Modeling Hg Reactive Transport in Soil Systems Using HP1

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Abstract

We developed a reactive transport model for simulating mercury (Hg) fate and transport in the unsaturated zone, in order to gain insight into the environmental fate of Hg originating from contaminated soil. The code was implemented using the module HP1 (Jacques et al., 2006; 2008), which couples HYDRUS-1D (Šimůnek et al., 2008) for water and solute transport with PHREEQC (Parkhurst and Appelo, 1999) for geochemical reactions. The main processes accounted for in the model are Hg aqueous speciation (including complexation with dissolved organic matter (DOM), humic and fulvic acids (HA and FA), and thiol groups), Hg sorption to solid organic matter (SOM, while also distinguishing between humic and fulvic acids and thiol groups), dissolution of solid phase Hg (e.g., cinnabar $HgS_{(s)}$), dissolution of Hg non-aqueous phase liquid (NAPL), sunlight-driven Hg^{II} reduction to Hg^0, Hg^0 diffusion in the gas phase and volatilization, and DOM sorption to soil minerals. Using a 50-year time series of daily weather data from Dessel (Belgium) and a 1-m deep sandy soil with deep groundwater (free drainage, oxic conditions), we implemented a sensitivity analysis using the elementary effects method (Morris, 1991). The most sensitive parameters determining Hg leaching or retardation were found to be the equilibrium constant for Hg sorption to humic and fulvic acids (i.e., the most abundant sorption sites in SOM), the initial concentration of Hg, and the concentration of DOM in the soil solution.

1. Introduction

Mercury (Hg) poses threats to human health and the environment, notably due to its persistence in the environment and its ability to bioaccumulate in ecosystems and the food chain. Anthropogenic sources are major contributors to the release of mercury into the atmosphere, water and soil. Soil contamination not only results from direct spills, but also indirectly, for example via deposition of prior atmospheric emissions. The main sources of mercury in soils are mercury mining activities, gold and silver mining (Hg^0 is used to amalgamate the metal), manufacturing (e.g., chlor-alkali plants, or manometer spills), wood preservation, and cemeteries (release of mercury from dental amalgams).

Mercury in soils can be present in different phases: the solid phase (most frequently cinnabar (HgS) and montroydite (HgO)), the solution phase (mainly Hg^{2+} bound to organic or inorganic ligands, but also methylmercury CH_3Hg^+ and dissolved Hg^0), the gas phase (Hg^0 or dimethylmercury $(CH_3)_2Hg$), and the non-aqueous liquid phase (NAPL), which may contain especially elemental mercury Hg^0 and is more dense than water. This complexity of multiple phases makes modeling of mercury transport in soils a particularly challenging task. As such, knowing the history of a given contaminated site is important because Hg species present in soils are closely related to the type of industry or activity that caused the contamination. The age of an Hg contaminated site is also important since the kinetics of phase transformations and retention processes may be relatively slow.

This study is focused on Hg fate and transport in the unsaturated zone following direct soil contamination from human activities. Our main objective was to develop a reactive transport model in order to gain insight into the fate and transport processes of Hg in soils under oxic conditions. The relative importance of different processes and parameters is assessed by means of with a sensitivity analysis based on the Morris (1991) method of elementary effects. The analysis is carried out for different initial speciations (dissolved, solid phase or NAPL) of Hg contamination.

2. Conceptual Model and Numerical Implementation in HP1

Figure 1 shows the conceptual model implemented in the HP1 simulator (Jacques et al., 2006; 2008). Aqueous complexation is treated using the database IM003_THERMODDEM (Blanc et al., 2012), augmented with some Hg speciation data from Skyllberg (2012). However, complexation with organic ligands is not included in IM003_THERMODDEM. Therefore, four hypothetical organic compounds (Ya, Yb and Yc representing oxygen sites of humic and fulvic acids, and Ys representing thiol groups) were added (Table 1, left column). Based on exchange capacity data, approximately 99% of the dissolved organic matter (DOM) ligands were modeled as humic and fulvic acids (88%, 11% and 1% for Ya, Yb and Yc, respectively), and about 1% as thiols (Gustafsson, 2001; Skyllberg, 2008).

