09E+02
B 20	2.13E+00	-3.66E+00	-4.56E+00	9.00E+00	3.82E+01	1.14E+00	4.00E-01	5.06E+00	1.00E+00	3.34E+00	9.95E-03	1.09E+02
B 21	2.13E+00	-3.66E+00	-4.56E+00	9.00E+00	3.82E+01	3.38E-01	4.00E-01	5.06E+00	1.00E+00	3.34E+00	9.95E-03	1.09E+02
B 22	2.13E+00	-3.66E+00	-4.56E+00	9.00E+00	1.29E+02	3.38E-01	4.00E-01	5.06E+00	1.00E+00	3.34E+00	9.95E-03	1.09E+02
B 23	2.13E+00	-3.66E+00	-4.56E+00	9.00E+00	1.29E+02	3.38E-01	4.00E-01	5.06E+00	1.00E+00	3.34E+00	2.91E-03	1.09E+02
B 24	3.33E+00	-3.66E+00	-4.56E+00	9.00E+00	1.29E+02	3.38E-01	4.00E-01	5.06E+00	1.00E+00	3.34E+00	2.91E-03	1.09E+02
B 25	3.33E+00	-2.46E+00	-4.56E+00	9.00E+00	1.29E+02	3.38E-01	4.00E-01	5.06E+00	1.00E+00	3.34E+00	2.91E-03	1.09E+02
B 26	3.33E+00	-2.46E+00	-4.56E+00	5.76E+01	1.29E+02	3.38E-01	4.00E-01	5.06E+00	1.00E+00	3.34E+00	2.91E-03	1.09E+02
B 27	3.33E+00	-2.06E+00	-4.96E+00	9.00E+00	3.82E+01	1.41E+00	0.00E+00	4.26E+00	8.00E-01	4.94E+00	7.60E-03	5.03E+02
B 28	3.33E+00	-2.06E+00	-4.96E+00	5.76E+01	3.82E+01	1.41E+00	0.00E+00	4.26E+00	8.00E-01	4.94E+00	7.60E-03	5.03E+02
B 29	3.33E+00	-2.06E+00	-4.96E+00	5.76E+01	3.82E+01	6.06E-01	0.00E+00	4.26E+00	8.00E-01	4.94E+00	7.60E-03	5.03E+02
B 30	3.33E+00	-2.06E+00	-4.96E+00	5.76E+01	3.82E+01	6.06E-01	0.00E+00	4.26E+00	8.00E-01	4.94E+00	5.60E-04	5.03E+02
B 31	3.33E+00	-2.06E+00	-6.16E+00	5.76E+01	3.82E+01	6.06E-01	0.00E+00	4.26E+00	8.00E-01	4.94E+00	5.60E-04	5.03E+02
B 32	3.33E+00	-2.06E+00	-6.16E+00	5.76E+01	3.82E+01	6.06E-01	0.00E+00	4.26E+00	8.00E-01	4.94E+00	5.60E-04	2.07E+02
B 33	3.33E+00	-3.26E+00	-6.16E+00	5.76E+01	3.82E+01	6.06E-01	0.00E+00	4.26E+00	8.00E-01	4.94E+00	5.60E-04	2.07E+02
B 34	3.33E+00	-3.26E+00	-6.16E+00	5.76E+01	3.82E+01	6.06E-01	0.00E+00	4.26E+00	8.00E-01	3.74E+00	5.60E-04	2.07E+02
B 35	3.33E+00	-3.26E+00	-6.16E+00	5.76E+01	3.82E+01	6.06E-01	6.00E-01	4.26E+00	8.00E-01	3.74E+00	5.60E-04	2.07E+02
B 36	3.33E+00	-3.26E+00	-6.16E+00	5.76E+01	1.29E+02	6.06E-01	6.00E-01	4.26E+00	8.00E-01	3.74E+00	5.60E-04	2.07E+02
B 37	3.33E+00	-3.26E+00	-6.16E+00	5.76E+01	1.29E+02	6.06E-01	6.00E-01	4.26E+00	2.00E-01	3.74E+00	5.60E-04	2.07E+02
B 38	3.33E+00	-3.26E+00	-0.10E+00	5./6E+01	1.29E+02	6.06E-01	6.00E-01	5.46E+00	2.00E-01	3.74E+00	5.60E-04	2.07E+02
B 39	2.13E+00	-3.20E+00	-0.10E+00	5.70E+01	1.29E+02	0.00E-01	6.00E-01	5.40E+00	2.00E-01	3.74E+00	5.00E-04	2.07E+02
B 40	3.33E+00	-2.80E+00	-0.10E+00	5.76E+01	3.82E+01	3.38E-01	6.00E-01	5.40E+00	8.00E-01	3.34E+00	9.95E-03	4.04E+02
D 41 D 42	3.335+00	-2.00E+00	-4.90E+00	5.700+01	3.020+01	3.30E-01	6.00E-01	5.400+00	0.00E-01	3.34E+00	9.956-05	4.04E+02
