

Bertrand Leterme & Diederik Jacques

Environ Sci Pollut Res
DOI 10.1007/s11356-015-4876-x



Your article is protected by copyright and all rights are held exclusively by Springer-Verlag Berlin Heidelberg. This e-offprint is for personal use only and shall not be self-archived in electronic repositories. If you wish to self-archive your article, please use the accepted manuscript version for posting on your own website. You may further deposit the accepted manuscript version in any repository, provided it is only made publicly available 12 months after official publication or later and provided acknowledgement is given to the original source of publication and a link is inserted to the published article on Springer's website. The link must be accompanied by the following text: "The final publication is available at link.springer.com".

A reactive transport model for mercury fate in contaminated soil—sensitivity analysis

Bertrand Leterme¹ · Diederik Jacques¹

Received: 16 February 2015 / Accepted: 10 June 2015
© Springer-Verlag Berlin Heidelberg 2015

Abstract We present a sensitivity analysis of a reactive transport model of mercury (Hg) fate in contaminated soil systems. The one-dimensional model, presented in Leterme et al. (2014), couples water flow in variably saturated conditions with Hg physico-chemical reactions. The sensitivity of Hg leaching and volatilisation to parameter uncertainty is examined using the elementary effect method. A test case is built using a hypothetical 1-m depth sandy soil and a 50-year time series of daily precipitation and evapotranspiration. Hg anthropogenic contamination is simulated in the topsoil by separately considering three different sources: cinnabar, non-aqueous phase liquid and aqueous mercuric chloride. The model sensitivity to a set of 13 input parameters is assessed, using three different model outputs (volatilized Hg, leached Hg, Hg still present in the contaminated soil horizon). Results show that dissolved organic matter (DOM) concentration in soil solution and the binding constant to DOM thiol groups are critical parameters, as well as parameters related to Hg sorption to humic and fulvic acids in solid organic matter. Initial Hg concentration is also identified as a sensitive parameter. The sensitivity analysis also brings out non-monotonic model behaviour for certain parameters.

Keywords Mercury · Hg · Sensitivity analysis · Morris · Vadose zone · Reactive transport modelling · HP1

Introduction

Mercury (Hg) poses threats for human health and the environment due to its ecotoxicity, exacerbated by its persistence in the environment and its ability to bioaccumulate in ecosystems (Liu et al. 2012). While there are some natural emissions of mercury from the earth's crust, anthropogenic sources are important contributors of Hg release to the atmosphere, hydrosphere and pedosphere (Pirrone et al. 2010; Kocman et al. 2013). Soil anthropogenic contamination can result from the wet and dry deposition of prior atmospheric emissions (coal combustion, artisanal and small-scale gold mining, cement production, etc.; Xu et al. 2015). More directly, soil contamination can also result from the disposal of liquid or solid Hg sources (accidental spilling, mine tailings, landfills, polluted sewage sludge, etc.).

The Hg species found in contaminated soils are highly related to the type of industry or activity that caused the contamination. The time elapsed since mercury contamination is also important, because Hg partitioning between different species or phases may evolve due to slow kinetics of transformation or retention mechanisms (Bloom et al. 2003). Mercury species found in contaminated soils are among others elemental Hg⁰(l) “globules” (or non-aqueous phase liquid; NAPL), cinnabar (HgS), corderoite (Hg₃S₂Cl₂), HgCl₂(s), Hg adsorbed to soil organic matter (Davis et al. 1997; Bernaus et al. 2006; Navarro et al. 2006; Santoro et al. 2010; Terzano et al. 2010; Skjellberg 2010).

Hg speciation analysis methods have greatly improved over the recent years (Leopold et al. 2010; Gao et al. 2012). In the same time, reactive transport codes have evolved

Responsible editor: Stuart Simpson

Electronic supplementary material The online version of this article (doi:10.1007/s11356-015-4876-x) contains supplementary material, which is available to authorized users.

✉ Bertrand Leterme
bleterme@sckcen.be

Diederik Jacques
djacques@sckcen.be

¹ Performance Assessments, Institute for Environment, Health and Safety, Belgian Nuclear Research Centre (SCK•CEN), Boeretang 200, 2400 Mol, Belgium

dramatically towards including a broad set of biogeochemical reactions, often coupled with water flow in saturated or unsaturated porous media (Steeffel et al. 2014). However, transcribing the complexity of Hg geochemistry in soil systems into a reactive transport model poses important challenges. For example, Hg interactions with natural organic matter are not accounted for in existing geochemical databases. Also, some (slow) Hg kinetics or phase transformations observed in the field are hardly compatible with a purely thermodynamic equilibrium approach.

To the best of our knowledge, the only published study of Hg fate and transport modelling in unsaturated media is by Bessinger and Marks (2010), who evaluated long-term Hg fate and remediation options. However, while they thoroughly substantiated the parameterisation of Hg reactions with dissolved and solid organic matter (DOM and SOM), investigating model sensitivity was briefly addressed with only three different model runs, varying one parameter at a time.

A reactive transport model for Hg fate in contaminated soils was developed with the multi-component reactive transport model for variably saturated soil HP1 (Jacques et al. 2006, 2008a, b) and presented in Leterme et al. (2014). A test case was developed, using different Hg sources and combinations of them. Although this already gave insights in the conceptual model benefits and limitations, the limited number of simulations in the test case could not illustrate potential complex Hg fate patterns (e.g. fast leaching or nearly immobile Hg resulting from complex parameter interactions) emerging from the different reactions involved. More generally, few information was given in Leterme et al. (2014) about parameter and process sensitivity, which constitute prerequisite information before any potential real-world applications. The present paper fills this gap by presenting a sensitivity analysis performed on the conceptual model developed by Leterme et al. (2014).

The sensitivity analysis is based on the elementary effect method (Morris 1991). In this method, parameters are varied one at a time along several trajectories, allowing an efficient screening of the parameter space (see section “Sensitivity analysis”). Several cases, having different initial Hg species associated with different sources of contamination, are evaluated. The first is cinnabar, which is frequently found in sites of anthropogenic contamination such as mercury or gold mine tailings (Slowey et al. 2005; Navarro et al. 2006), or in soils around chlor-alkali plants (Bernaus et al. 2006; Santoro et al. 2010). The second is elemental Hg ($\text{Hg}^0(\text{l})$ or NAPL). Although it is often rapidly oxidised to Hg^{2+} or volatilised to the atmosphere, $\text{Hg}^0(\text{l})$ can also be found at contaminated sites (Davis et al. 1997; Biester et al. 1999). The third is mercuric chloride (HgCl_2) in its aqueous form, which is a compound used for wood treatment (Bollen et al. 2008). Model outputs chosen for the sensitivity analysis are mass flux of Hg volatilised to the atmosphere, total mass of Hg remaining in

the horizon of initial contamination and mass flux of Hg leached at the bottom of the soil profile. These outputs are expressed in percentage of initial Hg contamination. We first shortly present the conceptual model used, the hypotheses on which the simulation cases are built and the sensitivity analysis design. Then, results are presented and discussed for three different initial contaminations (cinnabar, Hg NAPL and $\text{HgCl}_2(\text{aq})$). Finally, the main findings are summarised and discussed in light of the current status of Hg contamination modelling.

Material and methods

Model description

Leterme et al. (2014) detailed the conceptual model of Hg transport and transformations and its numerical implementation in HP1 (Jacques et al. 2006, 2008a, b). Hereafter, the main processes and model parameters are briefly summarised. Figure 1 shows the processes included in the one-dimensional model and depicts the hypothetical case assumptions (“Hypothetical case”) used in the sensitivity analysis.

The simulation of water flow in variably saturated conditions is based on Richards’ equation and accounts for daily variations in precipitation, root water uptake and evaporation. By accounting for these time-dependent boundary conditions, the water content, matric potential and water flux become a function of time and depth in the soil profile. Such soil hydrological conditions will affect Hg mobility and biogeochemical conditions for both equilibrium and kinetic reactions (Jacques et al. 2008a). Furthermore, it was shown by Jacques et al. (2008a) that the simulation of contaminant transport and leaching strongly depends on the flow conditions. Alterations between evaporation processes and precipitation may change

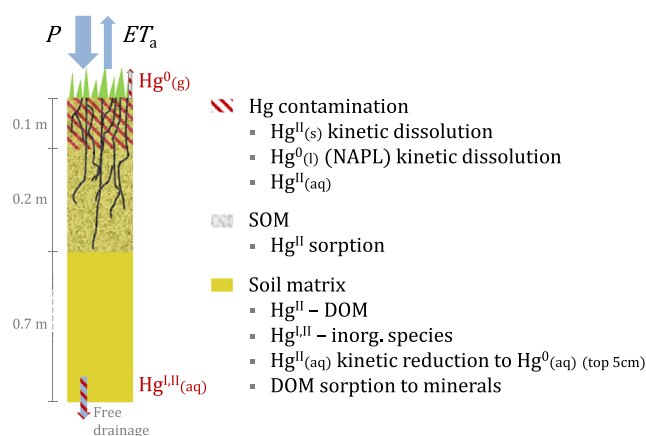


Fig. 1 Conceptual model and test case geometry for the simulation of Hg fate and transport in contaminated soil systems. P is the precipitation throughfall and ET_a the actual evapotranspiration

speciation and thus mobility. In particular, changing saturation degrees may change the diffusion of Hg in the gas phase.

