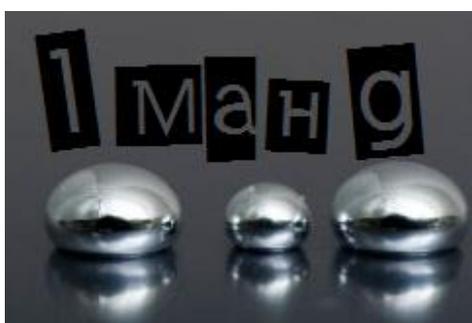**SNOWMAN NETWORK**
Knowledge for sustainable soils

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Enhanced knowledge in mercury fate and transport

for Improved Management of Hg soil contamination

Literature Review on Mercury Speciation Soil Systems Under Oxidizing Conditions

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WP coordinator: Diederik Jacques   (SCK•CEN)

Redactors: Bertrand Leterme (SCK•CEN), Diederik Jacques (SCK•CEN)

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Summary

This report consists of a literature review of factors and processes affecting mercury (Hg) fate in soils. Considering Hg cycle from the perspective of soil systems, Hg sources include atmospheric wet and dry deposition, geogenic sources and anthropogenic contamination. The main Hg sinks include volatilization to the atmosphere, and transport to groundwater or surface water. Plant root uptake from soils is extremely low and in general can be neglected.

Mercury can exist in three valence states: Hg^0, Hg^I and Hg^{II}. However, the presence of Hg^I in soils is negligible compared to Hg^0 and Hg^{II}, and the latter is dominant. The main dissolved Hg species in soil systems is Hg^{II} complexes with various inorganic and organic ligands. The key factors controlling Hg aqueous speciation are pH, ionic strength and redox potential. Concentrations of dissolved organic matter (DOM), dissolved oxygen, sulfide and suspended solids in solution can also play a role.

In oxidized soil conditions the predominant inorganic mercury species are $Hg(OH)_2$, $HgCl_2$, $HgOH^+$, HgS, and Hg^0. The first two are the most frequent. (Mono)methylmercury (MMHg) and dimethylmercury (DMHg) are the methylated forms of Hg that can be synthesized in soil or aqueous systems (by microbial activity). Generally, the concentration of MMHg is less than 2% of the total mercury concentration in soil systems, while DMHg is nearly absent.

Strong interactions between mercury and organic matter are observed. Hg complexes with thiol groups and humic and fulvic acids are particularly important. Migration of Hg to deeper soil layers is often suggested to be most effective if Hg is bound to soluble organic complexes (i.e. colloid-facilitated transport).

Different phase transitions of mercury occur in soil systems. Solid HgS (cinnabar) is the common ore of mercury. In the presence of Cl^- or DOM, HgS(s) dissolution is observed and precipitation is inhibited. In case of anthropogenic contamination, Hg can be present in the form of a (dense) non-aqueous phase liquid or (D)NAPL, which can further dissolve or volatilize in soil systems.

Similarly to what is observed for Hg aqueous complexation with organic ligands, sorption capability of Hg^{2+} is highest for humic and fulvic substances and for molecules containing a reactive thiol functional group. Adsorption rate depends mainly on initial Hg^{2+} concentration, organic matter content and ions in solution.

Volatilization of mercury occurs in soils and Hg vapor flux to the atmosphere can be important in case of anthropogenic contamination. Volatilization can be described as a three-step process, in which Hg^{II} is first reduced to Hg^0. Hg^0 is then diffused to the soil surface and finally volatilized across the soil-air boundary layer into the atmosphere. Sunlight and heat are the main factors driving Hg volatilization.

1   Mercury in the soil

1.1   Mercury cycle and transport

Many reviews or descriptions of mercury fate and transport in the environment take a global perspective (e.g. UNEP, 2002) where soils are only a compartment (pool) of Hg. If not assessed from a global perspective, Hg cycle is often restricted to either atmospheric (e.g. Schroeder and Munthe, 1998) or aqueous (wetland, river, lake, ocean; e.g. Sunderland, 2009) systems. Soils are then often seen as a sink/source of mercury, but to date we found no study giving a comprehensive description of all sources/sinks and transport processes relevant for Hg fate in soils. The cycle of Hg fate and transport from the perspective of soils is depicted in Figure 1. The objective of this figure is to give a qualitative rather than a quantitative description of mercury fate in soils. It is important to note that Figure 1 does not show all components and fluxes of the global Hg cycle, but only the most relevant for the vadose zone. For example, volatilization from ore deposits to the atmosphere, erosion and runoff of soil particles to surface water, or mercury fate in aqueous systems (river, lake, oceans, sediments…) are not shown.
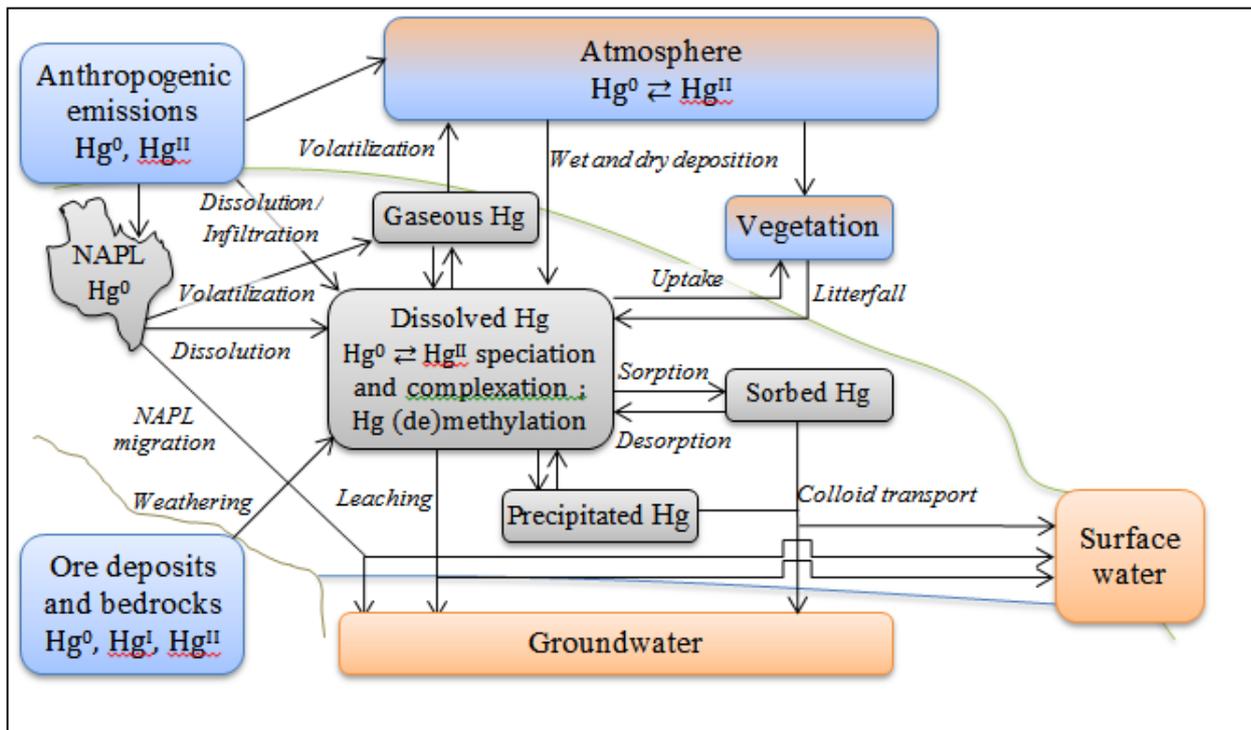
Figure 1 – Mercury sources (in blue), sinks (in orange) and phases in soil (in grey).