B 42	3.33L+00	-4.06E+00	-4.90L+00	5.76E+01	3.82E+01	1.14L+00	6.00E-01	5.46E+00	8.00L-01	3.34L+00	9.95E-03	4.04L+02
B 44	3.33E+00	-4.06E+00	-4 96E+00	5.76E+01	3.82E+01	1.14E+00	6.00E-01	5.46E+00	2 00E-01	3 34E+00	9.95E-03	4.04E+02
B 45	3.33E+00	-4.06F+00	-4.96F+00	5.76F+01	3.82F+01	1.14F+00	6.00F-01	5.46F+00	2.00F-01	3.34F+00	9.95F-03	1.09F+02
B 46	3.33E+00	-4.06E+00	-4.96E+00	5.76E+01	3.82E+01	1.14E+00	0.00E+00	5.46E+00	2.00E-01	3.34E+00	9.95E-03	1.09E+02
B 47	3.33E+00	-4.06E+00	-4.96E+00	9.00E+00	3.82E+01	1.14E+00	0.00E+00	5.46E+00	2.00E-01	3.34E+00	9.95E-03	1.09E+02
B 48	3.33E+00	-4.06E+00	-4.96E+00	9.00E+00	1.29E+02	1.14E+00	0.00E+00	5.46E+00	2.00E-01	3.34E+00	9.95E-03	1.09E+02
B 49	2.13E+00	-4.06E+00	-4.96E+00	9.00E+00	1.29E+02	1.14E+00	0.00E+00	5.46E+00	2.00E-01	3.34E+00	9.95E-03	1.09E+02
B 50	2.13E+00	-4.06E+00	-4.96E+00	9.00E+00	1.29E+02	1.14E+00	0.00E+00	5.46E+00	2.00E-01	3.34E+00	2.91E-03	1.09E+02
B 51	2.13E+00	-4.06E+00	-4.96E+00	9.00E+00	1.29E+02	1.14E+00	0.00E+00	5.46E+00	2.00E-01	4.54E+00	2.91E-03	1.09E+02
B 52	2.13E+00	-4.06E+00	-4.96E+00	9.00E+00	1.29E+02	1.14E+00	0.00E+00	4.26E+00	2.00E-01	4.54E+00	2.91E-03	1.09E+02
B 53	2.13E+00	-3.66E+00	-4.96E+00	4.14E+01	6.84E+01	6.06E-01	1.00E+00	4.26E+00	0.00E+00	2.94E+00	1.23E-02	5.03E+02
B 54	2.13E+00	-3.66E+00	-4.96E+00	4.14E+01	6.84E+01	1.41E+00	1.00E+00	4.26E+00	0.00E+00	2.94E+00	1.23E-02	5.03E+02
B 55	2.13E+00	-2.46E+00	-4.96E+00	4.14E+01	6.84E+01	1.41E+00	1.00E+00	4.26E+00	0.00E+00	2.94E+00	1.23E-02	5.03E+02
B 56	2.13E+00	-2.46E+00	-4.96E+00	4.14E+01	6.84E+01	1.41E+00	1.00E+00	4.26E+00	0.00E+00	2.94E+00	5.26E-03	5.03E+02
B 57	2.13E+00	-2.46E+00	-4.96E+00	4.14E+01	6.84E+01	1.41E+00	1.00E+00	4.26E+00	0.00E+00	2.94E+00	5.26E-03	2.07E+02
B 58	2.13E+00	-2.46E+00	-4.96E+00	4.14E+01	6.84E+01	1.41E+00	4.00E-01	4.26E+00	0.00E+00	2.94E+00	5.26E-03	2.07E+02
B 59	3.33E+00	-2.46E+00	-4.96E+00	4.14E+01	6.84E+01	1.41E+00	4.00E-01	4.26E+00	0.00E+00	2.94E+00	5.26E-03	2.07E+02
B 60	3.33E+00	-2.46E+00	-4.96E+00	9.00E+01	6.84E+01	1.41E+00	4.00E-01	4.26E+00	0.00E+00	2.94E+00	5.26E-03	2.07E+02
B 61	3.33E+00	-2.46E+00	-6.16E+00	9.00E+01	6.84E+01	1.41E+00	4.00E-01	4.26E+00	0.00E+00	2.94E+00	5.26E-03	2.07E+02
B 62	3.33E+00	-2.46E+00	-6.16E+00	9.00E+01	1.59E+02	1.41E+00	4.00E-01	4.26E+00	0.00E+00	2.94E+00	5.26E-03	2.07E+02
B 63	3.33E+00	-2.46E+00	-6.16E+00	9.00E+01	1.59E+02	1.41E+00	4.00E-01	5.46E+00	0.00E+00	2.94E+00	5.26E-03	2.07E+02
B 64	3.33E+00	-2.46E+00	-6.16E+00	9.00E+01	1.59E+02	1.41E+00	4.00E-01	5.46E+00	0.00E+00	4.14E+00	5.26E-03	2.07E+02
B 65	3.33E+00	-2.46E+00	-6.16E+00	9.00E+01	1.59E+02	1.41E+00	4.00E-01	5.46E+00	6.00E-01	4.14E+00	5.26E-03	2.07E+02