The model considers Hg aqueous speciation and complexation with organic and inorganic ligands, Hg sorption/desorption to/from SOM, Hg precipitation and dissolution, as well as Hg^{2+} reduction to Hg^0 and volatilisation. Colloid-facilitated Hg transport (Sen and Khilar 2006; Zhu et al. 2012) is implicitly considered by the transport of DOM-bound Hg.

Because the model was developed for soil systems having a Hg contamination more than a hundred times the background (worldwide mean concentration in soils is 1.1 mg/kg; Xu et al. 2015), some processes could be neglected (justifications in Leterme et al. 2014): vegetation uptake, atmospheric wet and dry deposition, NAPL migration and entrapment and Hg (de)methylation.

The database IM003_THERMODDEM (Blanc et al. 2012) is used for Hg aqueous complexation. Because complexation with dissolved organic compounds is not considered in IM003_THERMODDEM, four organic compounds (Ya, Yb, Yc representing different functional groups of humic and fulvic acids—HA and FA—and Ys representing thiols) are added. Hg interactions with these dissolved organic ligands are modelled as aqueous complexation reactions, using speciation data from Sklyberg (2012).

An approach based on multiple proton/ion exchangers (e.g. Jacques et al. 2008a) is used to describe the interactions between Hg and immobile SOM. Four reactive surface sites are considered (Xa, Xb, Xc representing oxygen sites of HA and FA, and Xs representing thiols).

Hg^{2+} reduction to Hg^0 is simulated in the soil top 5 cm with a pseudo-first-order kinetic reaction, accounting for sunlight and heat influence in the topsoil only. DOM sorption to mineral surfaces (typically Al and Fe hydroxides, clay minerals) is modelled using a Langmuir isotherm with parameters K_f (distribution coefficient) and S_{tot} (total concentration of sorption sites). DOM production is not explicitly considered in the model. Instead, DOM is brought to the system via the infiltrating rain water composition.

Certain processes in contaminated sites may be very specific due to local circumstances and thus may not be consistent with thermodynamic predictions. Therefore, some processes (e.g. Hg^{2+} reduction to Hg^0) need to be modelled following kinetics rather than thermodynamic laws (Leterme et al. 2014).

Hypothetical case

The hypothetical case built for the sensitivity analysis is based on the following assumptions. Mercury fate and transport are simulated in a 1-m-deep sandy soil profile with deep groundwater (i.e. free drainage boundary condition). The van Genuchten-Mualem model (van Genuchten 1980) is used to describe the relations between soil moisture content (θ), soil

water pressure head (h) and hydraulic conductivity (K). These relations are required to solve the Richards' equation for water flow (with evaporation and root water uptake in the top 30 cm accounting for a grass cover). The van Genuchten relations are as follows, Eqs. 1 and 2:

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

and

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

where θ_r is the residual water content [$\text{L}^3 \text{L}^{-3}$]; θ_s the saturated water content [$\text{L}^3 \text{L}^{-3}$]; α [L^{-1}], n [–] and m ($=1-1/n$) [–] shape parameters; l the pore connectivity parameter [–]; K_s the saturated hydraulic conductivity [L T^{-1}]; and $S_e = (\theta - \theta_r) / (\theta_s - \theta_r)$ the effective saturation [–].

The following hydraulic parameters are taken: $\theta_s = 0.43 \text{ cm}^3 \text{ cm}^{-3}$, $\theta_r = 0.045 \text{ cm}^3 \text{ cm}^{-3}$, $\alpha = 0.145 \text{ cm}^{-1}$, $n = 2.68$, $l = 0.5$ and $K_s = 712.8 \text{ cm day}^{-1}$.

Three different Hg contamination sources are tested. First, cinnabar (HgS) is used as a representation for a solid-phase contamination. Dissolution is simulated using a first-order rate equation based on parameters from Waples et al. (2005). The dissolution equation also includes DOM influence on the dissolution rate (i.e., cinnabar dissolution is enhanced by the interaction of DOM with the cinnabar surface; Waples et al. 2005). Second, release from a NAPL form is assessed by a simple dissolution model with a first-order rate equation (taken from Zhu and Sykes 2004). By instantaneous thermodynamical equilibrium, elemental Hg ($\text{Hg}^0(\text{l})$) first reacts to $\text{Hg}^0(\text{aq})$, which then oxidises to $\text{Hg}^{2+}(\text{aq})$. Finally, a case with Hg contamination present only in the aqueous phase (in the form of $\text{HgCl}_2(\text{aq})$) is tested. These three sources are among the most frequent species found in Hg-contaminated land. In all three cases, the initial Hg source is assumed to be homogeneously distributed in the soil profile top 10 cm (Fig. 1).

We use a 50-year time series of daily atmospheric precipitation conditions, derived from 25 years of observed precipitation and calculated potential evapotranspiration from Dessel (northern Belgium), repeated once. Initial soil solution and rainwater mineral composition that can be considered representative of northern Belgium are taken from the Dutch “National Precipitation Chemistry Network” (Stolk 2001). Besides, a constant DOM concentration is added to the initial and boundary solution composition. As mentioned above, Hg wet (and dry) deposition is neglected in the conceptual model. Cations present in rainwater (Na^+ , Mg^{2+} , Ca^{2+} , K^+) are competing with Hg for the reactive sites Xa, Xb, Xc and Xs, and for complexation with DOM Ya, Yb, Yc and Ys.

Simulation outputs include Hg mass flux at the bottom of the soil profile (leaching) and Hg volatilisation flux, as well as Hg concentration profile at different times (after 5, 10, 25 and 50 years). Concerning the sensitivity analysis, results are expressed as percentages of initial Hg of (i) Hg volatilised to the atmosphere, (ii) Hg leached out of the soil profile and (iii) Hg still present in the originally polluted soil horizon.

Sensitivity analysis

The sensitivity analysis is performed using the elementary effect method of Morris (1991). This method provides insights into which input factors may be considered to be negligible, or having a linear and additive effect, or non-linear and/or interacting effects with other factors (Campolongo et al. 2007). The input distributions of the k parameters are divided into p levels (or bins). A number r of sampling trajectories are then randomly designed across the parameter space, as described in detail in Morris (1991) and Campolongo et al. (2007). One trajectory consists of $k+1$ model realisations varying one parameter at a time, and keeping the “new” parameter value for the next realisation. Note that in the present method, correlations between parameters are not accounted for, but this would be required only in an uncertainty analysis.

One trajectory thus delivers k elementary effects, i.e. one per parameter. For each parameter, one computes then μ , the arithmetic mean of the r elementary effects, which assesses the factor overall influence on the output, and standard deviation σ , which estimates the ensemble of the factor's higher order effects, i.e. non-linear and/or interaction effects (Campolongo et al. 2007). Campolongo et al. (2007) further proposed to use μ^* (= mean of the absolute value of elementary effects) as a means of identifying model non-monotonicity (i.e. when for a given factor $|\mu| < \mu^*$ due to elementary effects of opposite signs).

A set of 13 input parameters are included in the sensitivity analysis. The parameters (or factors) are given in Table 1.

The range of initial Hg concentration (factor X_1) is arbitrarily set between 135 and 13,500 mg [Hg] kg⁻¹ [soil]. Concentrations of a few hundreds mg [Hg] kg⁻¹ [soil] are typical of anthropogenic contamination sites (e.g. Bloom et al. 2003; Bessinger and Marks 2010). At the higher bound, Bollen et al. (2008) reported Hg concentrations up to 11,000 mg [Hg] kg⁻¹ [soil]. For factor X_2 (cinnabar dissolution rate), the input bounds for the sensitivity analysis are based on the range of initial dissolution rates determined experimentally by Waples et al. (2005). The input range of Hg²⁺ reduction rate (factor X_3) is set as one order of magnitude below and above the value reported by Scholtz et al. (2003). Concerning DOM concentration (factor X_4), the input range 9 to 90 mg L⁻¹ encompasses one order of magnitude, centered around the range of DOM pore water concentrations measured by Don and

Schulze (2008; 30 and 70 mg L⁻¹ in spring and autumn, respectively) on a site (Kaltenborn) with a soil texture similar to that of the hypothetical case. Factor X_5 (exchange capacity of humic and fulvic acids, i.e. the density of HA and FA sorption sites) lower and upper bounds are based on Gustafsson (1999) value divided by 10 and multiplied by 2, respectively. For thiols (factor X_6), the exchange capacity value of Skjellberg (2008) is used, with the same rule for setting the lower and upper bounds. The log k values of Hg-DOM interactions (factors X_7 and X_8 for humic-fulvic acids and thiols, respectively) are based on Bessinger and Marks (2010) for humic and fulvic acids, and on Skjellberg (2008) for thiols. Half and double the log k values are arbitrarily chosen as input bounds for the sensitivity analysis. Similarly, the bounds of factors X_9 and X_{10} (log k values of Hg-SOM sorption for HA and FA and for thiols, respectively) are set to half and double the values determined experimentally by Bessinger and Marks (2010). Interactions between protons/cations (including Hg²⁺) and SOM HA and FA (and thiols) surface sites are treated as ion exchange reactions, X_9 (and X_{10}) being the equilibrium constants of these reactions. The higher the k value, the more preferentially a given aqueous species is attracted to the surface sites. Concerning DOM sorption on mineral surfaces (sorption coefficient K_f as factor X_{11} and total concentration of sorption sites S_{tot} as factor X_{12}), input ranges are taken from Kothawala et al. (2008) for the Langmuir isotherm—with final concentration in the formulation—fitted on seven Ah-horizon samples. The latter horizon type corresponds to the top horizon of our hypothetical soil profile. For factor X_{11} , the lower bound is set as the fitted value in Kothawala et al. (2008) decreased by one order of magnitude, while the upper bound is the double of it. The uncertainty range reported by Kothawala et al. (2008) is taken for factor X_{12} .