Mercury may be present under different phases in soil systems: (i) dissolved in the aqueous phase as a free ion (Hg^{2+}) or complexed with inorganic and/or organic ligands, (ii) metallic (or elemental) Hg^0 as a non-aqueous liquid phase (NAPL), (iii) sorbed on soil minerals and insoluble organic matter, (iv) in the gas phase, and (v) in solid (precipitated) phase. Aqueous speciation of mercury is reviewed in section 2 and phase transitions are discussed in section 3.

Sources of Hg in soils consist of (Figure 1): (i) atmospheric wet and dry deposition and litterfall, (ii) geogenic (or lithogenic) mercury, and (iii) anthropogenic contamination.

In the atmosphere, mercury in the form of gaseous Hg^0 is dominant (>95%; Zhang et al., 2009). Reviews of atmospheric mercury cycle, chemistry and modeling can be found in (Lin and Pehkonen, 1999; Schroeder and Munthe, 1998; Subir et al., 2011). Mercury wet and dry deposition is mostly in the form of inorganic Hg^{II} (Zhang et al., 2009), possibly in the form of $HgCl_2$; a large fraction being associated with particles (Schlüter, 2000). Deposition in the form of monomethylmercury (CH_3Hg^+) is usually reported to be less than 5% of total deposition (Schlüter, 2000). From the perspective of soil systems, litterfall can be considered as a Hg source. Atmospheric Hg is the main source of Hg in aboveground vegetation tissues and when these fall to the ground Hg can be further released in soils (Obrist et al., 2011).

Geogenic (or lithogenic) sources provide Hg via oxidation and weathering of ore deposits and bedrocks. Mercury may then transported to soils via Hg^0 degassing or via Hg^I/Hg^{II} transport in rising groundwater. One usually makes the distinction between Hg enriched areas (global "mercuriferous belt") and background areas (Schlüter, 2000). The former show high rates of mercury degassing and/or weathering. It is also in these areas that most of the mercury mines are found (mainly in the form of HgS(s) ore). More details on the location of Hg enriched areas and their origin can be found in (Gustin et al., 2006; Schlüter, 2000). Background areas are zones where the geogenic flux of mercury to soils and atmosphere is small or negligible. In the field, methods exist to discriminate between atmospheric and geogenic sources of soil Hg (Guedron et al., 2006).

Anthropogenic soil contamination can result from direct sources (spilling, mine tailing, landfills, polluted sewage sludge…) but it can also occur indirectly, for example via deposition of prior atmospheric emissions. Mason et al. (1994) estimated that about two thirds of atmospheric Hg is directly or indirectly from anthropogenic sources. Direct contamination of soils can occur in the form of a non-aquous phase liquid (NAPL) phase, which can then percolate, volatilize and dissolve. Specific aspects of soil contamination from anthropogenic sources and case studies are presented in section 1.2.

Mercury sinks from the perspective of soil systems are (Figure 1): (i) atmosphere, (ii) plants (via root uptake), (iii) groundwater, and (iv) surface water. Irreversible sorption sites are sometimes considered as a sink in the budget of soil Hg, but are not treated as sinks in this report, because this process does not change the total Hg budget in the soil.

Volatilization to soil gaseous phase and eventually to the atmosphere is discussed in section 3.3.

Plant root uptake from soils is extremely low and in general can be neglected (Pant et al., 2010; Schuster, 1991). Roots perform as a significant adsorption site and are therefore a barrier for Hg transport to foliage (Grigal, 2003). Therefore transport with the plants to the above ground parts is limited. It should be noted that some exceptions exist (e.g. Pérez-Sanz et al., 2012). Also, mercury phytoremediation can benefit from genetic engineering (Ruiz and Daniell, 2009) or association with rhizobacteria (Sorkhoh, 2010). Non terrestrial plants like mangroves can show significant Hg root uptake (Ding et al., 2011).

In the unsaturated zone, mercury transport to surface water (i.e. via subsurface flow) and to groundwater occurs via convection, dispersion, diffusion and colloid-facilitated transport. On sites of heavy contamination, the migration and entrapment of NAPL needs also to be taken into account. In the vadose zone, gaseous diffusion of mercury also participates in determining Hg fate in soils. Retardation of Hg in soils is mainly due to adsorption processes, which are examined in section 3.2.

1.2   Sites of anthropogenic contamination

Anthropogenic mercury contamination may result in much higher Hg concentrations in soil systems than from other sources. This has important consequences for assessing the fate and transport of Hg in soils, by affecting for instance Hg^{II} speciation in soils. Hg binding is preferentially on S-containing

functional groups of organic ligands. These are always in excess relative to Hg concentration in uncontaminated soils (see section 2.4), while contaminated sites may show much lower S/Hg ratios. It has also been found that in soil samples with anthropogenic contamination, the ratio of organomercury species to total mercury is usually lower than in uncontaminated areas (Boszke et al., 2008).

The activities most frequently cited as causes of anthropogenic contamination of the environment are (UNEP, 2002): mercury mining, gold and silver mining (Hg^0 is used to amalgamate the metal), manufacturing (chlor-alkali plants, manometer spill), wood preservation, cemeteries (release of mercury from dental amalgams).

Logically, the Hg species present in the soil highly depend on the type of industry or activity that led to the contamination. Bloom et al. (2003) illustrated the variety of Hg speciation found at contaminated sites (gold mine tailings, HgS mines, Hg^0 spill, chlor-alkali plant, $Hg(NO_3)_2$ contamination from hydrogen bomb production). They concluded that the source Hg compound was important but also the time (aging) since mercury contamination, because phase transformation or retention mechanisms can have relatively slow kinetics. For example, even after decades, elemental mercury discharged by manometer spills or as an amalgam for mining, may remain as Hg^0 "globules" or NAPL in the soil (Davis et al., 1997).