## 9.3.3 Group C

Simu	lation	X1	Х3	X4	X5	X6	X7	X8	X9	X10	X11	X12
		(log10)	(log10)				[0-1]	(log2)	[0-1]	(log2)		
C 01		2.13E+00	-4.16E+00	4.14E+01	3.82E+01	3.38E-01	6.00E-01	5.46E+00	6.00E-01	2.94E+00	7.60E-03	1.09E+02
C 02		2.13E+00	-4.16E+00	4.14E+01	3.82E+01	3.38E-01	0.00E+00	5.46E+00	6.00E-01	2.94E+00	7.60E-03	1.09E+02
C 03		2.13F+00	-4.16F+00	4.14F+01	1.29F+02	3.38F-01	0.00F+00	5 46F+00	6.00F-01	2.94F+00	7.60F-03	1.09F+02
C 04		2 13E+00	-4 16F+00	4 14F+01	1 29F+02	1 14F+00	0.00E+00	5.46F+00	6.00E-01	2 94F+00	7.60F-03	1.09E+02
C 05		2.13E+00	-4.16E+00	4.14E+01	1 29E+02	1.14E+00	0.00E+00	5.46E+00	6.00E-01	2.94E+00	5.60E-04	1.09E+02
C 06		2.13E+00	-4.16E+00	9 00F+01	1.29E+02	1.14E+00	0.00E+00	5.46E+00	6.00E-01	2.94E+00	5.60E-04	1.09E+02
C 07		2.132.00	4.165+00	0.005.01	1 205-02	1 145,00	0.000100	5.40E+00	6 00E 01	2.04E+00	5.00L 04	1.032102
C 07		2.135+00	4.100+00	9.00E+01	1.291-02	1.146+00	0.000000	1.26E+00	6.00E-01	2.946+00	5.00E-04	4.04E+02
C 00		2.135+00	4.165.00	9.000-01	1.291-02	1.140	0.0000000	4.201-00	6.00E-01	2.941-00	5.002-04	4.046+02
C 09		3.33E+00	-4.16E+00	9.00E+01	1.29E+02	1.14E+00	0.00E+00	4.265+00	6.00E-01	2.94E+00	5.60E-04	4.04E+02
0 10		3.33E+00	-5.36E+00	9.00E+01	1.29E+02	1.14E+00	0.00E+00	4.265+00	6.00E-01	2.94E+00	5.60E-04	4.04E+02
C 11		3.33E+00	-5.36E+00	9.00E+01	1.29E+02	1.14E+00	0.00E+00	4.26E+00	6.00E-01	4.14E+00	5.60E-04	4.04E+02
C 12		3.33E+00	-5.36E+00	9.00E+01	1.29E+02	1.14E+00	0.00E+00	4.26E+00	0.00E+00	4.14E+00	5.60E-04	4.04E+02
C 13		2.13E+00	-5.36E+00	9.00E+00	1.59E+02	1.14E+00	2.00E-01	3.86E+00	4.00E-01	2.94E+00	1.23E-02	1.09E+02
C 14		2.13E+00	-5.36E+00	9.00E+00	1.59E+02	1.14E+00	2.00E-01	3.86E+00	4.00E-01	2.94E+00	5.26E-03	1.09E+02
C 15		2.13E+00	-4.16E+00	9.00E+00	1.59E+02	1.14E+00	2.00E-01	3.86E+00	4.00E-01	2.94E+00	5.26E-03	1.09E+02
C 16		3.33E+00	-4.16E+00	9.00E+00	1.59E+02	1.14E+00	2.00E-01	3.86E+00	4.00E-01	2.94E+00	5.26E-03	1.09E+02
C 17	·	3.33E+00	-4.16E+00	9.00E+00	1.59E+02	1.14E+00	2.00E-01	5.06E+00	4.00E-01	2.94E+00	5.26E-03	1.09E+02
C 18		3.33E+00	-4.16E+00	9.00E+00	1.59E+02	3.38E-01	2.00E-01	5.06E+00	4.00E-01	2.94E+00	5.26E-03	1.09E+02
C 19		3.33E+00	-4.16E+00	9.00E+00	1.59E+02	3.38E-01	8.00E-01	5.06E+00	4.00E-01	2.94E+00	5.26E-03	1.09E+02
C 20		3.33E+00	-4.16E+00	9.00E+00	1.59E+02	3.38E-01	8.00E-01	5.06E+00	1.00E+00	2.94E+00	5.26E-03	1.09E+02
C 21		3.33E+00	-4.16E+00	9.00E+00	1.59E+02	3.38E-01	8.00E-01	5.06E+00	1.00E+00	2.94E+00	5.26E-03	4.04E+02
C 22		3.33E+00	-4.16E+00	5.76E+01	1.59E+02	3.38E-01	8.00E-01	5.06E+00	1.00E+00	2.94E+00	5.26E-03	4.04E+02