Using the 13 parameters of Table 1 and $p=6$ levels, 5 trajectories are produced for each Hg initial contamination type (cinnabar, NAPL and HgCl₂(aq)). Usually, between 10 and 50 trajectories are defined (Campolongo et al. 2007). However, repeating the analysis with three different pollution types provides complementary coverage of the input parameter space, even if in the present case, the 5×3 trajectories cannot strictly be considered as an ensemble of 15 trajectories. The sampling design is implemented in Matlab[®] according to Campolongo et al. (2007), who refined Morris original sampling strategy by maximising the distances between trajectories in the parameter space.

Results and discussion

A set of simulations with fixed parameter values were presented in Leterme et al. (2014). Mercury release in the pore water depends on the dissolution rate in the case of cinnabar and NAPL initial contamination. Note that with the average

Table 1 List of parameters included in the sensitivity analysis

Factor		Unit	Lower bound	Upper bound	Ref.
X ₁	Initial Hg concentration in soil	mg kg ⁻¹	135	13500	-
X ₂	Cinnabar dissolution rate	day ⁻¹ g _{OC} ⁻¹	4.57 × 10 ⁻⁴	1.42 × 10 ⁻²	(a)
X ₃	Hg ^{II} reduction rate	day ⁻¹	6.91 × 10 ⁻⁷	6.91 × 10 ⁻⁵	(b)
X ₄	DOM concentration (in boundary solution)	mg L ⁻¹	9	90	(c)
X ₅	Exchange capacity of HA and FA (SOM top 30 cm)	meq g _{OC} ⁻¹	0.53	10.6	(d)
X ₆	Exchange capacity of thiols (SOM top 30 cm)	meq g _{OC} ⁻¹	0.0047	0.094	(e)
X ₇	log <i>k</i> complexation Hg-DOM (HA and FA)	-	HgYa ₂ : -2.2 HgYb ₂ : -15.2 HgYc ₂ : -3.6 HgOHYa: -6.0 HgOHYb: 0.9 HgOHYc: 1.0	-0.55 -3.8 -0.9 -1.5 3.6 4.0	(f)
X ₈	log <i>k</i> complexation Hg-DOM (thiols)	-	HgYs ₂ : 11.0	44.0	(e)
X ₉	log <i>k</i> sorption Hg-SOM (HA and FA)	-	HgXa ₂ : 1.75 HgXb ₂ : 2.15 HgXc ₂ : 2.54 HgOHXa: 3.85 HgOHXb: 3.85 HgOHXc: 5.1	7.0 8.6 10.16 15.4 15.4 20.4	(f)
X ₁₀	log <i>k</i> sorption Hg-SOM (thiols)	-	HgXs ₂ : 7.7	30.8	(f)
X ₁₁	Sorption coeff. DOM to soil minerals	-	5.6 × 10 ⁻⁴	1.23 × 10 ⁻²	(g)
X ₁₂	Max. adsorption capacity of DOM to minerals	mg kg ⁻¹	109	601	(g)
X ₁₃	NAPL dissolution rate	day ⁻¹	8.64 × 10 ⁻⁵	8.64 × 10 ⁻³	-

(a) Waples et al. (2005)

(b) Scholtz et al. (2003)

(c) Don and Schulze (2008)

(d) Gustafsson (1999)

(e) Skyllberg (2008)

(f) Bessinger and Marks (2010)

(g) Kothawala et al. (2008)

NAPL non-aqueous phase liquid, DOM dissolved organic matter, SOM solid organic matter, HA humic acids, FA fulvic acids

The input distributions are uniform on a log₁₀ scale for factors X₁, X₃ and X₁₃; uniform on a log₂ scale for factors X₈ and X₁₀; and uniform for the others

dissolution rates, all Hg NAPL is dissolved after 25 simulated years, and half of the cinnabar after 50 years. After dissolution—or immediately in the case of HgCl₂(aq) as initial contamination—Hg mobility is mainly controlled by two processes: sorption to SOM and complexation with DOM. SOM thiol groups are occupied first early in the simulation but are generally outnumbered due to the high Hg concentrations typical of anthropogenic contaminations. Therefore, HA and FA sorption sites progressively sorb the additional Hg²⁺ released from cinnabar/NAPL dissolution.

Complexes with DOM thiol groups are the most important Hg leaching species. However, Hg complexation with inorganic ligands is important in the case of mercuric chloride as the initial Hg contamination, due to the massive and immediate Hg release to pore water.

In the simulations presented here, volatilisation is very low because the Hg²⁺ reduction rate is a function of Hg²⁺ concentration in pore water, which is always found to be very low.

The following paragraphs present the results of the sensitivity analysis, grouped by the species of the Hg initial contamination (cinnabar, NAPL, mercuric chloride).

Cinnabar as Hg contamination source

Model outputs for which parameter sensitivity is evaluated are the % of Hg volatilised, the % of Hg leached below the bottom of the 1-m-deep soil profile and the % of Hg remaining in the top 10 cm of the soil profile. Figure 2 plots μ^* and σ values for the Morris trajectories with cinnabar (HgS) as initial contamination. High μ^* values denote influential parameters,

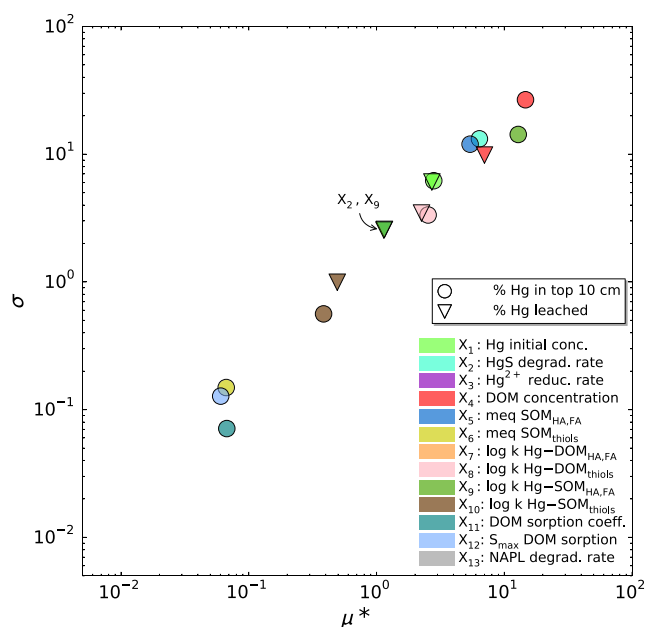


Fig. 2 Sensitivity analysis plot showing μ^* (mean of the absolute value of elementary effects) and σ (standard deviation of elementary effects) for 12 parameters (X_{13} NAPL dissolution rate being not relevant) and 5 trajectories with cinnabar (HgS) as Hg initial contamination

while σ reflects the degree of parameter interactions and non-linear effects. All μ^* (and μ) values for the indicator % Hg volatilised are zero (Online Resource 1), because Hg volatilisation is always very limited, as reported in Table 2 (max. 0.00002 % after 50 years). Therefore, this indicator is not visible in Fig. 2.

Because volatilisation is very low, factor sensitivity ranking is very similar between the indicators % Hg in top 10 cm and % Hg leached. These indicators are negatively correlated, as shown by their μ values (Online Resource 1).

X_4 (DOM concentration) is the most sensitive factor for the indicators % Hg leached and % Hg remaining in top horizon. A higher DOM concentration in infiltrating water increases Hg leaching in two ways. First, because the dissolution rate

is directly proportional to DOM concentration (Eq. 8 in Leterme et al. 2014), more cinnabar is dissolved, and thus, more Hg is potentially mobilised. Second, Hg complexation with DOM thiol groups increases, forming the mobile species $\text{HgYs}_2(\text{aq})$, which, in most cases, is favoured over the sorbed species HgXa_2 , HgOHXa , etc. (compare $\log k$ values of $\text{HgYs}_2(\text{aq})$ and $\log k$ values of Hg-SOM complexes in Table 1).

The percentage of Hg leached after 50 years varies from 0 to 14.3 % in the sensitivity analysis (Table 2). In comparison to other test cases (see “NAPL as Hg contamination source” and “ $\text{HgCl}_2(\text{aq})$ as Hg contamination source”), this lower percentage is due to the cinnabar dissolution rate. Among all 65 simulations of these 5 trajectories (with cinnabar as Hg initial contamination), the percentage of cinnabar dissolved after 50 years ranges between 1 and 82 %. However, it is less than 10 % in 21 simulations and above 50 % in 19 simulations.

Concerning the % Hg remaining in the top horizon after 50 simulated years, the second most sensitive parameter is the $\log k$ value of Hg sorption on HA and FA (factor X_9). Figure 3 shows the depth distribution of cinnabar and Hg sorbed to SOM after 5, 10, 25 and 50 years. Hg sorption on HA and FA is stronger in Fig. 3b than in Fig. 3a simulation, the rest of the parameter set being identical. The total Hg leaching after 50 simulated years is similar between the two simulations (12 and 9 % of the initial Hg contamination, respectively). However, Fig. 3 shows how factor X_9 variations result in qualitatively different patterns of vertical Hg distribution in the soil profile. Higher X_9 values mean that Hg^{2+} is sorbing more strongly to SOM HA and FA surface sites, and therefore, Hg^{2+} sorption becomes increasingly favoured compared to complexation with organic (HA and FA, thiols) or inorganic (mainly OH^- and Cl^-) mobile ligands. The percentage of Hg remaining in the top 10 cm of the soil profile after 50 years varies between 0 and 100 % (Table 2). Small Hg amounts are present as dissolved species, the rest being either (undissolved) cinnabar or Hg sorbed to SOM.