In a study of soil and aquifer contamination by $HgCl_2$ used for wood preservation, Bollen et al. (2008) found that most Hg in soil was Hg bound to mineral soil compounds (e.g. iron/aluminium oxides and hydroxides or clay minerals), whereas in the aquifer reduction to Hg^0 could be observed.

Boszke et al. (2008) analysed Hg speciation after a Hg^0 industrial contamination (spill). The main transformations were volatilization to the atmosphere and oxidation to Hg^{II} followed by binding to humic matter and sulfides (Boszke et al., 2008). Indeed, even after high contamination events, very few Hg^0 persists in the liquid form: Hg^0 is either rapidly volatilized or more slowly oxidized to Hg^{II} (Biester et al., 2002).

In a study of Hg speciation from historical gold mine tailing, Slowey et al. (2005b) found that Hg^0 had been oxidized and transformed to mineral and organic sorption complexes, highly insoluble cinnabar (HgS), Hg oxides and Hg chloride. Moreover, colloidal transport of cinnabar was identified as the dominant leaching mechanism in the mine tailings (Slowey et al., 2005b). Lowry et al. (2004) similarly observed colloidal HgS as the dominant transported form of Hg from gold mine waste materials.

Other speciation analyses of gold mine tailings illustrate how Hg speciation can vary from one site to another. In one instance, thermodynamic calculations indicated that >99.8% of mobilized Hg was in the form of Hg-CN complexes (Shaw et al., 2006). Palmieri et al. (2006) found that most of the mercury in a gold mining area was associated with organic matter and sulfur.

In samples from a mercury mining area, Biester et al. (1999) found differences in speciation depending on the time of contamination: older incomplete ore roasting gave more cinnabar than younger tailings in which mineral sorbed Hg^0 (see section 3.2.1) and unbound Hg^0 predominated. Studying speciation in another mercury mining area, Navarro et al. (2006) indicated that predominant Hg species in soils and mine wastes was cinnabar (HgS), mainly formed from the weathering of Hg-rich pyrite and elemental Hg^0 in the matrix, whereas in calcines and tailings the dominant species was Hg^0. In the area of the former Almadén (Spain) mercury mining industry, fractionation analyses of soil samples showed predominant Hg sulfides, then associated with Fe-Mn oxyhydroxides and with organic matter, and traces of Hg^0 (Millan et al., 2011). Land use influence on Hg speciation was also indicated by different speciation results in agricultural and pastoral areas (Millan et al., 2011).

Lechler et al. (1997) studied Hg speciation in soils contaminated by former gold and silver mines. They found that after dissolution of the source Hg^0, deeper, high-sulfur soil (reducing) horizons appeared to fix a significant part of the mercury as HgS.

Bernaus et al. (2006) assessed Hg speciation in soils polluted by Hg^0 wastes from a chlor-alkali plant. Speciation was observed to quite insoluble inorganic coumpounds: cinnabar and metacinnabar (HgS), corderoite ($Hg_3S_2Cl_2$), and and small quantities of $HgSO_4$ and HgO. Similar speciation results were found by Santoro et al. (2010) and Terzano et al. (2010) at a different site contaminated by a chlor-alkali plant. HgO(s) and $HgCl_2$(s) are typically species that are sometimes found in highly contaminated soils but not under background conditions (Skyllberg, 2010).

Renneberg and Dudas (2001) studied Hg0 speciation in the presence of co-contamination by hydrocarbons. They found that over time Hg has transformed to HgII and is mostly sorbed to soil organic and mineral materials. Association of Hg with hydrocarbon was significant in one of the five analysed samples (Renneberg and Dudas, 2001).

Bessinger and Marks (2010) investigated soil and cinder contamination in a site of historical mercury fulminate ($Hg(CNO)_2$) production. Elemental mercury was not found, and methylmercury was detected at low level. Mercury sulfides were detected in both samples (soil and cinder), and other forms of mercury (i.e. adsorbed Hg) were likely present but not analysed. Bessinger and Marks (2010) further developed a geochemical model for simulating in-situ remediation by incorporation of activated carbon (see report Part 2 – Conceptual and Mathematical model for Mercury Fate and Transport in Soil Systems).

Gray et al. (2006) showed that methylation and demethylation (see section 2.2) processes were significant in mercury mine tailings. Methylmercury concentrations were positively correlated with Hg^{2+}, organic carbon and total sulfur concentrations. Different conclusions were drawn in study of soils contaminated by a former chlor-alkali plant. Methylmercury concentrations in soil were negatively correlated to total Hg concentrations, organic carbon and total sulfur concentrations (Remy et al., 2006). High methylmercury/Hg_{tot} ratios were mainly related to a combination of low Hg_{tot}, low organic C/N ratios and relatively low pH (Remy et al., 2006). Frohne et al. (2011) studied methylation in floodplain soils contaminated by the textile and metal industries. They suggested that the dissolved organic carbon (DOC)/Hg_{tot} ratio might be a more important factor for the Hg net methylation (with a positive correlation) than DOC alone. Other important factors influencing methylation were changes in DOC, sulfur cycle, and microbial community structure, whereas Eh and pH values, dissolved Fe^{3+}/Fe^{2+} and Cl^- concentrations seemed to play a minor role (Frohne et al., 2011).

2 Aqueous speciation of mercury

The main dissolved Hg species in soil systems is Hg^{II} complexes with various inorganic and organic ligands (Loux, 1998; Skyllberg, 2012). Dissolved Hg^0 and organic Hg forms (mainly monomethylmercury and dimethylmercury) are also present (Ullrich et al., 2001). Methylmercury forms are present in small amounts in soils, but are very important in terms of toxicity because they have the potential to bioaccumulate owing to their lipophilic and proteinbinding properties (Schlüter, 2000; Ullrich et al., 2001). Factors controlling Hg speciation are pH, ionic strength, redox potential, and concentrations of dissolved organic matter (DOM), dissolved oxygen, sulfide and suspended solids in solution. The first three (pH, ionic strength, redox potential) are by far the most important (Gabriel and Williamson, 2004).

Water solubility of Hg compounds varies, e.g. CH_3HgCl and CH_3HgOH more soluble than $HgCl_2$ and $Hg(OH)_2$ (Gabriel and Williamson, 2004). Highest water solubility occurs in oxygenated environment Eh = 350-400 mV; this is typical of most soils (Schuster, 1991).