C 23		3.33E+00	-4.16E+00	5.76E+01	1.59E+02	3.38E-01	8.00E-01	5.06E+00	1.00E+00	4.14E+00	5.26E-03	4.04E+02
C 24		3.33E+00	-4.16E+00	5.76E+01	6.84E+01	3.38E-01	8.00E-01	5.06E+00	1.00E+00	4.14E+00	5.26E-03	4.04E+02
C 25		4.13E+00	-6.16E+00	7.38E+01	3.82E+01	7.00E-02	2.00E-01	3.86E+00	4.00E-01	3.34E+00	5.26E-03	6.01E+02
C 26		4.13E+00	-4.96E+00	7.38E+01	3.82E+01	7.00E-02	2.00E-01	3.86E+00	4.00E-01	3.34E+00	5.26E-03	6.01E+02
C 27		2.93E+00	-4.96E+00	7.38E+01	3.82E+01	7.00E-02	2.00E-01	3.86E+00	4.00E-01	3.34E+00	5.26E-03	6.01E+02
C 28		2.93E+00	-4.96E+00	7.38E+01	3.82E+01	8.74E-01	2.00E-01	3.86E+00	4.00E-01	3.34E+00	5.26E-03	6.01E+02
C 29		2.93E+00	-4.96E+00	7.38E+01	3.82E+01	8.74E-01	8.00E-01	3.86E+00	4.00E-01	3.34E+00	5.26E-03	6.01E+02
C 30		2.93E+00	-4.96E+00	7.38E+01	1.29E+02	8.74E-01	8.00E-01	3.86E+00	4.00E-01	3.34E+00	5.26E-03	6.01E+02
C 31		2.93E+00	-4.96E+00	7.38E+01	1.29E+02	8.74E-01	8.00E-01	3.86E+00	1.00E+00	3.34E+00	5.26E-03	6.01E+02
C 32		2.93E+00	-4.96E+00	7.38E+01	1.29E+02	8.74E-01	8.00E-01	5.06E+00	1.00E+00	3.34E+00	5.26E-03	6.01E+02
C 33		2.93F+00	-4.96F+00	7.38F+01	1.29F+02	8.74F-01	8.00F-01	5.06F+00	1.00F+00	4.54F+00	5.26F-03	6.01F+02
C 34		2.93E+00	-4.96E+00	7 38F+01	1 29F+02	8 74F-01	8.00F-01	5.06E+00	1.00E+00	4 54F+00	1 23F-02	6.01E+02
C 35		2.93E+00	-4.96E+00	7 38F+01	1.29E+02	8 7/F=01	8 00F-01	5.06E+00	1.00E+00	4.54E+00	1.23E-02	3.06F+02
C 36		2.035+00	-4.965+00	2 52E+01	1 20E+02	8 7/E-01	8 00E-01	5.00E+00	1.00E+00	4.54E+00	1.23E-02	3.065+02
C 27		4 125-00	E 26E+00	E 76E+01	6.94E+01	1 415-00	0.00L-01	2 465+00	2 00E 01	4.541+00	E 26E 02	5.00L+02
C 20		4.132+00	-3.30E+00	5.701	6.04E+01	6 06E 01	0.00E-01	2.465+00	8.00E-01	4.346+00	5.20E-03	6.01E+02
C 20		4.130-00	-3.30E+00	5.701	0.04ETUI	6.06F.01	0.00E-01	3.401+00	8.00E-01	2.245.00	5.200-03	6.010102
C 39		4.130+00	-5.50E+00	5.700+01	0.04E+01	0.002-01	0.00E-01	3.40E+00	8.00E-01	3.34E+00	3.202-03	0.01E+02
C 40		4.130+00	-5.50E+00	5.700+01	0.04E+01	0.000-01	8.00E-01	3.40E+00	0.00E-01	3.34E+00	1.235-02	0.01E+02
C 41		4.13E+00	-5.30E+00	5.76E+01	0.84E+01	6.06E-01	8.00E-01	3.46E+00	2.00E-01	3.34E+00	1.23E-02	6.01E+02
C 42		2.93E+00	-5.36E+00	5.762+01	0.84E+01	6.06E-01	8.00E-01	3.46E+00	2.00E-01	3.34E+00	1.23E-02	6.01E+02
C 43		2.93E+00	-5.36E+00	5./6E+01	1.59E+02	0.06E-01	8.00E-01	3.46E+00	2.00E-01	3.34E+00	1.23E-02	0.01E+02
C 44		2.93E+00	-5.36E+00	5./6E+01	1.59E+02	6.06E-01	2.00E-01	3.46E+00	2.00E-01	3.34E+00	1.23E-02	6.01E+02
C 45		2.93E+00	-5.36E+00	9.00E+00	1.59E+02	6.06E-01	2.00E-01	3.46E+00	2.00E-01	3.34E+00	1.23E-02	6.01E+02
C 46		2.93E+00	-4.16E+00	9.00E+00	1.59E+02	6.06E-01	2.00E-01	3.46E+00	2.00E-01	3.34E+00	1.23E-02	6.01E+02