Concerning the binding strength of Hg to SOM, factor X_9 (HA and FA) has a higher sensitivity than factor X_{10} (thiols).

Table 2 Simulation results after 50 years, for the different Hg initial contamination types

Hg initial contamination type	Hg volatilised (%)	Hg leached (%)	Hg in top 10 cm (%)	Hg between 11 and 100 cm (%)
Cinnabar	<0.0001	0 - 14.3	Hg-SOM, 0.046 - 81.9 $\text{Hg}^{2+}(\text{aq})$, 0 - 0.004 HgS, 18.0 - 99.3	Hg-SOM, 0 - 39.8 $\text{Hg}^{2+}(\text{aq})$, 0 - 0.063
Hg NAPL	0 - 0.0024	0 - 89.9	Hg-SOM, 0 - 99.9 $\text{Hg}^{2+}(\text{aq})$, 0 - 0.008 Hg NAPL, 0 - 19.4	Hg-SOM, 0.0002 - 49.4 $\text{Hg}^{2+}(\text{aq})$, 0 - 0.136
$\text{HgCl}_2(\text{aq})$	0 - 0.0638	0 - 100	Hg-SOM, 0 - 99.1 $\text{Hg}^{2+}(\text{aq})$, 0 - 0.006	Hg-SOM, 0.001 - 48.5 $\text{Hg}^{2+}(\text{aq})$, 0 - 0.204

The minimum and maximum outputs of all sensitivity analysis runs are given, expressed in percentage of the initial Hg contamination

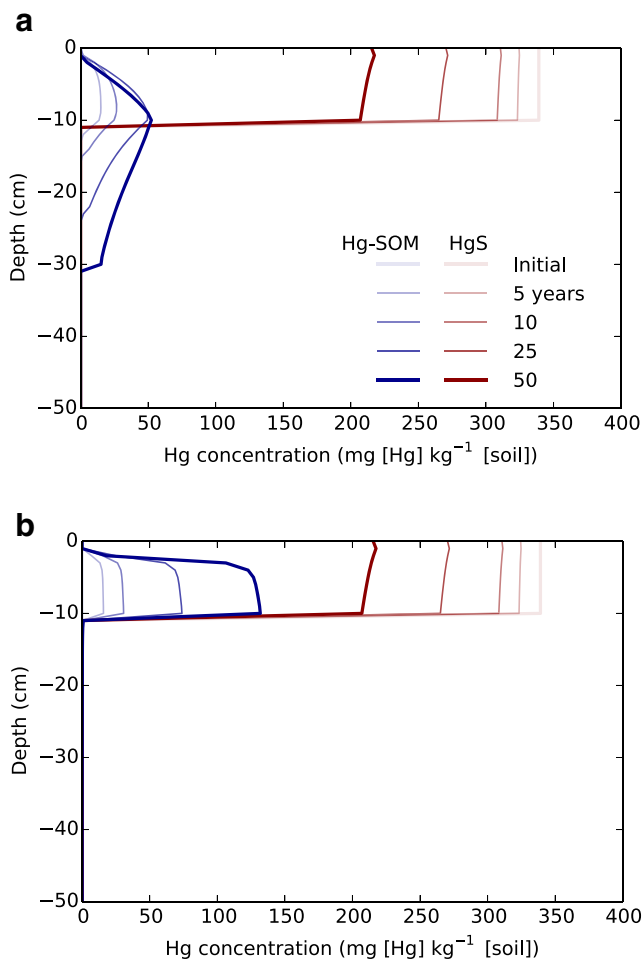


Fig. 3 Depth distribution of cinnabar (HgS; red lines) and Hg sorbed to SOM (blue lines) at $t=0, 5, 10, 25$ and 50 years; from two simulations of the same trajectory, with cinnabar as Hg initial contamination. Only factor X_9 ($\log k$ of Hg sorption on humic and fulvic acids) differs between simulations **a** and **b**. **a** $X_9=0.4$ and **b** $X_9=1$; reporting $X_9 \log k$ values of each oxygen site reactivity on a normalized $[0-1]$ interval. Note that for clarity, the y-axis stops at 50-cm depth

Two processes explain this. First, the binding capacity of thiol groups (see Table 1) is always large enough so that ‘stronger’ or ‘weaker’ binding does not really matter. Second, the less strongly binding, but much more abundant HA and FA sites, can be more readily accessed by other speciation reactions in their variability range (Table 1). Therefore, factor sensitivity is higher than for thiols.

The relatively high sensitivity of factor X_1 (initial Hg concentration) is partly a consequence of the indicators being expressed in terms of percentage of the initial Hg contamination. The crucial element for Hg mobility is the abundance of sorption sites relative to the Hg contamination. In soils with background Hg concentrations, sorption sites provided by thiols are in excess compared to Hg (Skylberg 2010) and the sorption strength on HA and FA is probably not so sensitive. For highly Hg contaminated soils, thiol sites may be saturated and Hg

sorption on HA and FA then becomes important. Thus, the influence of factor X_1 (initial Hg concentration), as captured by elementary effects, can vary depending on, e.g. the abundance of thiol or HA/FA sorption sites (factors X_5 and X_6). For example, a moderate increase of initial Hg concentration might have no effect on the amount of Hg leaching if strongly sorbing HA and FA sites are still available, whereas it has when no free sorbing HA and FA sites are available. When elementary effect values of one parameter show a high variability between trajectories, this results in higher σ values (Fig. 2) reflecting these important parameter interactions.

The mechanism explaining factor X_2 (cinnabar dissolution rate) sensitivity is as follows: the faster HgS dissolves, the more Hg potentially leaves the horizon originally contaminated.

Factors X_3 (Hg^{2+} reduction rate), X_6 ($\text{SOM}_{\text{thiols}}$ exchange capacity), X_7 ($\log k$ Hg-DOM_{HA,FA}), X_{11} and X_{12} (related to DOM sorption to mineral surfaces) are at the lower end of sensitivity ranking. Factor X_7 low sensitivity is explained by the higher affinity of Hg^{2+} with OH^- (and Cl^-) anions compared to HA and FA: $\text{Hg-DOM}_{\text{thiols}} > \text{Hg-inorganic} (\text{OH}^-, \text{Cl}^-) > \text{Hg-DOM}_{\text{HA,FA}}$. When DOM thiol sites are Hg saturated, any exceeding Hg^{2+} in pore water mainly complexes to $\text{Hg}(\text{OH})_2(\text{aq})$ or $\text{HgOHCl}(\text{aq})$. Figure 4 shows, in the absence of SOM, how Hg speciation in the soil water evolves with increasing Hg concentration. At low Hg concentrations ($<0.001 \text{ mmol L}^{-1}$), Hg^{2+} reacts exclusively with DOM thiol groups (to form $\text{HgYs}_2(\text{aq})$). When DOM thiol groups are saturated, $\text{HgCl}_2(\text{aq})$ is first formed, before $\text{HgOHCl}(\text{aq})$ and $\text{Hg}(\text{OH})_2(\text{aq})$. It can be noted that Hg complexation with DOM HA and FA does not occur. Therefore, DOM HA and FA ligands do not influence Hg mobility.

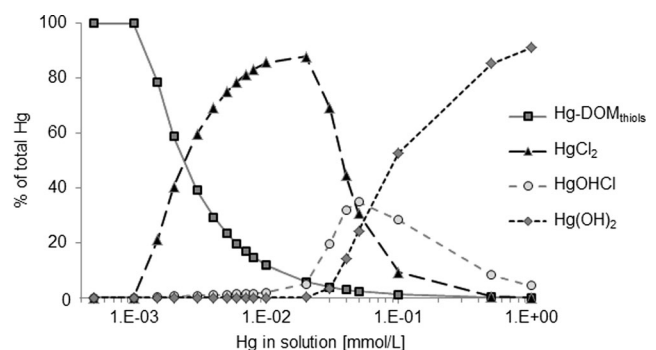


Fig. 4 Hg speciation in the soil water as a function of Hg total concentration, calculated in the absence of SOM. The DOM concentration is 50 mg L^{-1} and reaction constants are the initial values (middle of Table 1 input ranges). The species shown are Hg-DOM_{thiols} ($\text{HgYs}_2(\text{aq})$; squares), $\text{HgCl}_2(\text{aq})$ (triangles), $\text{HgOHCl}(\text{aq})$ (circles) and $\text{Hg}(\text{OH})_2(\text{aq})$ (diamonds)

NAPL as Hg contamination source

For the simulations with NAPL as Hg source, the percentage of Hg volatilised after 50 years was never above 0.0024 % of the initial mercury (Table 2). Kinetically based NAPL dissolution leads to Hg^0 which immediately oxidises to Hg^{2+} ; the rate-limiting factor in the modelled volatilisation process is the Hg^{2+} concentration (Leterme et al. 2014).

Results of the elementary effect analysis for the indicators % Hg in top 10 cm and % Hg leached are shown in Fig. 5. Hg sorption strength to HA and FA (factor X_9) and initial concentration (X_1) are the most sensitive parameters for both indicators. Compared to the case with cinnabar as the contamination source (Fig. 2), more Hg is released to the soil system because of a generally higher Hg NAPL dissolution rate. Therefore, the exchange capacity of SOM thiol sites is more likely to be exceeded, and sorption to HA and FA becomes more sensitive than in the case with cinnabar as Hg source.