Colloidal transport of Hg (Sen and Khilar, 2006; Zhu et al., 2012) is implicitly considered by the transport of Hg bound to DOM. While numerical solutions exists for simulating more realistically colloid formation and migration exist (Šimůnek et al., 2006), they generally demand numerous specific parameters that were not available for the present case.

For Hg sorption to soil organic matter (SOM) we used the EXCHANGE command of PHREEQC for simulating multiple proton/ion exchangers. Similarly to Hg complexation with DOM, four reactive surface sites were considered (Table 1, right column): Xa, Xb, Xc (representing the ~99% oxygen exchange sites from fulvic and humic acids) and Xs (representing ~1% thiol exchange sites). Sorption of DOM on soil minerals was modeled using the PHREEQC function SURFACE for surface complexation, with a Langmuir isotherm and parameters fitted by Kothawala et al. (2008).

Starting with Hg^{2+} in the aqueous phase, mercury volatilization requires two steps: (i) reduction of Hg^{II} to Hg^0, and (ii) a phase change from $Hg^0(aq)$ to $Hg^0(g)$. Our model at present was developed for oxic conditions, which thermodynamically does not favor volatilization. For this reason we decided to implement a (pseudo-first-order) kinetic reaction in HP1 for the reduction of Hg^{II} to $Hg^0(aq)$ (cf. Figure 1).

Two other kinetic reactions were necessary to allow dissolution of cinnabar ($HgS_{(s)}$) and NAPL (cf. Figure 1). Cinnabar dissolution is dependent upon DOM (Waples et al., 2005) and represented by a zero-order rate equation, while NAPL dissolution is modeled by means of a first-order rate law (this was done somewhat arbitrarily due to the absence of data on Hg NAPL dissolution).
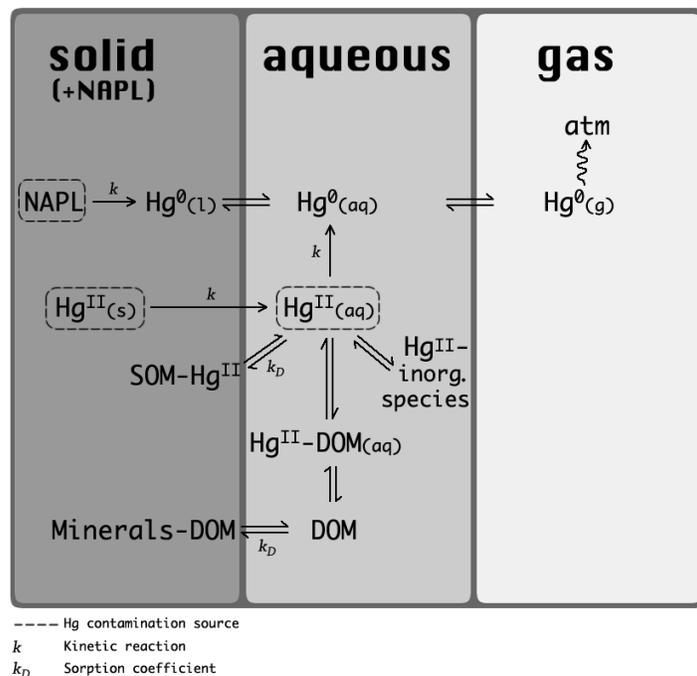
Figure 1. Conceptual model of Hg speciation and reactions in the solid, aqueous and gas phases. Initial mercury contamination can be simulated as non-aqueous phase liquid (NAPL), solid, or aqueous phase.

Table 1. Equilibrium constants for Hg-DOM complexes (left column) and for sorption of Hg to SOM (ion exchange assemblage; right column).