C 47		2.93E+00	-4.16E+00	9.00E+00	1.59E+02	6.06E-01	2.00E-01	3.46E+00	2.00E-01	3.34E+00	1.23E-02	3.06E+02
C 48		2.93E+00	-4.16E+00	9.00E+00	1.59E+02	6.06E-01	2.00E-01	4.66E+00	2.00E-01	3.34E+00	1.23E-02	3.06E+02
C 49		2.93E+00	-5.36E+00	2.52E+01	3.82E+01	6.06E-01	6.00E-01	3.86E+00	1.00E+00	3.34E+00	7.60E-03	1.09E+02
C 50		2.93E+00	-5.36E+00	2.52E+01	1.29E+02	6.06E-01	6.00E-01	3.86E+00	1.00E+00	3.34E+00	7.60E-03	1.09E+02
C 51		2.93E+00	-5.36E+00	2.52E+01	1.29E+02	6.06E-01	0.00E+00	3.86E+00	1.00E+00	3.34E+00	7.60E-03	1.09E+02
C 52		2.93E+00	-5.36E+00	2.52E+01	1.29E+02	6.06E-01	0.00E+00	3.86E+00	1.00E+00	4.54E+00	7.60E-03	1.09E+02
C 53		2.93E+00	-5.36E+00	2.52E+01	1.29E+02	6.06E-01	0.00E+00	3.86E+00	1.00E+00	4.54E+00	7.60E-03	4.04E+02
C 54		2.93E+00	-5.36E+00	2.52E+01	1.29E+02	6.06E-01	0.00E+00	3.86E+00	1.00E+00	4.54E+00	5.60E-04	4.04E+02
C 55		2.93E+00	-5.36E+00	2.52E+01	1.29E+02	1.41E+00	0.00E+00	3.86E+00	1.00E+00	4.54E+00	5.60E-04	4.04E+02
C 56		2.93E+00	-5.36E+00	2.52E+01	1.29E+02	1.41E+00	0.00E+00	5.06E+00	1.00E+00	4.54E+00	5.60E-04	4.04E+02
C 57		4.13E+00	-5.36E+00	2.52E+01	1.29E+02	1.41E+00	0.00E+00	5.06E+00	1.00E+00	4.54E+00	5.60E-04	4.04E+02
C 58		4.13E+00	-4.16E+00	2.52E+01	1.29E+02	1.41E+00	0.00E+00	5.06E+00	1.00E+00	4.54E+00	5.60E-04	4.04E+02
C 59		4.13E+00	-4.16E+00	7.38E+01	1.29E+02	1.41E+00	0.00E+00	5.06E+00	1.00E+00	4.54E+00	5.60E-04	4.04E+02
C 60		4.13E+00	-4.16E+00	7.38E+01	1.29E+02	1.41E+00	0.00E+00	5.06E+00	4.00E-01	4.54E+00	5.60E-04	4.04E+02

### 9.3.4 Group E

Simulation	¥1	V12	¥2	V4	V5	¥6	¥7	٧Q	٧Q	V10	V11	V12
Simulation		×15	^5	^4	~5	70	~/	<u>^o</u>	<u></u>	×10	×11	×12
	(log10)	(log10)	(log10)				[0-1]	(log2)	[0-1]	(log2)		
E 01	3.73E+00	-2.86E+00	-6.16E+00	5.76E+01	7.95E+00	3.38E-01	0.00E+00	5.06E+00	2.00E-01	3.74E+00	2.91E-03	4.04E+02
E 02	3.73E+00	-2.86E+00	-6.16E+00	5.76E+01	7.95E+00	3.38E-01	0.00E+00	5.06E+00	2.00E-01	3.74E+00	2.91E-03	1.09E+02
E 03	3.73E+00	-2.86E+00	-6.16E+00	5.76E+01	7.95E+00	3.38E-01	0.00E+00	5.06E+00	2.00E-01	3.74E+00	9.95E-03	1.09E+02
E 04	2.53E+00	-2.86E+00	-6.16E+00	5.76E+01	7.95E+00	3.38E-01	0.00E+00	5.06E+00	2.00E-01	3.74E+00	9.95E-03	1.09E+02
E 05	2 53E+00	-2 86E+00	-6 16E+00	9 00F+00	7 95E±00	3 38F-01	0.00E+00	5.06E+00	2 00F-01	3 7/F+00	9 95F-03	1 09F+02
E 05	2.531+00	-2.80L+00	-0.101+00	9.001+00	7.951+00	3.301-01	0.000	5.001+00	2.000-01	3.741+00	9.951-03	1.091+02
E 06	2.53E+00	-2.86E+00	-0.16E+00	9.00E+00	7.95E+00	1.14E+00	0.00E+00	5.06E+00	2.00E-01	3.74E+00	9.95E-03	1.09E+02
E 07	2.53E+00	-2.86E+00	-6.16E+00	9.00E+00	7.95E+00	1.14E+00	0.00E+00	3.86E+00	2.00E-01	3.74E+00	9.95E-03	1.09E+02