The exchange capacity of SOM thiol sites (factor X_6) is also a sensitive parameter, contrary to the previous case (cinnabar as Hg source). Detailed investigation of the results illustrates how parameter interactions play an important role. In the case of factor X_6 , the calculated elementary effect is (quasi-)null for four out of the five trajectories (not shown). Thus, X_6 sensitivity visible in Fig. 5 stems from just one trajectory (or elementary effect). Hg^{2+} leaching fluxes for the simulations corresponding to that particular elementary effect are shown in Fig. 6. It can be seen that

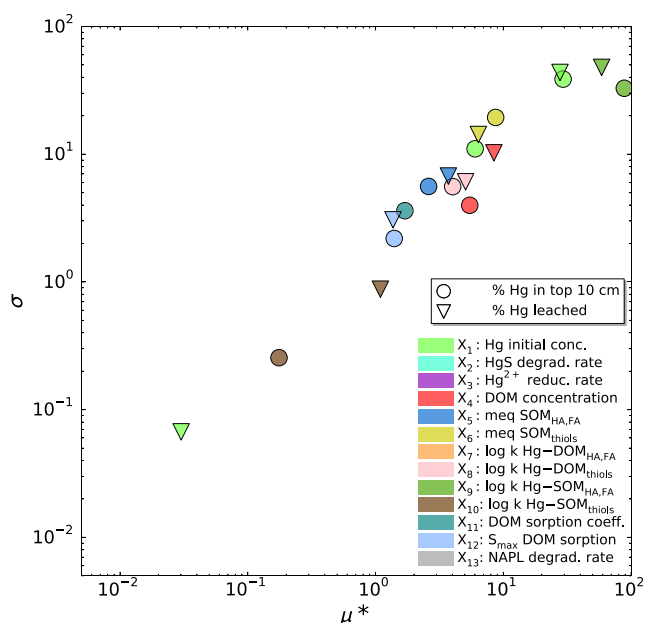


Fig. 5 Sensitivity analysis plot showing μ^* (mean of the absolute value of elementary effects) and σ (standard deviation of elementary effects) for 12 parameters (X_2 cinnabar dissolution rate being not relevant) and 5 trajectories with NAPL as Hg initial contamination

factor X_6 influence on leaching appears after approximately 23 simulated years only. At that time, the maximum sorption capacity of thiol groups in the soil top 30 cm has been reached in one simulation (green line; lower X_6), but not in the second one (orange line; higher X_6). As a consequence, Hg^{2+} leaching flux in the former simulation is higher from then on. Compared to the elementary effects calculated in other trajectories, the two simulations shown in Fig. 6 are characterised by a low initial Hg concentration (X_1) associated to a very low HA and FA sorption strength (X_9). Factor X_6 sensitivity appears only at low initial concentration because at higher Hg concentrations changes of the thiol exchange capacity—much smaller compared to that of HA and FA—would not affect much the results expressed in percentage of the initial Hg.

For factor X_4 , μ^* is larger than $|\mu|$ which denotes a non-monotonic behaviour of the model (μ values in Online Resource 1). This means, for instance, that more DOM does not necessarily lead to more Hg leaching, but that—a priori counter-intuitively—it can also cause less leaching. A detailed investigation of the results shows that one elementary effect (out of five) is responsible for the observed non-monotonicity. The corresponding simulations are characterised by a very weak sorption to $\text{SOM}_{\text{HA,FA}}$ (X_9) compared to the other trajectories. In this case, Hg inorganic species in solution are dominant (mainly in the form of $\text{Hg}(\text{OH})_2$). Increasing DOM concentrations then leads to more HgOH^+ sorption onto HA and FA at the expense of $\text{Hg}(\text{OH})_2(\text{aq})$ complexation, thereby decreasing Hg leaching. This is illustrated in Fig. 7, in which a replicated Phreeqc batch simulation shows the effect of increasing DOM concentrations on Hg speciation, depending on factor X_9 value. Continuous lines correspond to Hg speciation in the case of a very weak Hg sorption to $\text{SOM}_{\text{HA,FA}}$ (X_9 lower bound; Table 1), while the dashed lines use $\log k$ values corresponding to the third quartile of the input range. Model non-monotonicity is detected in the former case, i.e. when higher DOM concentration causes more Hg sorption and less leaching as opposed to the sensitivity observed in other trajectories.

NAPL degradation rate (X_{13}) has a relatively high sensitivity with respect to the indicator % Hg in top 10 cm, but it should be noted that sensitivity depends partly on the input range, which was set arbitrarily (Table 1).

Sensitivity to factors X_3 (Hg^{2+} reduction rate) and X_7 ($\log k$ Hg- $\text{DOM}_{\text{HA,FA}}$) is negligible (Fig. 5). Factors X_{11} and X_{12} (related to DOM sorption to mineral surfaces) generally show a higher sensitivity than in the case of cinnabar as Hg source. Here also, the sensitivity detected for these factors essentially comes from the trajectory characterised by a very low sorption to $\text{SOM}_{\text{HA,FA}}$ (X_9). Because of the effect of DOM concentrations on Hg sorption (Fig. 7), simulation results are similarly affected by any change in DOM pore water concentration due to DOM sorption to mineral surfaces.

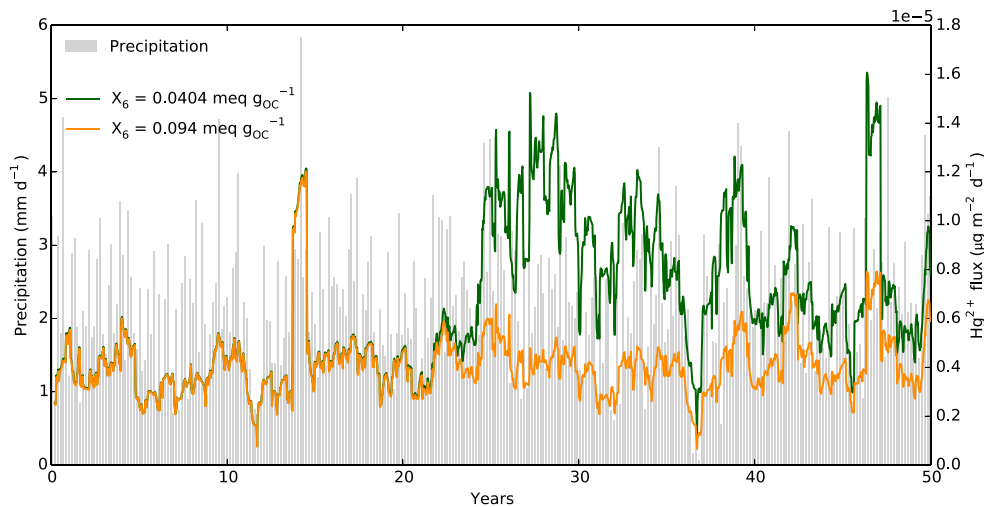


Fig. 6 Comparison of Hg^{2+} leaching flux vs time, for two simulations from the same trajectory, with NAPL as Hg initial contamination. Only factor X_6 (exchange capacity of thiol groups) differs between the two parameter sets. Plotted fluxes are a moving average (31-day window)

calculated from the daily data. After 50 simulated years, cumulative Hg leaching is 35 % (orange line; higher X_6) and 54 % (green line; lower X_6) of the initial contamination. Grey bars show the surface precipitation input (averaged every 2 months for clarity)

$\text{HgCl}_2(\text{aq})$ as Hg contamination source

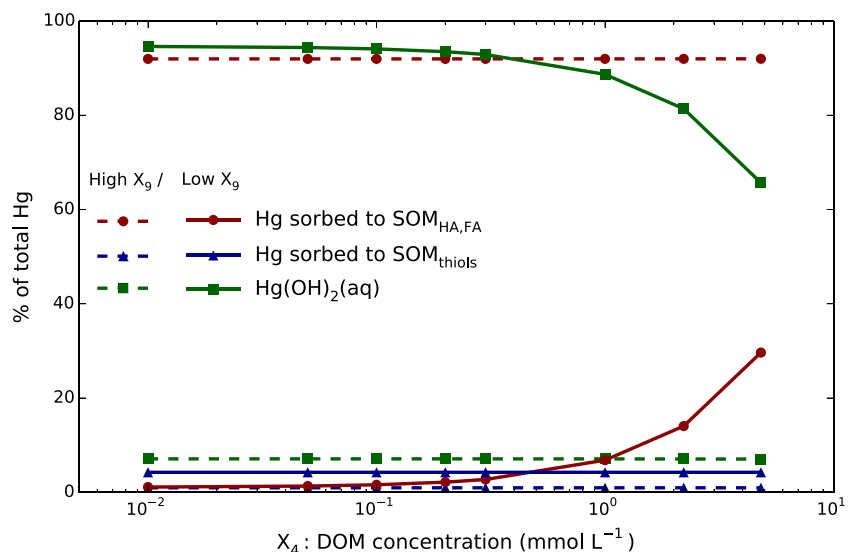
When the contamination source is $\text{HgCl}_2(\text{aq})$, all Hg is immediately mobilisable. This leads to mostly higher leaching rates (up to 100 % of the initial Hg after 50 simulated years; Table 2) compared to the previous simulations with cinnabar or NAPL as Hg sources. Sorption mechanisms are less efficient to prevent Hg leaching, due to higher Hg pore water concentrations. Another consequence is that Hg^{2+} reduction and volatilisation increase, although not exceeding 0.0638 % of the initial Hg among all simulation runs (Table 2).