Section 2.1 presents oxido-reduction reactions, while section 2.2treats the formation and degradation of methylmercury. Sections 2.3 and 2.4 give an overview of (methyl)mercury speciation with inorganic and organic ligands, respectively

2.1 Mercury oxidation and reduction

In soil systems, depending on redox conditions, mercury can exist in three valence states: Hg^0, Hg^I and Hg^{II} (Gabriel and Williamson, 2004). In the presence of dissolved ligands and organic matter, Hg^I and Hg^{II} exist as free species Hg_2^{2+} and Hg^{2+} but also in many complexed forms. However, most Hg_2^{2+} compounds, when exposed to air and light, will oxidize to Hg^{2+} (Davis et al., 1997). Therefore, the presence of Hg^I in soils is negligible compared to Hg^0 and Hg^{II}, and the latter is dominant (Schlüter, 2000).

The most widely noted Hg reaction in soils is the reduction of Hg^{2+} to Hg^0 (Gabriel and Williamson, 2004). Reduction to Hg^0 is usually the first step of mercury volatilization from soil to atmosphere (see section 3.3). Hg^{2+} reduction in soils can be biotic or abiotic, and takes place more easily in lower or saturated horizons which are generally reducing environments (Schlüter, 2000).

Abiotic reduction can be mediated by reductants such as dissolved organic matter (humic and fulvic acids) or Fe^{2+} (Gabriel and Williamson, 2004; Schlüter, 2000). Mercury reduction by humic and fulvic acids was shown to be affected by solution pH, concentrations of dissolved oxygen, and chloride (Ravichandran, 2004).

Abiotic reduction is influenced by adsorption, because free Hg^{2+} in solution has a higher potential for reduction than an adsorbed Hg compound (Mishra et al., 2011; Schlüter, 2000; Schuster, 1991). As a consequence, the reduction of Hg^{2+} by reaction with dissolved organic matter (DOM) in the soil upper layers may benefit from the availability of recently deposited atmospheric Hg^{2+}, which has not yet been incorporated into the soil matrix and is still relatively available (Schlüter, 2000).

Abiotic reduction of Hg^{2+} (and CH_3Hg^+) to Hg^0 can also result from photochemical reactions in the first few millimeters of soil (Gabriel and Williamson, 2004; Ravichandran, 2004).

Biotic reduction of Hg^{2+} to Hg^0 can be mediated by various microorganisms (Gabriel and Williamson, 2004). Similarly to abiotic reduction, an increase in DOM inhibits biotic reduction due to the relative unavailability of adsorbed Hg compounds.

2.2 Mercury methylation and demethylation

(Mono)methylmercury (MMHg) and dimethylmercury (DMHg) are the most common methylated forms synthesized by microbial activity (Davis et al., 1997). DMHg is practically insoluble in water and is highly volatile, while MMHg has a much higher water solubility (Gabriel and Williamson, 2004).

Generally, the concentration of MMHg is less than 2% of the total mercury concentration in soil (Schlüter, 2000), but this percentage can be higher in wetland or riparian zones (EPA, 1997; Skyllberg et al., 2003). There seems to be an increase in the percentage of MMHg as one goes further from the source of Hg deposition (Skyllberg et al., 2003; Ullrich et al., 2001). The percentage of MMHg compared to the total Hg is generally higher in the aqueous phase compared to the solid phase (Skyllberg, 2012).

Factors controlling methylation and demethylation of Hg have often been studied in aqueous systems such as wetlands, rivers and lakes; because these are the proximate pools of methylmercury before bioaccumulation in the food chain. Ullrich et al. (2001) provided an extensive review of mercury methylation in aqueous systems. Some points of their review are reported here, because the soil solution can be considered as an aqueous system but it should be reminded that most of the literature they cite is specific to surface water.

Mercury methylation can occur in both aerobic and anaerobic environments, but in sediments biotic methylation and MMHg stability appear to be enhanced under anaerobic conditions (Ullrich et al., 2001).

The concentration of bioavailable Hg^{II} (rather than the total Hg pool) is a primary factor controlling methylation (Ullrich et al., 2001). For example in a study of arctic soils over one summer period, Oiffer and Siciliano (2009) found a net loss of MMHg because most of the mercury seemed to be complexed with DOM and hence unavailable for methylation. Hg^{2+} dissolved in soil solution is more available for methylation processes than adsorbed Hg^{2+} (Gabriel and Williamson, 2004; Skyllberg et al., 2003). Using isotope tracers, Jonsson et al. (2012) confirmed that methylation rate can vary a lot depending on the Hg^{II} species. Methylation rate constants in estuarine sediments were ranked as follows : metacinnabar < cinnabar < Hg^{II} reacted with mackinawite (Fe,Ni sulfide mineral) < Hg^{II} bounded to DOM < $Hg(NO_3)_2(aq)$.

The efficiency of microbial Hg methylation depends also on microbial activity, which in turn is influenced by temperature, pH and redox potential. Moderately high temperatures likely stimulate microbial activity and contribute to explain higher MMHg production rates usually observed during summer in aqueous systems. Besides, enhanced rates of MMHg production (in aqueous systems) seem to be associated with low pH and the presence of decomposable organic matter in reducing environments (Ullrich et al., 2001). For example, Munthe et al. (2001) found more rapid methylation in wetland soils than in dry forest soils.

The influence of organic matter on Hg methylation is not fully elucidated and may have conflicting effects. On the one hand, organic carbon can enhance methylation by stimulating microorganisms or through direct abiotic methylation of Hg by humic or fulvic substances (Ullrich et al., 2001). On the other hand, high DOM concentrations can decrease the bioavailability of Hg to bacteria particularly in the neutral pH range (Ullrich et al., 2001).

It is important to note that due to demethylation, MMHg concentrations reflect net methylation rather than actual rates of MMHg production (Ullrich et al., 2001). To our knowledge, no studies have examined demethylation in soils. In aqueous systems, MMHg is kinetically stable but is efficiently degraded by microbial action and can also be decomposed by photochemical reactions. MMHg degradation by bacteria mainly involves Hg^{II} reduction to Hg^0 and appears to be favored under aerobic conditions (Ullrich et al., 2001). However, oxidative demethylation – up to 8-10 % per day – in sediments (and production of CO_2) has also been established (Hines et al., 2000; Ullrich et al., 2001).

2.3 Inorganic complex forms

The main factors affecting inorganic complex formation are pH, redox conditions, dissolved OH^-, Cl^- and S^- ions and DOM. Due to their abundance and high stability with Hg^{II}, the main inorganic Hg-complexes are with chloride and hydroxyl (Gabriel and Williamson, 2004).

In oxidized soil conditions the predominant inorganic mercury species are $Hg(OH)_2$, $HgCl_2$, $HgOH^+$, HgS, and Hg^0. $Hg(OH)_2$ and $HgCl_2$ are the most frequent (see also Figure 2(a)) due to high abundance and stability of OH^- and Cl^- (Gabriel and Williamson, 2004). $HgCl_2$ is more easily transported in soils than the other inorganic mercury species (less sorption), and typically serves as the substrate for mercury methylation (Han et al., 2006). Mercuric oxide (HgO) can also be encountered in contaminated environments (Ullrich et al., 2001).