E 08	2.53E+00	-2.86E+00	-6.16E+00	9.00E+00	7.95E+00	1.14E+00	6.00E-01	3.86E+00	2.00E-01	3.74E+00	9.95E-03	1.09E+02
E 09	2.53E+00	-2.86E+00	-6.16E+00	9.00E+00	7.95E+00	1.14E+00	6.00E-01	3.86E+00	2.00E-01	4.94E+00	9.95E-03	1.09E+02
E 10	2.53E+00	-2.86E+00	-6.16E+00	9.00E+00	9.86E+01	1.14E+00	6.00E-01	3.86E+00	2.00E-01	4.94E+00	9.95E-03	1.09E+02
F 11	2 53E+00	-2 86F+00	-4 96F+00	9 00F+00	9 86F+01	1 1/F+00	6 00F-01	3 86F+00	2 00F-01	4 94F+00	9 95F-03	1 09F+02
E 11	2.552100	4.000100	4.000	0.005.00	0.800101	1.140.00	C.00E.01	3.802100	2.000 01	4.045:00	0.055.03	1.005.02
E 12	2.53E+00	-4.06E+00	-4.96E+00	9.00E+00	9.80E+U1	1.14E+00	6.00E-01	3.80E+00	2.00E-01	4.94E+00	9.95E-03	1.09E+02
E 13	2.53E+00	-4.06E+00	-4.96E+00	9.00E+00	9.86E+01	1.14E+00	6.00E-01	3.86E+00	8.00E-01	4.94E+00	9.95E-03	1.09E+02
E 14	2.13E+00	-2.46E+00	-4.96E+00	9.00E+00	7.95E+00	8.74E-01	4.00E-01	5.06E+00	8.00E-01	2.94E+00	1.23E-02	5.03E+02
E 15	2.13E+00	-2.46E+00	-4.96E+00	9.00E+00	7.95E+00	8.74E-01	4.00E-01	3.86E+00	8.00E-01	2.94E+00	1.23E-02	5.03E+02
E 16	2.13E+00	-3.66E+00	-4.96E+00	9.00E+00	7.95E+00	8.74E-01	4.00E-01	3.86E+00	8.00E-01	2.94E+00	1.23E-02	5.03E+02
F 17	2 13E+00	-3 66F+00	-4 96F+00	9 00F+00	7 95E+00	8 74F-01	4 00F-01	3 86F+00	8 00F-01	2 94F+00	1 23F-02	2 07F+02
E 19	2 12 5±00	2 665+00	-6 16E+00	0 00E+00	7.05 E+00	9 74E 01	4.005.01	2 865+00	9 00E 01	2 0/ E+00	1 225 02	2.075+02
L 10	2.131+00	-3.001+00	-0.101+00	5.001+00	7.951+00	0.741-01	4.000-01	3.001+00	0.000-01	2.941+00	1.230-02	2.071+02
E 19	2.13E+00	-3.66E+00	-6.16E+00	5.76E+01	7.95E+00	8.74E-01	4.00E-01	3.86E+00	8.00E-01	2.94E+00	1.23E-02	2.07E+02
E 20	2.13E+00	-3.66E+00	-6.16E+00	5.76E+01	7.95E+00	8.74E-01	4.00E-01	3.86E+00	8.00E-01	2.94E+00	5.26E-03	2.07E+02
E 21	2.13E+00	-3.66E+00	-6.16E+00	5.76E+01	7.95E+00	8.74E-01	1.00E+00	3.86E+00	8.00E-01	2.94E+00	5.26E-03	2.07E+02
E 22	2.13E+00	-3.66E+00	-6.16E+00	5.76E+01	7.95E+00	8.74E-01	1.00E+00	3.86E+00	8.00E-01	4.14E+00	5.26E-03	2.07E+02
F 23	2 13E+00	-3 66F+00	-6 16F+00	5 76F+01	7 95E+00	7 00F-02	1 00F+00	3 86F+00	8 00F-01	4 14F+00	5 26F-03	2 07F+02
E 24	2 12 5±00	2 665+00	-6 16E+00	5 765+01	0.965+01	7.005.02	1.005+00	2 865+00	9 00E 01	1 1/E+00	5 265 02	2.075+02
L 24	2.131+00	-3.001+00	-0.101+00	5.701+01	9.801+01	7.000-02	1.001+00	3.802+00	8.001-01	4.14L+00	5.201-03	2.071+02
E 25	3.33E+00	-3.66E+00	-0.10E+00	5.76E+01	9.86E+01	7.00E-02	1.00E+00	3.86E+00	8.00E-01	4.14E+00	5.26E-03	2.07E+02
E 26	3.33E+00	-3.66E+00	-6.16E+00	5.76E+01	9.86E+01	7.00E-02	1.00E+00	3.86E+00	2.00E-01	4.14E+00	5.26E-03	2.07E+02