Figure 8 shows the results of the Morris sensitivity analysis for the three indicators. Factor X_9 ($\log k$ Hg-SOM_{HA,FA}) is the most influential factor, similarly to the case with NAPL as the contamination source. In the present case, most of the initial

Hg^{2+} ions released in the aqueous phase rapidly sorb to SOM (within a few days). Actually, Hg sorbed to SOM could be viewed as the initial Hg pool. This explains why factors X_5 and X_6 (determining SOM exchange capacity) are also ranking high regarding their sensitivity. Other factors having an important impact include X_1 (initial Hg concentration), X_4 (DOM concentration) and X_8 ($\log k$ Hg-DOM_{thiols}). Concerning Hg volatilisation, X_1 , X_3 (Hg^{2+} reduction rate) and X_9 ($\log k$ Hg-SOM_{HA,FA}) are the most sensitive factors. Factors X_1 and X_9 determine the amount of Hg^{2+} in the soil solution, being available for reduction and volatilisation.

Figure 9 illustrates the sensitivity of simulated Hg volatilisation to changes in the initial concentration. Four simulations from two trajectories are plotted, with only factor X_1 varying between the parameter sets of a same trajectory.

Fig. 7 Hg speciation as a function of dissolved organic matter (DOM) concentration (factor X_4), for two contrasting values of factor X_9 ($\log k$ values of Hg sorption to SOM humic and fulvic acids (HA, FA)). The case with a high X_9 (upper quartile of the input range) is plotted using dashed lines, while the case with a low X_9 (lower bound of the input range) is plotted using continuous lines. The latter case illustrates a parameter set for which a DOM concentration increase results in a Hg leaching decrease



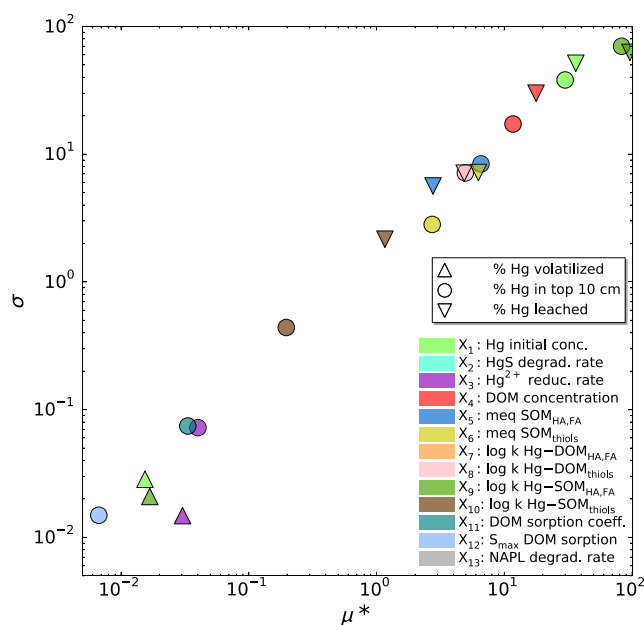


Fig. 8 Sensitivity analysis plot showing μ^* (mean of the absolute value of elementary effects) and σ (standard deviation of elementary effects) for 11 parameters (X_2 and X_{13} cinnabar and NAPL dissolution rates being not relevant) and 5 trajectories with $\text{HgCl}_2(\text{aq})$ as Hg initial contamination

Although partly an artefact due to model indicators being expressed in % of the initial Hg, elementary effects indicate that the model is non-monotonic with respect to factor X_1 . For trajectory 1 in Fig. 9, X_1 increase from 135 to 2138 mg [Hg] kg^{-1} [soil] results in proportionally less volatilisation (0.06 and 0.03 % of the initial Hg contamination, respectively). On the contrary, for trajectory 2 in Fig. 9, increasing X_1 value results in a higher total volatilisation (from 0.001 to 0.02 % of the initial contamination). The explanation of this non-

monotonic behaviour is not clear but lies in the influence of factor X_9 ($\log k \text{ Hg-SOM}_{\text{HA,FA}}$).

Sensitivity to factor X_7 ($\log k \text{ Hg-DOM}_{\text{HA,FA}}$) is negligible. Factors related to DOM sorption to mineral surfaces (X_{11} and X_{12}) also have a very low influence (see Fig. 8).

Discussion

Figure 10 visualises all calculated parameter sensitivities (μ^*), including the different indicators (% Hg volatilised, % Hg in top 10 cm, % Hg leached) and the three Hg contamination sources (cinnabar, NAPL, $\text{HgCl}_2(\text{aq})$). This helps getting an overview of the general model sensitivity.

For the indicators % Hg in top 10 cm and % Hg leached, Fig. 10 shows that factors X_1 (initial Hg concentration), X_4 (DOM concentration), X_8 ($\log k \text{ Hg-DOM}_{\text{thiols}}$) and X_9 ($\log k \text{ Hg-SOM}_{\text{HA,FA}}$) are in general the most sensitive.

Factor sensitivity is also high for X_5 and X_6 (SOM exchange capacity), except when cinnabar is the contamination source. This is due to the lower Hg concentrations simulated in the latter case, which less frequently leads to sorption site saturation.

Factors X_2 and X_{13} (cinnabar and NAPL degradation rates) are also important when the corresponding contamination source is considered and is, at least for cinnabar, as sensitive as X_1 .

However, it should be noted that a precise factor ranking is not the primary objective of a Morris analysis. Instead, it is better used to determine which factors have or not have an influence on model output (Morris 1991). In this respect, Fig. 10 shows that factors X_3 (Hg^{2+} reduction rate) and X_7

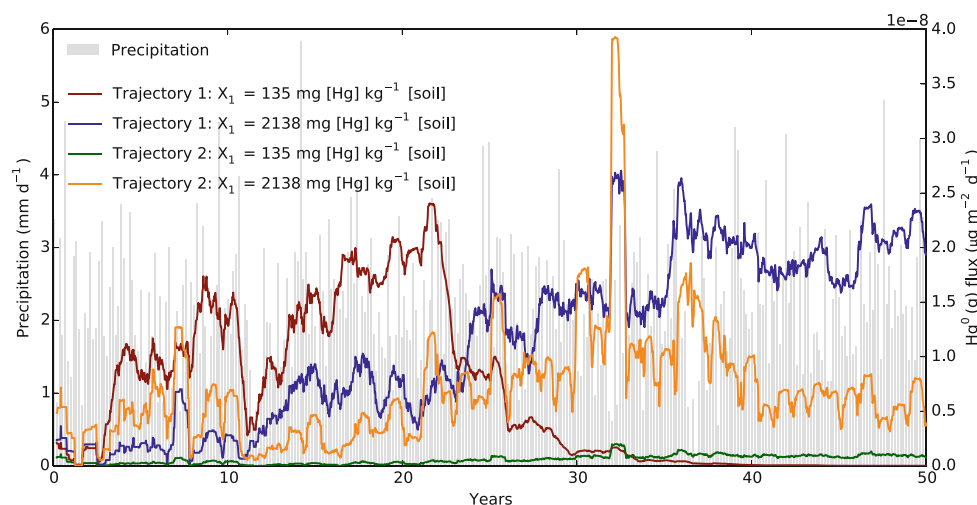


Fig. 9 Comparison of $\text{Hg}^0(\text{g})$ volatilisation flux vs time, for four simulations from two trajectories, with $\text{HgCl}_2(\text{aq})$ as Hg initial contamination. Only factor X_1 (initial Hg concentration) differs between the two parameter sets of each trajectory. Plotted fluxes are a moving average (31-day window) calculated from the daily data. After 50

simulated years, cumulative Hg volatilisation is 0.064 % (red line), 0.030 % (blue line), 0.019 % (green line) and 0.029 % (orange line) of the initial contamination. Grey bars show the surface precipitation input (averaged every 2 months for clarity)

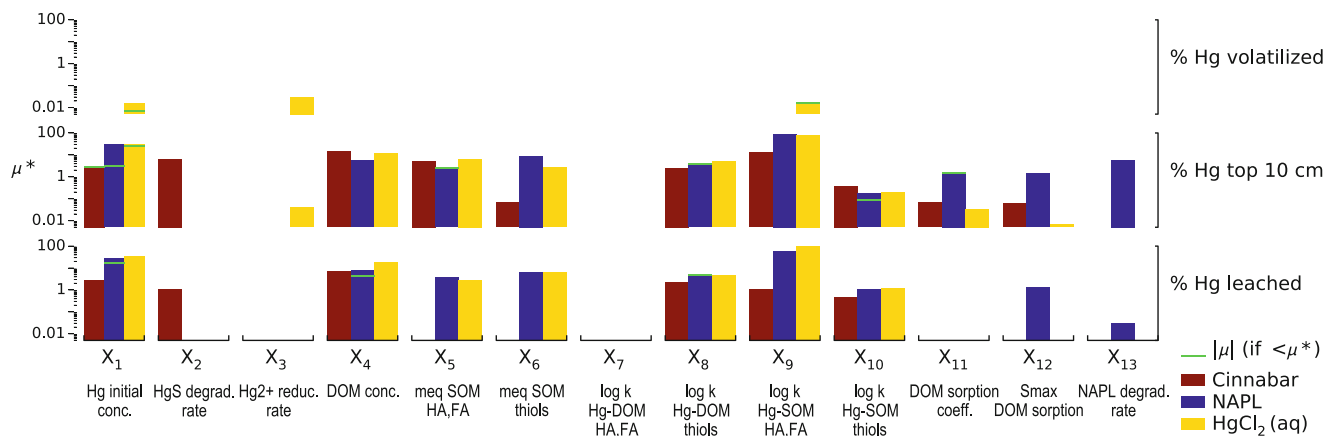


Fig. 10 Summary of factor sensitivities (μ^*) for the 13 parameters (X_1 to X_{13}) included in the sensitivity analysis, and for the three chosen indicators (% Hg volatilised, % Hg in top 10 cm and % Hg leached). The bar colour refers to the Hg contamination source: cinnabar (red),