Complexation Hg-DOM	Log k	Sorption Hg-SOM	Log k
$HYa + 0.5Hg^{2+} = Hg_{0.5}Ya + H^+$	-1.1[a]	$Hg^{2+} + 2Xa^- = HgXa_2$	3.5[a]
$HYb + .5Hg^{2+} = Hg_{0.5}Yb + H^+$	-7.6[a]	$Hg^{2+} + 2Xb^- = HgXb_2$	4.3[a]
$HYc + .5Hg^{2+} = Hg_{0.5}Yc + H^+$	-1.8[a]	$Hg^{2+} + 2Xc^- = HgXc_2$	5.08[a]
$HYa + HgOH^+ = HgOHYa + H^+$	-3[a]	$HgOH^+ + Xa^- = HgOHXa$	7.7[a]
$HYb + HgOH^+ = HgOHYb + H^+$	1.8[a]	$HgOH^+ + Xb^- = HgOHXb$	7.7[a]
$HYc + HgOH^+ = HgOHYc + H^+$	2.0[a]	$HgOH^+ + Xc^- = HgOHXc$	10.2[a]
$2HYs + Hg^{2+} = HgYs_2 + 2H^+$	22.0[b]	$Hg^{2+} + 2HXs = HgXs_2 + 2H+$	15.4[b]

[a] Bessinger and Marks (2010)
[b] Skyllberg (2008)

Within the context of Hg contamination from anthropogenic sources, mercury uptake by vegetation and atmospheric wet and dry deposition could be ignored since they generally generate relatively small Hg fluxes compared to those included in our model.

3. Sensitivity Analysis

We applied Hg reactive transport model to a synthetic case, consisting of a 1-m course-textured soil having a uniform SOM content in the top 30 cm, initial Hg contamination in the top 10 cm, and a grass cover with uniform rooting depth until 30 cm (no Hg uptake). The soil surface hydraulic boundary condition consisted of atmospheric input (precipitation and potential evapotranspiration rates) obtained from a 50-year time series of daily observations in Dessel (Belgium). The lower hydraulic boundary condition was set to free drainage in order to ensure oxic conditions.

Given these assumptions, a sensitivity analysis (SA) was performed using the elementary effects method of Morris (1991). Sampling trajectories were randomly designed across parameter space (each parameter range being divided into p levels), with successive deviations in the trajectories resulting in quantification of the elementary effects. One computes then μ (the average elementary effect) which assesses the overall influence of the factor on the output, and also σ (standard deviation) which estimates the ensemble of the factor's higher order effects (i.e., non-linear and/or interaction effects). Campolongo et al. (2007) further proposed the use of μ^* (the mean 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 in the measure of μ).

Thirteen parameters were included in the SA (Table 2), while the following model outputs were selected: leached Hg, Hg still in the originally polluted horizon, and Hg below the top 30-cm thick horizon (all expressed as % of the initial Hg contamination). The SA was repeated at three different simulation times (after 5, 25 and 50 years) and with three different contamination sources (cinnabar, Hg NAPL and aqueous mercuric chloride). Only a few representative results are presented hereafter.

Figure 2 shows plots of μ vs. σ and μ^* vs. σ for the percentage of Hg being leached after 50 years in case of cinnabar being the contamination source. Among the parameters tested, X_4 (DOM concentration of infiltrating rainwater) had the highest sensitivity. This is due to (i) Hg^{II} migration occurring mainly via Hg-DOM complexes and (ii) cinnabar dissolution rate depending upon the DOM concentration of soil water. Other parameters showing a high sensitivity were X_1 (initial cinnabar concentration) and X_8 (log k Hg-DOM (thiols)). For X_1, the high sensitivity was partly explained by the model output being expressed in a relative way (% of initial Hg), and by incomplete cinnabar dissolution over the simulation time.