E 27	4.13E+00	-2.46E+00	-4.96E+00	9.00E+00	3.82E+01	7.00E-02	6.00E-01	5.06E+00	0.00E+00	4.94E+00	1.23E-02	5.03E+02
E 28	4.13E+00	-2.46E+00	-4.96E+00	9.00E+00	3.82E+01	8.74E-01	6.00E-01	5.06E+00	0.00E+00	4.94E+00	1.23E-02	5.03E+02
F 29	4 13F+00	-2 46F+00	-4 96F+00	5 76F+01	3 82F+01	8 74F-01	6 00F-01	5 06F+00	0.00F+00	4 94F+00	1 23F-02	5 03F+02
E 20	4.12E+00	2.46E+00	4.965+00	5.76E+01	1 205+02	9 74E 01	6 00E 01	5.00E+00	0.0000-000	4.04E±00	1 225 02	5.03E+02
L 30	4.131+00	-2.401+00	-4.901+00	5.701+01	1.291+02	0.741-01	0.001-01	5.002+00	0.002+00	4.941+00	1.231-02	5.03L+02
E 31	4.13E+00	-2.46E+00	-4.96E+00	5.76E+01	1.29E+02	8.74E-01	6.00E-01	5.06E+00	0.00E+00	4.94E+00	5.26E-03	5.03E+02
E 32	4.13E+00	-2.46E+00	-4.96E+00	5.76E+01	1.29E+02	8.74E-01	6.00E-01	5.06E+00	6.00E-01	4.94E+00	5.26E-03	5.03E+02
E 33	4.13E+00	-2.46E+00	-4.96E+00	5.76E+01	1.29E+02	8.74E-01	0.00E+00	5.06E+00	6.00E-01	4.94E+00	5.26E-03	5.03E+02
E 34	4.13E+00	-3.66E+00	-4.96E+00	5.76E+01	1.29E+02	8.74E-01	0.00E+00	5.06E+00	6.00E-01	4.94E+00	5.26E-03	5.03E+02
E 35	4.13E+00	-3.66E+00	-6.16E+00	5.76E+01	1.29E+02	8.74E-01	0.00E+00	5.06E+00	6.00E-01	4.94E+00	5.26E-03	5.03E+02
E 36	2 93E+00	-3 66E+00	-6 16E+00	5 76F+01	1 29F+02	8 7/F-01	0.00E+00	5.06E+00	6.00F-01	/ 9/F+00	5 26F-03	5.03E+02
E 30	2.931+00	-3.001+00	-0.101+00	5.701+01	1.291+02	0.741-01	0.000	5.001+00	0.001-01	4.941+00	5.201-03	3.031+02
E 37	2.93E+00	-3.66E+00	-6.16E+00	5.76E+01	1.29E+02	8.74E-01	0.00E+00	5.06E+00	6.00E-01	4.94E+00	5.26E-03	2.07E+02
E 38	2.93E+00	-3.66E+00	-6.16E+00	5.76E+01	1.29E+02	8.74E-01	0.00E+00	5.06E+00	6.00E-01	3.74E+00	5.26E-03	2.07E+02
E 39	2.93E+00	-3.66E+00	-6.16E+00	5.76E+01	1.29E+02	8.74E-01	0.00E+00	3.86E+00	6.00E-01	3.74E+00	5.26E-03	2.07E+02
E 40	2.13E+00	-3.26E+00	-5.36E+00	7.38E+01	7.95E+00	3.38E-01	1.00E+00	4.26E+00	1.00E+00	4.94E+00	5.60E-04	6.01E+02
E 41	2.13E+00	-3.26E+00	-5.36E+00	7.38E+01	9.86E+01	3.38E-01	1.00E+00	4.26E+00	1.00E+00	4.94E+00	5.60E-04	6.01E+02
E /12	2 13E+00	-3 26E+00	-5 36E+00	2 52F+01	9.86F+01	3 38F-01	1.00E+00	4 26E+00	1.00E+00	/ 9/F+00	5.60E-04	6.01E+02
L 42	2.131+00	-3.201+00	-3.30L+00	2.521+01	0.0001	2.205.01	1.000+00	4.201+00	1.000+00	4.34L+00	5.000-04	0.011+02
E 43	2.13E+00	-3.26E+00	-5.36E+00	2.52E+01	9.80E+U1	3.38E-U1	1.00E+00	4.20E+00	1.00E+00	3.74E+00	5.60E-04	0.01E+02
E 44	2.13E+00	-3.26E+00	-5.36E+00	2.52E+01	9.86E+01	3.38E-01	4.00E-01	4.26E+00	1.00E+00	3.74E+00	5.60E-04	6.01E+02
E 45	2.13E+00	-3.26E+00	-5.36E+00	2.52E+01	9.86E+01	1.14E+00	4.00E-01	4.26E+00	1.00E+00	3.74E+00	5.60E-04	6.01E+02
E 46	2.13E+00	-3.26E+00	-5.36E+00	2.52E+01	9.86E+01	1.14E+00	4.00E-01	4.26E+00	1.00E+00	3.74E+00	7.60E-03	6.01E+02