NAPL (blue) or mercuric chloride (yellow). Non-monotonic model behaviour is detected when $|\mu| < \mu^*$ and is indicated by a green line (at $|\mu|$ y-value). Note the logarithmic y-scale

(log k Hg-DOM_{HA,FA}) do not play a significant role in the model. For X_3 , this information has to be taken with caution given the limitations mentioned above about Hg volatilisation modelling. As discussed above (Fig. 4), that factor X_7 has a negligible sensitivity is a consequence of the log k constants chosen for organics (Table 1) compared to inorganic complexation assessed with IM003_THERMODDEM database. Once thiol groups are saturated, free Hg^{2+} in the aqueous phase preferentially binds to inorganic anions. This is contradicting previous simulations with the MINTEQ database (Reddy and Aiken 2001). The wide range of log k constants attributed to Hg-DOM interactions in the literature (over 25 orders of magnitude in the review of Ravichandran 2004) illustrates the difficulty to correctly model Hg speciation. There is an agreement on Hg preferential binding to sulphur groups (thiols), but currently no definitive answer on Hg relative affinity between inorganic ligands and oxygen-containing functional groups. However, this can have a very important effect on Hg mobility as shown in the present study.

Non-monotonic model behaviour is indicated in Fig. 10 by plotting the value of $|\mu|$ (green line) when it is lower than μ^* . Non-monotonic model behaviour is mostly detected when NAPL is the Hg contamination source. Our interpretation is that this is a consequence of the NAPL source release function being an intermediate between those based on $\text{HgCl}_2(\text{aq})$ (instantaneous Hg release at high concentrations) and on cinnabar (low degradation rate and incomplete release). This produces, in the case of NAPL simulations, a broader spectrum of sensitive parameter sets and hence a higher probability of more complex model behaviour. Overall, the sensitivity analysis performed with three different Hg contamination sources had a cumulative effect on the input parameter space coverage by the Morris trajectories. Therefore, the total number of trajectories seems sufficient for encompassing the model complexity.

It is obvious in Fig. 10 that the low (or null) simulated volatilisation rates had a strong impact on the calculated sensitivities for this indicator. Only when the initial Hg contamination is $\text{HgCl}_2(\text{aq})$, three parameters were showing some sensitivity (X_1 , X_3 and X_9). If compared to volatilisation rates measured on some polluted sites, the model does not simulate Hg volatilisation realistically. For example, Rinklebe et al. (2010) reported 0.01 to $0.85 \mu\text{g m}^{-2} \text{h}^{-1}$ Hg emission from heavily polluted floodplain soils. Llanos et al. (2011) monitored Hg volatilisation on contaminated soil samples from the Almadén mercury mining area. Total Hg concentrations in the soil were up to $\sim 10,000 \text{ mg kg}^{-1}$ and the maximum volatilisation rate measured exceeded $10 \mu\text{g m}^{-2} \text{h}^{-1}$.

In contrast, among all simulations performed for the present sensitivity analysis, Hg volatilisation rarely exceeded $10^{-7} \mu\text{g m}^{-2} \text{h}^{-1}$, i.e. five orders of magnitude lower than emission rates commonly measured on contaminated soils. This value is even lower than estimates obtained for soils that are not severely contaminated. In a study of Hg fate in UK soils, Tipping et al. (2011) derived Hg leaching rate from the partitioning of OM between solid and solution, and volatilisation rate from published field observations or estimates of volatilisation fluxes and corresponding Hg soil pools. With initial Hg topsoil concentrations ranging from 0.035 to 0.5 mg kg^{-1} , their results showed Hg volatilisation and leaching fluxes to be of the same order of magnitude ($\sim 10^{-4}$ to $10^{-2} \mu\text{g m}^{-2} \text{h}^{-1}$).

In our model, Hg^{2+} reduction rate depends on the total Hg^{2+} concentration in the aqueous phase and not on sorbed species (Leterme et al. 2014). Because Hg^{2+} concentration in the aqueous phase is relatively low at any time, Hg reduction and volatilisation remain limited. If applied to a real case showing significant Hg volatilisation, an effective model calibration could require to drastically increase Hg^{2+} reduction rate beyond factor X_3 input range (Table 1).

Finally, it should be noted here that the unrealistic conceptualisation of DOM production in the model (i.e. input via rainwater; factor X_4) weakens the reliability of long-term predictions. As already reported by Bessinger and Marks (2010), DOM dynamics in the soil profile are a key element for predicting Hg long-term fate. The model would therefore greatly benefit of integrating a specific description of soil DOM dynamics (e.g. Kalbitz et al. 2000; Neff and Asner 2001; Braakhekke et al. 2011; Ota et al. 2013).

Even though computation time is relatively high (about 6 h on a standard 4-core laptop, processor Intel® Core™ i5-3360 M CPU @ 2.80 GHz for one 50-year simulation with boundary conditions defined at a daily time step), a screening of the full parameter space is indispensable given the many parameter interactions observed (e.g. between Hg total concentration, abundance and binding strength of sorption sites). Sigma values demonstrate that factor interactions are important; these would not be captured by a one-at-a-time sensitivity analysis. Also, examining the elementary effects individually allows to detect particular parameter sets resulting in a high sensitivity for a given factor. For example, DOM sorption to mineral surfaces was found especially sensitive for simulations characterised by factor X_4 non-monotonic influence, with NAPL as Hg source.

Conclusions

A sensitivity analysis was applied to a Hg reactive transport model using Morris method of elementary effects. This allowed to identify the most critical parameters and processes for different contamination sources and different indicators.

Parameter sensitivity differs from one scenario to the other depending on pollution type (cinnabar, NAPL or $\text{HgCl}_2(\text{aq})$) and on the indicator assessed (volatilised Hg, leached Hg, Hg in soil horizon originally polluted). In general, DOM concentration in soil water is a critical parameter due to the strong interaction between Hg^{2+} and the thiol groups. The log k constant used to characterise $\text{Hg-DOM}_{\text{thiols}}$ complexation is accordingly found to be a sensitive parameter. Other important parameters are those related to Hg sorption on SOM (in particular with the fulvic and humic acids). Initial Hg concentration is also often identified as a sensitive parameter, because it interacts with SOM exchange capacity to determine Hg immobilisation potential in the soil system. Interactions between factors and non-linear effects as measured by the elementary effect method are generally important, but again depend on the contamination type and indicator. Several simulation runs were presented in more details to illustrate the model capability to represent complex behaviour. In this respect, non-monotonic model behaviour was appropriately detected by the sensitivity analysis method applied here.

Soil physical and climate parameters were not included in the sensitivity analysis. While they would probably be sensitive for the fluxes between the different model compartments

(e.g. faster/slower leaching depending on effective infiltration rate), their influence on Hg speciation should be rather limited. Seuntjens et al. (2002) analysed the sensitivity of field-scale Cd leaching flux to variations in chemical and soil physical parameters. In nearly all the scenarios that they considered, the effect of water retention curves parameters was insignificant compared to chemical parameters. Only the hydraulic conductivity of the humus top layers was found to have an influence on the maximum Cd leaching flux.

Comparison with estimated or measured Hg volatilisation fluxes suggests that the model underestimates Hg^{2+} reduction and/or $\text{Hg}^0(\text{g})$ volatilisation. This shows that, if used for example to study remediation options at a particular contaminated site, cautious model parameterisation and calibration is needed first.

For future developments, it may be desirable to better characterise DOM input and cycle rather than introducing it through rainwater composition. Given the importance of DOM in the fate and transport of Hg, better insights in the processes related to Hg-DOM interactions could be gained by integrating a submodel of DOM-SOM cycle in the soil.

Acknowledgments The present study is part of the IMaHg project, which aims at providing recommendations to improve management of sites contaminated by mercury within the SNOWMAN funding framework. This particular work was done with the financial support of the Public Waste Agency of Flanders (OVAM).