Figure 3 shows plots of the concentration of Hg^{II} in the leachate over time, obtained from one SA simulation using cinnabar as the contamination source. Results indicate that Hg^{II} leaching occurs after only about 30 years. Also, after the initial breakthrough, the variability in the Hg^{II} concentration spans about two orders of magnitude. These are important findings, for example within the context of designing a sampling strategy, or for planning (temporal) objectives of soil remediation and/or risk assessment.

Table 2. List of parameters included in the sensitivity analysis, and their lower and upper bounds (uniform distributions).

Factor		Unit	Lower bound	Upper bound
X_1	Initial Hg concentration	mg kg^{-1}	135	13500
X_2	Cinnabar dissolution rate	day^{-1} g$_{OC}$$^{-1}$	4.59×10^{-4}[a]	1.42×10^{-2} [a]
X_3	Hg^{II} reduction rate	day^{-1}	6.91×10^{-7}	6.91×10^{-5}
X_4	DOM (in rainwater boundary solution)	mg L^{-1}	9 [c,d]	90 [c,d]
X_5	Exchange capacity of HA and FA (SOM top 30 cm)	meq dm^{-3}	7.95	159
X_6	Exchange capacity of thiols (SOM top 30 cm)	meq dm^{-3}	0.0705	1.41
X_7	log k 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
X_8	log k complexation Hg-DOM (thiols)	-	11.0	44.0
X_9	log k 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
X_{10}	log k sorption Hg-SOM (thiols)		7.7	30.8
X_{11}	K_L sorption DOM to soil minerals	-	5.6×10^{-4}	1.23×10^{-2} [g]
X_{12}	S_{max} max. adsorption capacity of DOM to minerals	mg kg^{-1}	109 [g]	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] Mertens et al. (2007)

[d] Don and Schulze (2008)

[e] Skyllberg (2008)

[f] Bessinger and Marks (2010)

[g] Kothawala et al. (2008)

Figure 4 presents results for the percentage of Hg still present in the top horizon (0-10 cm) after 50 years, with Hg NAPL being the contamination source. Parameter X_9 (log k Hg-SOM (HA, FA)) was the most sensitive parameter. The corresponding parameter for thiols, X_{10}, showed no sensitivity due to the high proportion of HA and FA sites compared to thiols. Factor X_1 (Hg initial concentration) was the second most important parameter. This parameter is characterized by μ values indicating non-monotonic behavior of the model. Nonlinearities and interactions with other parameters are also important for X_9 and X_1 (high σ values).
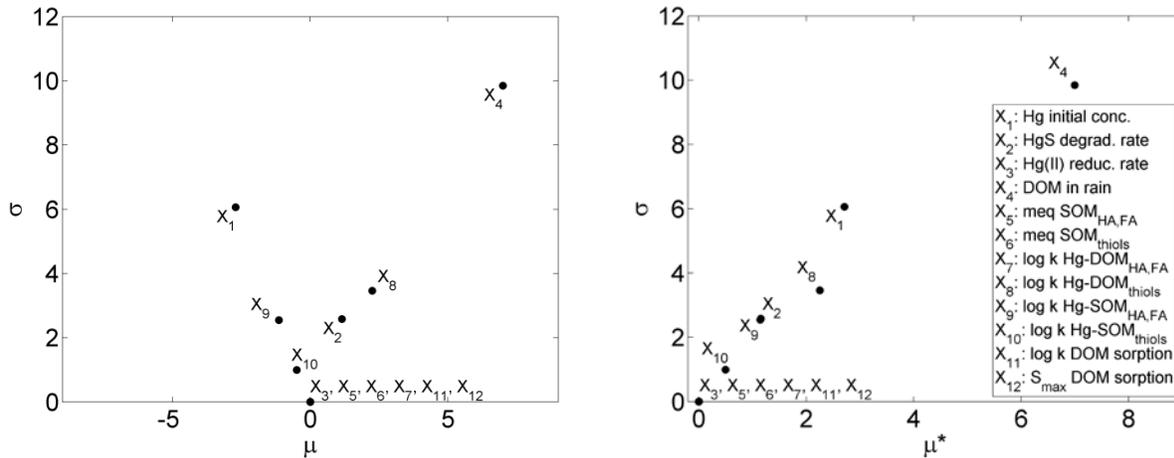
Figure 2. Plots of μ vs. σ and μ^* vs. σ for elementary effects of the percentage Hg leaching after 50 years, using 5 trajectories and cinnabar (HgS$_{(s)}$) was the contamination source.