E 47	2.13E+00	-3.26E+00	-5.36E+00	2.52E+01	9.86E+01	1.14E+00	4.00E-01	4.26E+00	1.00E+00	3.74E+00	7.60E-03	3.06E+02
E 48	2.13E+00	-3.26E+00	-5.36E+00	2.52E+01	9,86E+01	1.14E+00	4.00F-01	5.46E+00	1.00E+00	3.74E+00	7.60E-03	3.06E+02
F 10	2 13E±00	-3 26F±00	-5 36F+00	2 52F±01	9 86F±01	1 1/F±00	4 00F 01	5 46E±00	4 00F 01	3 7/15-00	7 60F 02	3 065-02
E E0	2.135-00	3.200700	5.30ETUU	2.326701	0.0000101	1.140100	4.000-01	5.400100	4.005-01	3.745.00	7.000-03	3.000002
E 50	2.13E+00	-2.06E+00	-5.36E+00	2.52E+01	9.86E+01	1.14E+00	4.00E-01	5.46E+00	4.00E-01	3.74E+00	7.60E-03	3.06E+02
E 51	3.33E+00	-2.06E+00	-5.36E+00	2.52E+01	9.86E+01	1.14E+00	4.00E-01	5.46E+00	4.00E-01	3.74E+00	7.60E-03	3.06E+02
E 52	3.33E+00	-2.06E+00	-4.16E+00	2.52E+01	9.86E+01	1.14E+00	4.00E-01	5.46E+00	4.00E-01	3.74E+00	7.60E-03	3.06E+02
E 53	4.13E+00	-2.86E+00	-5.36E+00	4.14E+01	3.82E+01	8.74E-01	4.00E-01	4.66E+00	2.00E-01	4.14E+00	1.23E-02	2.07E+02
E 54	4.13E+00	-2.86E+00	-5.36E+00	4.14E+01	3.82E+01	8.74E-01	4.00E-01	3.46E+00	2.00E-01	4.14E+00	1.23E-02	2.07E+02
E 55	1 135+00	-2 865-00	-5 365+00	A 1/E+01	3 875+01	87/5.01	1 005 01	3 465+00	2 005 01	2 9/5+00	1 235 02	2 075+02
E 55	+.13E+00	2.000000	5.30ETUU	4.145.01	3.02ETU1	0.745-01	4.000-01	3.400100	2.005-01	2.346700	1.235-02	2.075.02
E 30	2.93E+00	-2.80E+UU	-3.30E+UU	4.14E+U1	3.82E+U1	0.74E-U1	4.00E-01	3.40E+00	2.00E-01	2.94E+00	1.23E-02	2.07E+02
E 57	2.93E+00	-2.86E+00	-5.36E+00	4.14E+01	3.82E+01	8.74E-01	4.00E-01	3.46E+00	2.00E-01	2.94E+00	1.23E-02	5.03E+02
E 58	2.93E+00	-2.86E+00	-5.36E+00	4.14E+01	3.82E+01	8.74E-01	4.00E-01	3.46E+00	2.00E-01	2.94E+00	5.26E-03	5.03E+02
E 59	2.93E+00	-4.06E+00	-5.36E+00	4.14E+01	3.82E+01	8.74E-01	4.00E-01	3.46E+00	2.00E-01	2.94E+00	5.26E-03	5.03E+02
E 60	2.93F+00	-4.06F+00	-5.36F+00	4.14F+01	3.82F+01	8.74F-01	1.00F+00	3.46F+00	2.00F-01	2.94F+00	5.26F-03	5.03F+02
E 61	2 93F±00	-4 06F+00	-5 36F+00	9 00F±01	3 82F±01	8 7/ F_01	1 00F+00	3 46F+00	2 00F-01	2 94F±00	5 26F-02	5 03F+02
	2.551+00	4.0001+00	5.301+00	0.005-01	3.021-01	0.745.01	1.000-000	3.400-00	2.001-01	2.045.00	5.201-03	5.031+02
E 62	2.93E+00	-4.06E+00	-5.30E+00	9.00E+01	3.82E+01	8.74E-01	1.00E+00	3.46E+00	8.00E-01	2.94E+00	5.26E-03	5.03E+02
E 63	2.93E+00	-4.06E+00	-5.36E+00	9.00E+01	1.29E+02	8.74E-01	1.00E+00	3.46E+00	8.00E-01	2.94E+00	5.26E-03	5.03E+02
E 64	2.93E+00	-4.06E+00	-5.36E+00	9.00E+01	1.29E+02	7.00E-02	1.00E+00	3.46E+00	8.00E-01	2.94E+00	5.26E-03	5.03E+02
E 65	2.93E+00	-4.06E+00	-4.16E+00	9.00E+01	1.29E+02	7.00E-02	1.00E+00	3.46E+00	8.00E-01	2.94E+00	5.26E-03	5.03E+02

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