In reduced conditions, mercury usually complexes with sulfides to form compounds such as HgS_2^{-2}, $HgS(H_2S)_2$, $Hg(SH)_2$, $HgSH^+$, HgOHSH, and HgClSH (Gabriel and Williamson, 2004; Skyllberg, 2012; Ullrich et al., 2001). Relatively insoluble cinnabar (HgS) can also be formed (Skyllberg, 2010) eventually leading to HgS precipitation (see also section 3.1.1). The dominant factor controlling the speciation of mercury in the presence of sulfide is the redox potential, which determines whether sulfur is in a reduced or oxidized form (Gabriel and Williamson, 2004). In reducing conditions, S^{2-} is normally present in large quantities; therefore HgS is mainly formed under reducing conditions (Gabriel and Williamson, 2004; Schuster, 1991). Accumulation of stable HgS will result in highly insoluble cinnabar or meta-cinnabar, which further precipitate. However, competing ions (Cl^-, DOC, Fe^{2+}) can prevent HgS formation (Gabriel and Williamson, 2004; Skyllberg, 2012).

The speciation characteristics of MMHg are similar to those of Hg^{2+}. CH_3Hg^+ has the following order of affinities for common inorganic ligands: $SH^- > OH^- > Cl^-$. In neutral pH range the following forms predominate due to ion abundance: $CH_3HgCl > CH_3HgOH >$ free CH_3Hg^+ (Gabriel and Williamson, 2004).

2.4 Organic complex forms

Hg and MMHg complexation with dissolved organic matter has been extensively studied (e.g. Haitzer et al., 2002; 2003; Khwaja et al., 2010; Ravichandran, 2004).

In soils, strong interactions between mercury and organic matter are observed. Mainly the sulfur-containing functional groups (especially thiol groups) are considered to be important for Hg and MMHg binding to DOM (Gabriel and Williamson, 2004; Ravichandran, 2004; Skyllberg, 2012). The thermodynamic calculations of Skyllberg (2012; Table 7.2) including common organic and inorganic ligands found Hg complexes with thiol groups by far the dominant aqueous species in freshwater and wetland soils.

In soils not contaminated by anthropogenic sources strong binding sites in organic matter exceed by far the amount of mercury available (Ravichandran, 2004) even if it assumed that only about 2% of the reduced sulfur is available for binding with mercury (Haitzer et al., 2002). The complexation of Hg to NOM, except under extreme conditions of contamination, outcompetes $Hg(OH)_2(aq)$ and $HgCl_2(aq)$ (Skyllberg, 2012). Besides, it is often the case that inorganic Hg species, although quite soluble, are further complexed with organic ligands (mainly fulvic and humic acids) and mineral colloids (EPA, 1997; Gabriel and Williamson, 2004).

Even in the presence of sulfide (for which Hg has a strong affinity), some interaction is observed between Hg and DOM, possibly reflecting the formation of a DOM-Hg-sulfide complex or the hydrophobic partitioning of neutral Hg-sulfide complexes into higher-molecular-weight DOM (Miller et al., 2007).

As illustrated in Figure 2(b) for oxic conditions, two-coordinated Hg^{2+} complex with organic thiols in DOM is probably the dominant form of mercury organic complexation (Hesterberg et al., 2001; Skyllberg, 2012). Three or four-coordinated complexes may also form under neutral and alkaline pH and high S/Hg ratios (Skyllberg, 2012). Concerning MMHg, the dominant form is the one-coordinated complex MMHg-thiol (see Figure 2(c)).

In case of extreme (industrial) Hg contamination, if Hg is in excess compared to DOM sulfur-containing groups it may then bound to oxygen-containing functional groups such as carboxyl or phenol groups (Reddy and Aiken, 2001; Xia et al., 1999).

Figure 3 shows the dominance diagram of Hg species in soils and sediments as a function of pe and pH (Skyllberg, 2012). This diagram differs from traditionally published dominance diagrams by including Hg complexed by thiol groups associated with DOM, and it can be noticed that the $Hg(SR-NOM)_2$ complex dominates over the whole pH scale (Skyllberg, 2012).
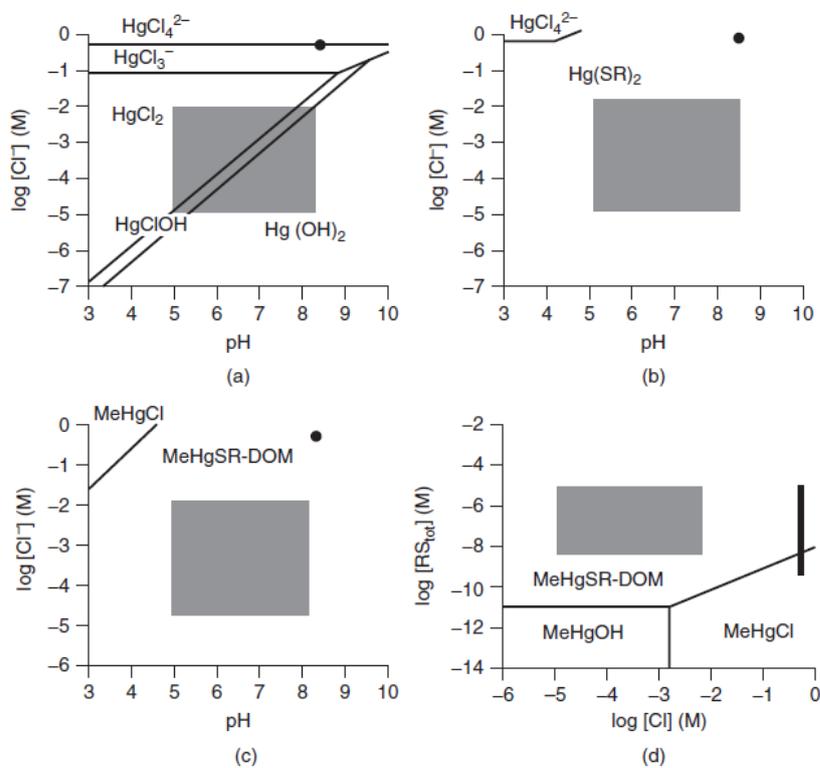
Figure 2 – Dominant Hg aqueous species under oxic conditions (a) in the absence and (b) in the presence of 10 nM of low molecular mass thiols (RS), and (c) for MeHg under oxidized conditions in the presence of DOC 50 mg/L (having 2.3 µM of thiol functional groups, DOM-RS) and (d) a pH of 7. Marine conditions are indicated by black areas, and freshwater conditions by gray areas. Source : Skyllberg (2012).
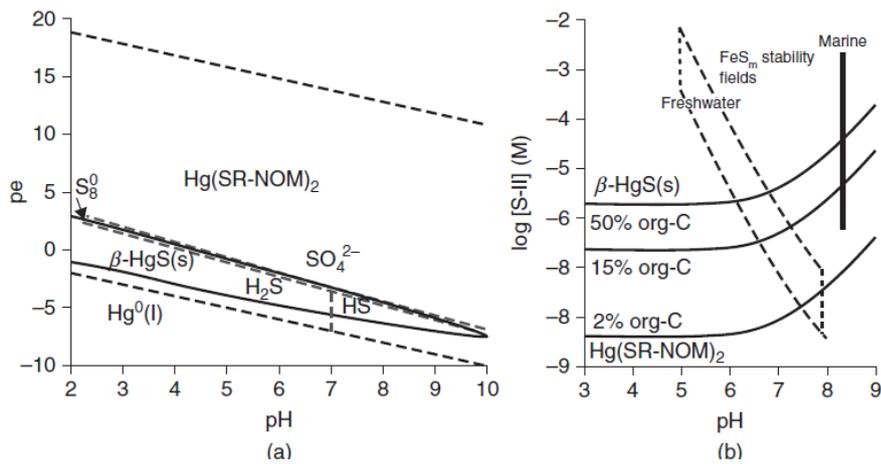
Figure 3 – Dominance diagrams for soils and sediments with 100 ng Hg/g dry mass and 90 mass% pore water content. (a) The solid phase contains 15% organic C (NOM having a concentration of thiol functional groups corresponding to 0.8 mM on a pore water basis): the concentration of inorganic sulfur is 0.1 mM. Solid lines show the stability of mercury species, black broken lines show the stability of water and grey broken lines show the stability of sulfur species. (b) Limiting concentrations of S(−II)(= [H₂S] + [HS⁻]) for the precipitation of metacinnabar in sediments with different concentrations of organic C. Regulation of S(−II) by the solubility of FeSm is indicated at freshwater (area bordered by dotted line) and marine conditions (black field). The stability of FeSm is in equilibrium with Fe²⁺ concentrations of 10⁻³ to 5×10⁻⁵ M in freshwater and 10⁻⁶ to 5×10⁻⁸ in marine environments. Source : Skyllberg (2012).