Figure 3. Hg^{II} concentration (μg L^{-1}) in the leachate over time, from one of the 60 HP1 runs of the sensitivity analysis using cinnabar (HgS$_{(s)}$) as the contamination source.

Two simulations illustrating model nonlinearity and the interaction effects are shown in Figure 5. Figure 5a indicates that no more Hg is present in the top horizon (0-10 cm) after 50 years, while the percentage is still 32.5% of the initial Hg in Figure 5b (= the maximum of all simulations of the 5 trajectories). Both simulations were carried out using the same initial concentration (X_1) and a low value of X_9. Differences between the two simulations is mainly due to interactions between X_1 and X_6 (exchange capacity of thiols). Even though thiol sorption sites are less abundant than HA and FA sites, the interaction of low X_1 and high X_6 in Figure 5b means that thiols in SOM are sufficient to retain a significant percentage of the initial Hg in the topsoil.
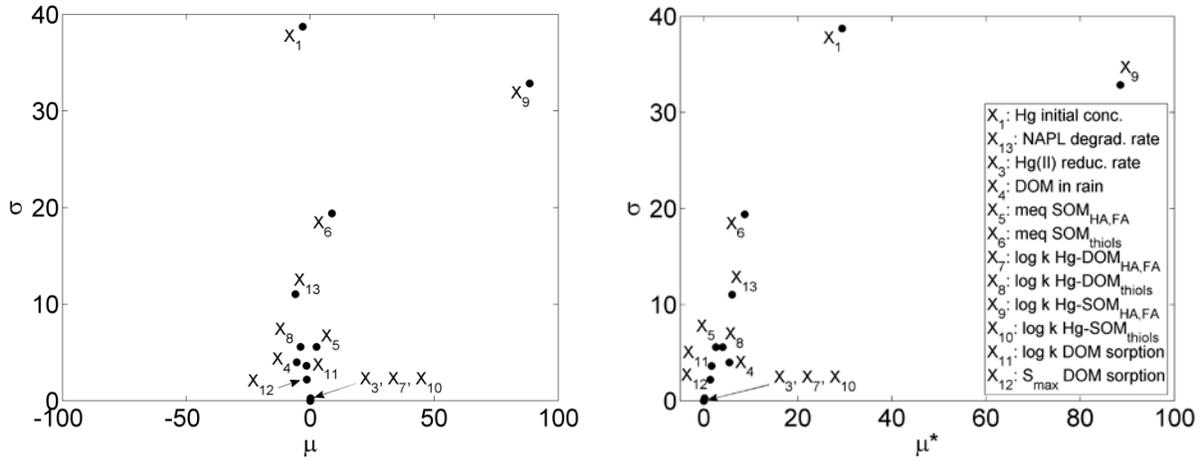
Figure 4. Plots of μ vs. σ and μ^* vs. σ for elementary effects of the percentage Hg still in the surface horizon initially polluted after 50 years, using 5 trajectories and Hg NAPL as contamination source.
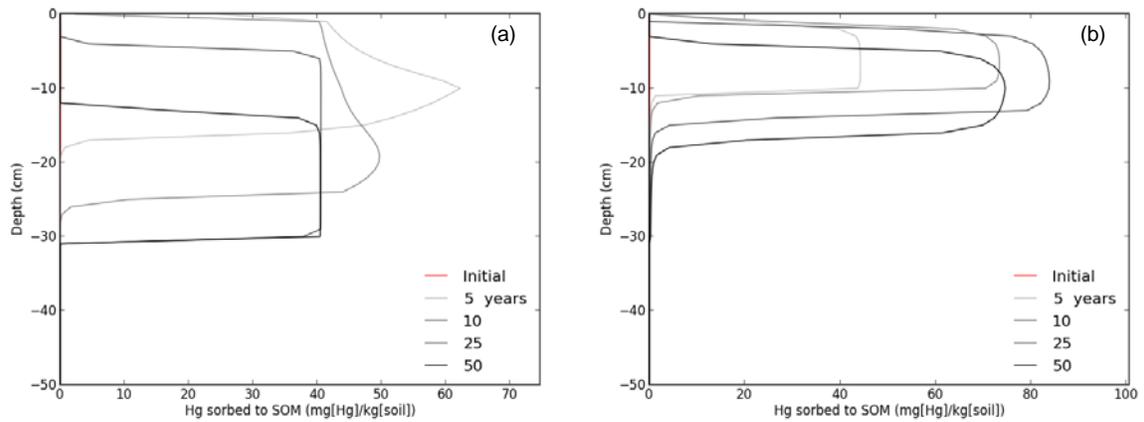
Figure 5. Depth distribution over time of Hg sorbed to SOM at $t = 0$, 5, 10, 25 and 50 years for two simulations with contrasting percentages of Hg in the top horizon after 50 years: 0% for (a) and 32.5% for (b). The initial contamination Hg NAPL was (135 mg[Hg]/kg[soil]).