References

- Bernaus A, Gaona X, van Ree D, Valiente M (2006) Determination of mercury in polluted soils surrounding a chlor-alkali plant: Direct speciation by X-ray absorption spectroscopy techniques and preliminary geochemical characterisation of the area. *Anal Chim Acta* 565(1):73–80
- Bessinger BA, Marks CD (2010) Treatment of mercury-contaminated soils with activated carbon: A laboratory, field, and modeling study. *Remediat J* 21(1):115–135. doi:10.1002/rem.20275
- Biester H, Gosar M, Müller G (1999) Mercury speciation in tailings of the Idrija mercury mine. *J Geochem Explor* 65(3):195–204
- Blanc P, Lassin A, Piantone P (2012) THERMODDEM a database devoted to waste minerals. BRGM, Orléans, France. <http://thermoddem.brgm.fr>
- Bloom NS, Preus E, Katon J, Hiltner M (2003) Selective extractions to assess the biogeochemically relevant fractionation of inorganic mercury in sediments and soils. *Anal Chim Acta* 479(2):233–248
- Bollen A, Wenke A, Biester H (2008) Mercury speciation analyses in HgCl_2 -contaminated soils and groundwater-Implications for risk assessment and remediation strategies. *Water Res* 42(1-2):91–100
- Braakhekke MC, Beer C, Hoosbeek MR, Reichstein M, Kruijt B, Schrumph M, Kabat P (2011) SOMPROF: A vertically explicit soil organic matter model. *Ecol Model* 222(10):1712–1730. doi:10.1016/j.ecolmodel.2011.02.015
- Campolongo F, Cariboni J, Saltelli A (2007) An effective screening design for sensitivity analysis of large models. *Environ Model Softw* 22(10):1509–1518
- Davis A, Bloom NS, Que Hee SS (1997) The Environmental Geochemistry and Bioaccessibility of Mercury in Soils and

- Sediments: A Review. *Risk Anal* 17(5):557–569. doi:10.1111/j.1539-6924.1997.tb00897.x
- Don A, Schulze E-D (2008) Controls on fluxes and export of dissolved organic carbon in grasslands with contrasting soil types. *Biogeochemistry* 91(2):117–131. doi:10.1007/s10533-008-9263-y
- Gao Y, Shi Z, Long Z, Wu P, Zheng C, Hou X (2012) Determination and speciation of mercury in environmental and biological samples by analytical atomic spectrometry. *Microchem J* 103(0):1–14. doi:10.1016/j.microc.2012.02.001
- Gustafsson JP (1999) WinHumicV For Win95/98/NT. Retrieved from <http://www2.lwr.kth.se/English/OurSoftWare/WinHumicV/index.htm>
- Jacques D, Šimůnek J, Mallants D, Van Genuchten MT (2006) Operator-splitting errors in coupled reactive transport codes for transient variably saturated flow and contaminant transport in layered soil profiles. *J Contam Hydrol* 88:197–218
- Jacques D, Šimůnek J, Mallants D, van Genuchten MT (2008a) Modeling Coupled Hydrologic and Chemical Processes: Long-Term Uranium Transport following Phosphorus Fertilization. *Vadose Zone J* 7(2): 698–711. doi:10.2136/vzj2007.0084
- Jacques D, Šimůnek J, Mallants D, Van Genuchten MT (2008b) Modelling coupled water flow, solute transport and geochemical reactions affecting heavy metal migration in a podzol soil. *Geoderma* 145(3–4):449–461
- Kalbitz K, Solinger S, Park JH, Michalzik B, Matzner E (2000) Controls on the dynamics of dissolved organic matter in soils: a review. *Soil Sci* 165(4):277–304
- Kocman D, Horvat M, Pirrone N, Cinnirella S (2013) Contribution of contaminated sites to the global mercury budget. *Environ Res*. doi:10.1016/j.envres.2012.12.011i
- Kothawala DN, Moore TR, Hendershot WH (2008) Adsorption of dissolved organic carbon to mineral soils: A comparison of four isotherm approaches. *Geoderma* 148(1):43–50
- Leopold K, Foulkes M, Worsfold P (2010) Methods for the determination and speciation of mercury in natural waters—A review. *Anal Chim Acta* 663(2):127–138. doi:10.1016/j.aca.2010.01.048
- Leterme B, Blanc P, Jacques D (2014) A reactive transport model for mercury fate in soil—application to different anthropogenic pollution sources. *Environ Sci Pollut Res* 21:12279–12293. doi:10.1007/s11356-014-3135-x
- Liu G, Cai Y, O'Driscoll N, Feng X, Jiang G (2012) Overview of mercury in the environment. In: Liu G, Cai Y, O'Driscoll N (eds) *Environmental chemistry and toxicology of mercury*. John Wiley & Sons, Inc., Hoboken, New Jersey, pp 1–12. doi:10.1002/9781118146644.ch1
- Llanos W, Kocman D, Higuera P, Horvat M (2011) Mercury emission and dispersion models from soils contaminated by cinnabar mining and metallurgy. *J Environ Monit* 13(12):3460–3468. doi:10.1039/C1EM10694E
- Morris MD (1991) Factorial Sampling Plans for Preliminary Computational Experiments. *Technometrics* 33(2):161–174
- Navarro A, Biester H, Mendoza JL, Cardellach E (2006) Mercury speciation and mobilization in contaminated soils of the Valle del Azogue Hg mine (SE, Spain). *Environ Geol* 49(8):1089–1101. doi:10.1007/s00254-005-0152-6
- Neff JC, Asner GP (2001) Dissolved organic carbon in terrestrial ecosystems: synthesis and a model. *Ecosystems* 4(1):29–48. doi:10.1007/s100210000058
- Ota M, Nagai H, Koarashi J (2013) Root and dissolved organic carbon controls on subsurface soil carbon dynamics: A model approach. *J Geophys Res Biogeosci* 118(4):1646–1659. doi:10.1002/2013JG002379
- Pirrone N, Cinnirella S, Feng X, Finkelman R, Friedli H, Leaner J, Mason R, Mukherjee A, Stracher G, Streets D (2010) Global mercury emissions to the atmosphere from anthropogenic and natural sources. *Atmos Chem Phys* 10(13):5951–5964
- Ravichandran M (2004) Interactions between mercury and dissolved organic matter: a review. *Chemosphere* 55(3):319–331
- Reddy MM, Aiken GR (2001) Fulvic Acid-Sulfide Ion Competition for Mercury Ion Binding in the Florida Everglades. *Water Air Soil Pollut* 132(1):89–104. doi:10.1023/a:1012073503678
- Rinklebe J, During A, Overesch M, Du Laing G, Wennrich R, Stärk H-J, Mothes S (2010) Dynamics of mercury fluxes and their controlling factors in large Hg-polluted floodplain areas. *Environ Pollut* 158(1): 308–318
- Santoro A, Terzano R, Blo G, Fiore S, Mangold S, Ruggiero P (2010) Mercury speciation in the colloidal fraction of a soil polluted by a chlor-alkali plant: a case study in the South of Italy. *J Synchrotron Radiat* 17(2):187–192. doi:10.1107/S0909049510002001
- Scholtz MT, Van Heyst BJ, Schroeder WH (2003) Modelling of mercury emissions from background soils. *Sci Total Environ* 304(1–3):185–207
- Sen TK, Khilar KC (2006) Review on subsurface colloids and colloid-associated contaminant transport in saturated porous media. *Adv Colloid Interf Sci* 119(2–3):71–96
- Seuntjens P, Mallants D, Šimůnek J, Patyn J, Jacques D (2002) Sensitivity analysis of physical and chemical properties affecting field-scale cadmium transport in a heterogeneous soil profile. *J Hydrol* 264(1):185–200
- Skyllberg U (2008) Competition among thiols and inorganic sulfides and polysulfides for Hg and MeHg in wetland soils and sediments under suboxic conditions: Illumination of controversies and implications for MeHg net production. *J Geophys Res* 113:G00C03. doi:10.1029/2008jg000745
- Skyllberg U (2010) Mercury biogeochemistry in soils and sediments. *Dev Soil Sci* 34:379–410
- Skyllberg U (2012) Chemical speciation of mercury in soil and sediment. In: Liu G, Cai Y, O'Driscoll N (eds) *Environmental chemistry and toxicology of mercury*. John Wiley & Sons, Inc., Hoboken, New Jersey, pp 219–258. doi:10.1002/9781118146644.ch7
- Slowey AJ, Rytuba JJ, Brown GE (2005) Speciation of Mercury and Mode of Transport from Placer Gold Mine Tailings. *Environ Sci Technol* 39(6):1547–1554. doi:10.1021/es049113z
- Steeff CI, Appelo CAJ, Arora B, Jacques D, Kalbacher T, Kolditz O, Lagneau V, Lichtner PC, Mayer KU, Meeussen JCL, Molins S, Moulton D, Shao H, Šimůnek J, Spycher N, Yabusaki SB, Yeh GT (2014) Reactive transport codes for subsurface environmental simulation. *Comput Geosci*, pp 1–34. doi:10.1007/s10596-014-9443-x
- Stolk AP (2001) Landelijk Meetnet Regenwatersamenstelling - Meetresultaten 1999. Dutch National Precipitation Chemistry Network. Monitoring results for 1999. Rijksinstituut voor Volksgezondheid en Milieu RIVM, Bilthoven, the Netherlands, p 61.
- Terzano R, Santoro A, Spagnuolo M, Vekemans B, Medici L, Janssens K, Göttlicher J, Denecke MA, Mangold S, Ruggiero P (2010) Solving mercury (Hg) speciation in soil samples by synchrotron X-ray microspectroscopic techniques. *Environ Pollut* 158(8):2702–2709
- Tipping E, Wadsworth RA, Norris DA, Hall JR, Ilyin I (2011) Long-term mercury dynamics in UK soils. *Environ Pollut* 159(12):3474–3483
- van Genuchten MT (1980) A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sci Soc Am J* 44:892–898
- Waples JS, Nagy KL, Aiken GR, Ryan JN (2005) Dissolution of cinnabar (HgS) in the presence of natural organic matter. *Geochim Cosmochim Acta* 69(6):1575–1588
- Xu J, Bravo AG, Lagerkvist A, Bertilsson S, Sjöblom R, Kumpiene J (2015) Sources and remediation techniques for mercury contaminated soil. *Environ Int* 74(0):42–53. doi:10.1016/j.envint.2014.09.007
- Zhu J, Sykes JF (2004) Simple screening models of NAPL dissolution in the subsurface. *J Contam Hydrol* 72(1–4):245–258
- Zhu Y, Ma LQ, Gao B, Bonzongo JC, Harris W, Gu B (2012) Transport and interactions of kaolinite and mercury in saturated sand media. *J Hazard Mater* 213–214:93–99. doi:10.1016/j.jhazmat.2012.01.061