3   Phase transitions of mercury

3.1   Dissolution

3.1.1   Dissolution of HgS(s) and HgO(s)

HgS(s) is the common ore of mercury. It is mainly encountered in its most stable crystalline α-form (cinnabar) or cubic β-form (metacinnabar). Weathering of HgS(s) ore is a common geogenic source of mercury in the environment (section 1.1).

Formation of HgS(s) in soil solution can immobilize mercury, but in the presence of Cl^- or DOM, HgS(s) formation is inhibited and solubility and dissolution of HgS(s) are enhanced (Gabriel and Williamson, 2004; Miller et al., 2007; Reddy and Aiken, 2001; Skyllberg, 2012; Waples et al., 2005). Based on the stability constants of Hg-DOM and Hg-sulfide complexes, it is not likely that HgS would be thermodynamically favorable (Miller et al., 2007). Instead, interactions between DOM and HgS surface have been suggested, resulting in the dissolution of HgS and formation of a dissolved Hg-DOM complex (Waples et al., 2005): HS–Hg–OH + HR = HS–Hg–R + H2O. It has also been suggested that not all DOM types affect HgS(s) dissolution rates in the same way (Gerbig et al., 2012).

Skyllberg (2012) showed that under certain conditions (presence of S_8^0 and pH>8) polysulfides increase HgS(s) solubility.

In an experimental study, Waples et al. (2005) found linear dissolution rates of HgS with time. Rates approached constant values at a specific ratio of DOM concentration to cinnabar surface area, suggesting a maximum surface coverage by dissolution-reactive DOM.

Dissolution of montroydite (HgO) was studied by Hocsman et al. (2006) among others. They concluded that montroydite will only occur in nature in highly contaminated sites and that Hg oxidation products formed at the Hg^0(l)/water interface may dissolve rapidly.

3.1.2   Dissolution from non-aqueous liquid form

In case of anthropogenic contamination (see also section 1.2), Hg can be present in the form of a (dense) non-aqueous phase liquid or (D)NAPL, which can further dissolve or volatilize in soil systems.

NAPLs behave differently than dissolved solutes in soil systems. This behavior depends on fluid properties such as interfacial tension, viscosity and density; i.e. properties associated with volatilization and aqueous solubility (Mercer and Cohen, 1990). Mass transfer produces vapor and solute transport in the vadose zone.

Mercury NAPL has a high density and high interfacial tension with water (Devasena and Nambi, 2010). Liquid Hg also has the rare property for a liquid of preferentially wetting air rather than solids (Mercer and Cohen, 1990).

Devasena and Nambi (2010) noted that due to its properties, migration and entrapment of mercury DNAPL cannot be fully described using existing theories and models of DNAPL fate (e.g. Fure et al., 2006; Grant and Gerhard, 2007; Kueper et al., 2003). Models of DNAPL dissolution usually describe the mass transfer via changes in interfacial area as a residual non-wetting phase dissolves. The work of Devasena and Nambi (2010) is to our knowledge the only experimental study devoted to mercury DNAPL in soils, and provides useful inputs for two phase flow models specific to mercury-water systems (see also Annex 6.1). Tsakiroglou and Payatakes (1998) also studied mercury intrusion and capillary pressure curves in porous media, but using artificial glass pore networks.

3.2 Sorption

3.2.1 Types of sorbent

The literature on mercury adsorption focuses on Hg^{2+} because it has a high reactivity and high solubility (Gabriel and Williamson, 2004). However, since the dominant Hg^{II} species in solution are uncharged complexes, the dominant mechanism for sorption on the solid phase is stable insoluble inorganic and organic complex formation rather than ion exchange (Schuster, 1991).

Sorbents can be mineral or organic surfaces. Sorbents can also be categorized as particulate (>0.45 µm) and colloidal (<0.45 µm and >1 nm) sorbents (Aiken et al., 2011; Gabriel and Williamson, 2004). Due to their large surface area, the finest particles (i.e. colloidal particles) have the highest adsorption capacities (Gabriel and Williamson, 2004). It should be noted that all fulvic acids (i.e. humic acids having a lower molecular weight and higher oxygen content) are colloids according to the International Humic Substances Society.

Sorption capability of Hg^{2+} is highest for organic matter in the particulate and dissolved phases (especially humic and fulvic substances). In conditions of low Hg/DOM ratio (i.e. no high Hg contamination), sorption of Hg to DOM is controlled by a small fraction of DOM molecules containing a reactive thiol functional group (Haitzer et al., 2002; Ravichandran, 2004).