Overall (i.e., including results not shown in this paper), parameter sensitivity for a given model output was found to depend on the type of mercury contamination. However, trends could be drawn by ranking the 13 parameters based on the sensitivity after 25 and 50 years for all types of contamination. For leaching, the most sensitive parameters were X_1, X_9 and X_4 (decreasing sensitivity ; see Table 2 for parameter names and ranges). For the percentage of Hg remaining in the topsoil, the ranking was: X_9, X_1 and X_4. For Hg below the horizon of contamination (11-30 cm), the most sensitive parameters were X_9, and X_1, X_4, X_2, X_{13}. Parameters that could generally be considered negligible based on the SA results were X_3, X_7, X_{11}, X_{12}.

Simulated Hg volatilization was found to be negligible (<0.1%). This is mainly due to the fact that the reduction rate depends on the total Hg^{II} concentration in the aqueous phase, i.e. the free species of Hg^{2+}, the inorganic and organic aqueous complexes of Hg^{II}, not being sorbed. Since

Hg^{II} concentration in the aqueous phase were relatively low at all times, Hg reduction and volatilization were consequently very limited.

4. Conclusions

The HP1 module of HYDRUS-1D was used to implement a numerical model of mercury fate and transport in soils. The processes included in the model are relevant for oxic conditions and pollution from anthropogenic sources. These simulated processes were Hg transport and speciation in the gaseous and aqueous phases, Hg sorption to SOM, cinnabar and Hg NAPL dissolution, Hg^{II} reduction and volatilization, and DOM sorption to minerals. Hg-DOM complexes in the aqueous phase were considered as a surrogate for colloid transport.

Three different phases of initial mercury contamination were tested: solid (cinnabar), non-aqueous phase liquid Hg, and aqueous mercuric chloride. The dominant processes for Hg fate in soils were identified by means of a parameter sensitivity analysis using the method of elementary effects. Overall, the most sensitive parameters were the equilibrium constant for Hg sorption to humic and fulvic acids (i.e., the most abundant sorption sites of SOM), the Hg initial concentration, and the DOM concentration of the infiltrating rainwater. Interactions between factors and nonlinear effects as measured by the elementary effect method were generally important. They depended on the type of contamination and on the time at which the indicators were evaluated.

More comprehensive modeling of the DOM cycle in soils should improve performance of the model, given the importance of DOM and SOM on Hg dynamics. Finally, we note that no model calibration was performed in the present study, but this is considered a necessary step in the future.

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