Other potentially important sorbents are oxides, hydroxides, oxyhydroxides of Fe/Mn/Al (best sorbents MnOOH and FeOOH), armophous FeS under reducing conditions, and clay minerals (Gabriel and Williamson, 2004). However, except under highly contaminated conditions and/or low organic matter environments, Hg and MMHg will not directly bind to oxygen functional groups (Skyllberg, 2012). Therefore, when using Hg/DOM distribution coefficients for modeling the fate and transport of Hg, it is important to take into account the Hg/DOM ratios at which they were determined. For example, at Hg/DOM ratios <1 µg of Hg/mg of DOM, Haitzer et al. (2002) observed very strong Hg-thiol bonds. At Hg/DOM ratios >10 µg of Hg/mg of DOM (as used in most laboratory studies), much lower distribution coefficients are found, indicative of Hg binding mainly to oxygen (carboxyl and phenol) functional groups (Drexel et al., 2002; Haitzer et al., 2002).

Detailed modeling of Hg^{2+} binding to DOM showed the existence of bidentate binding by one thiol group and one other group (statistical mixture of functional groups containing oxygen, nitrogen or sulfur; Haitzer et al., 2003), and indirect adsorption can occur through $Hg(SR)_2$ or $MMHg(SR)$ forming ternary complexes with reactive –XOH groups (Senevirathna et al., 2011; Skyllberg, 2012).

Although highly volatile (see section 3.3), elemental mercury (Hg^0) can also be adsorbed to soil material and has a stronger sorption affinity for DOM than for minerals (metal oxides) (Schlüter, 2000). Hg^0 adsorption increases with sorbent surface area, but the physical structure of soils can also play a role, for example through restricted migration in clay horizons increasing the contact time between Hg^0 and the soil matrix and therefore increasing adsorption (Schlüter, 2000).

In a study of Hg distribution in soil profiles near chlor-alkali plants, migration of Hg to deeper soil layers was suggested to be most effective if Hg was bound to soluble organic complexes (cf. colloid-facilitated transport), whereas Hg bound to mineral components or weak Hg complexes (e.g. Hg^0 bound to inner-sphere sorption sites) were effectively retained in the uppermost soil layer (5 cm) (Biester et al., 2002).

Sorption to colloids is very important to understand the fate of mercury in soils, because colloidal-facilitated transport is sometimes referred to as the main Hg transport process (Gao et al., 2011; Slowey et al., 2005a; Slowey et al., 2005b). Interaction between heavy metals and colloids can potentially be of three types : adsorption, precipitation and cation exchange (Gao et al., 2011). However, among these adsorption is the predominant and most influential for heavy metal mobility in soils.

The three main active colloidal constituents in soils are clay minerals, metal oxides and organic matter (humic and fulvic acids). Colloids may also be classified by surface functional groups: surface hydroxyl, carbonyl, or organic complexation group (Gao et al., 2011). Besides, the sorptive behavior of colloidal particles is not the simple sum of the contributions of the single constituents (it is less because of blockage or loss of accessibility of many functional groups; Cruz-Guzmán et al., 2003).

Studying Hg^{2+} (at high concentration) sorption on soil humic acid, ferrihydrite and montmorillonite colloidal particles, Cruz-Guzmán et al. (2003) found that sorption was much higher on humic acids than on ferrihydrite and montmorillonite. This can be interpreted as the result of strong sorbed complexes with organic S-containing functional groups and a much higher CEC for humic substances than for these minerals (Gao et al., 2011).

Studying the distribution of colloidal Hg in soil, Santoro et al. (2012) found a positive correlation between the concentration of Hg in the colloidal fraction and OM content in samples polluted by a former chlor-alkali plant. Rather than attributing this correlation to sorption of Hg on DOM, they suggested that HgS sorption to DOM could prevent the growth of HgS colloids into larger crystals. This would therefore augment Hg colloidal fraction and increase the risk of Hg mobilization. The effect of colloid sorption to DOM was experimentally investigated by Morales et al. (2011) using polystyrene and carboxylated spheres as colloids. They observed that humic acids could electrosterically stabilize colloids and thus enhanced colloid transport significantly, while fulvic acids hardly affected transport.

More information on colloid-facilitated transport in soils in Flury and Qiu (2008) and in Gao et al. (2011).

3.2.2 Effect of dissolved species (S^{2-}, Cl^- and DOC), pH and heat

Chloride has been shown to interfere with Hg^{2+} adsorption in soils. In general (but not always), an increase in Cl^- concentration reduces adsorption of Hg^{2+} and CH_3Hg^+ to inorganic and organic adsorbents (Gabriel and Williamson, 2004). Similarly, mercury forms a covalent bond with OH^-. This highly stable dissolved complex minimizes the bond between the mineral surface (oxide) and OH^-. As a result, the overall mercury adsorption to mineral surfaces decreases (Schuster, 1991).

The formation of mercury-DOC complexes has an impact on Hg adsorption as generally known for heavy metals, but contrasting effects have been found for mercury (Schuster, 1991). On the one hand, a decrease in Hg adsorption to mineral surfaces could be due to the strong DOC-Hg complex stability that prevents mercury from adsorbing to the mineral surface. On the other hand, an increase in Hg adsorption could be due to a high affinity of the dissolved organic ligand for the mineral surface (Gabriel and Williamson, 2004; Schuster, 1991).

Mercury adsorption is also influenced by soil pH (Gabriel and Williamson, 2004). When pH is <4.5-5, organic matter is the most efficient mercury sorbent. In neutral to alkaline soil, mineral components are more efficient sorbents. As with all metals, adsorption generally decreases with decreasing pH, due to H+ removing and replacing Hg ions (Gabriel and Williamson, 2004). However, it has sometimes been stated that mercury adsorption to humic matter increases at lower pH (e.g. Jing et al., 2007; Sarkar et al., 2000).

Heat has been shown to decrease Hg^{2+} adsorption (Biester and Scholz, 1996). However, in terms of natural occurring temperatures, heat influence on mercury desorption was found only for $HgCl_2$ (Biester and Scholz, 1996; Gabriel and Williamson, 2004).

3.2.3 Equilibrium or kinetic sorption, hysteresis

Kinetic studies, such as that reported by Liao et al. (2009), showed that between 24 and 48h, Hg adsorption reached a quasi-equilibrium state. Amacher et al. (1990) stated that generally multiple

reaction kinetics (e.g. rapid and slow reversible reactions and irreversible reaction) were needed to fit Hg^{2+} sorption.

In a study on four loamy soils at pH 6, Yin et al. (1997b) found that both Hg^{2+} adsorption and desorption were characterized by a biphasic pattern, a fast step (a few minutes) followed by a slow step (<24 h in total). Besides, adsorption and desorption rate coefficients were inversely correlated with the soil organic C content.

In their study on three different soils, Liao et al. (2009) found rapid and nonlinear Hg^{2+} adsorption with the sorption capacities for clay > loam > sand. A multi-reaction model (based on Zhang and Selim, 2006) including sequential and parrallel equilibrium and/or sorption reactions was also used to fit the adsorption data. Yin et al. (1997a) similarly advocated the use of a multireaction model to describe Hg retention in soils, justified by the many different solid phases that can immobilize Hg. Indeed, even in the absence of soil organic matter, Hg transport can be highly retarded due to adsorption to mineral sorbents (Jing et al., 2008). This was confirmed by Liao et al. (2009) who similarly found significant Hg adsorption in the absence of soil organic matter.

S-type isotherms have also been proposed to fit experimental data of Hg adsorption, characterized by limited sorption at low initial concentrations followed increasing adsorption as Hg concentration in solution increases (Yin et al., 1997a). Isotherms of the S-type may be due to the early complexation of Hg by DOM. When Hg^{2+} concentration exceeds DOM complexation capacity, adsorption to soil particle surface becomes competitive (Yin et al., 1997a).

In a review of adsorption isotherms of heavy metals and other chemicals, Ho and McKay (1999) found that pseudo-first order model fitted well the initial period of the adsorption reaction, but that pseudo-second order model provided the best fit on a longer period. Recently, the question on how these pseudo-first and second order models can be interpreted in view of the Langmuir theoretical model has been debated (Liu and Shen, 2008; Marczewski, 2010; Plazinski et al., 2009; Saeid, 2004).

Hysteresis of mercury adsorption/desorption in soils has frequently been demonstrated (e.g. Jing et al., 2008; Liao et al., 2009; Miretzky et al., 2005; Yin et al., 1997b). Besides, the fraction of Hg irreversibly sorbed was shown to be correlated with soil organic content (e.g. Jing et al., 2007; Liao et al., 2009). It has been suggested that irreversible sorption may be due to diffusion of Hg^{II} through intraparticle micropores of soil organic matter (Jing et al., 2007; Yin et al., 1997b), and to high affinity for S-containing groups (Yin et al., 1997b).

In the study of Jing et al. (2007), the influence of pH on Hg^{2+} desorption displayed a "U" pattern; i.e. a decrease with increasing pH in the lower pH range (3-5) and an increase with increasing pH for pH>7. Strong adsorption of metal hydroxo complexes ($HgOH^+$ and $Hg(OH)_2^0$), hydrolysis of Al on exchange sites, competition of protons for adsorbing sites, and acid catalyzed dissolution of reactive oxide sites were suggested to explain this "U" pattern (Jing et al., 2007).

CH_3Hg^+ is less strongly adsorbed to soil than Hg^{2+} (Gabriel and Williamson, 2004).

3.3 Volatilization

Volatilization of mercury from soils has been extensively studied, but it still represents the major uncertainty in global/regional annual budget of non point source mercury transport (Grigal, 2002).

Volatilization is assumed to require three steps: (i) reduction of Hg^{II} to Hg^0, (ii) diffusion or mass transport of Hg^0 to the soil surface (in gaseous and aqueous phases), and (iii) diffusion or mass transport of the Hg^0 across the soil–air boundary layer into the atmosphere (Schlüter, 2000). DMHg is also volatile and can contribute to mercury volatilization from soils, while MMHg and Hg^{II} salts are of minor importance. CH_3HgOH and CH_3HgCl are volatile compounds, but MMHg volatility decreases due to the high affinity to solute and solid organic matter (Schlüter, 2000).

Sunlight (UV radiation) and heat emitted from sunlight (air and soil temperature) are considered the main factors stimulating Hg^0 volatilization (through enhanced reduction of Hg^{2+} to Hg^0) (Gabriel and Williamson, 2004). Looking at the kinetics of Hg emission data, Quinones and Carpi (2011) suggested that mercury emissions from soil samples may follow a multicompartment model (driven by exposure to light) in which one compartment of the emissions spectrum is limited to the surface (<2 cm) of the soil matrix and a second is driven by a subsurface phenomenon.

Apart from sunlight and heat, all factors having an impact on Hg^{II} reduction (section 2.1) are also expected to influence volatilization. For instance, Hg^{2+} volatilization decreases with increasing DOM/Cl^- content, and decreasing moisture content (Schlüter, 2000). Soil moisture content is generally found to be very important to determine the volatilization rate (Schlüter, 2000). Generally, mercury volatilization increases with increasing water content up to a certain level (Rinklebe et al., 2010; Song and Van Heyst, 2005).

Fritsche et al. (2008) suggested that biotic processes are partially controlling Hg^0 volatilization in uncontaminated soils. Biotic action could be direct (biotic reduction of Hg^{2+}) or indirect (microbiological degradation of organic matter followed by Hg^{2+} abiotic reduction). Biological reduction of Hg^{2+} to Hg^0 is favoured in soils of high Hg^{2+} availability and microbiological activity. Abiological reduction is favoured in soils of high organic matter content and/or low Eh. Microbiological reactions can cause considerably higher mercury evaporation rates than abiologically mediated evaporation (Schlüter, 2000).

In a study of uncontaminated (background) forest soils, soil temperature, redox conditions and organic matter were significant factors affecting gaseous mercury concentrations (Moore and Castro, 2012).

Other factors influencing volatilization – via point (ii) above – are soil physical characteristics, sorption capacity, mercury species and content and pH (Schlüter, 2000).

Finally, meteorological conditions (wind speed, relative humidity, turbulent mixing of air layers, etc.) can affect Hg volatilization by limiting or stimulating transport and release – points (ii) and (iii) above (Gabriel and Williamson, 2004; Schlüter, 2000). Meteorological factors may become especially important in Hg enriched or contaminated areas, while in background areas formation of Hg^0 (or DMHg) will be the rate limiting factor (Schlüter, 2000).

Values of mercury emission rates from background areas reported in the literature are usually <0.2 µg m^{-2} h^{-1} and significantly smaller than from mercury enriched or contaminated soils (Schlüter, 2000; Schroeder and Munthe, 1998; Schroeder et al., 1989). Emissions from uncontaminated urban soils varied significantly between different land uses and ranged from 8.7×10^{-4} to 4.5×10^{-3} µg m^{-2} h^{-1} (Gabriel et al., 2005). For comparison, Rinklebe et al. (2010) measured 0.01 to 0.85 µg m^{-2} h^{-1} Hg emission from heavily polluted floodplain soils. Volatilization losses in the subsurface from NAPLs can also be expected, especially where NAPL is close to the surface or in dry sandy soils (Mercer and Cohen, 1990).

Transport of gaseous mercury can also be significant laterally. Walvoord et al. (2008) observed long-distance (several tens or hundreds of meters) migration of elemental mercury released from a buried landfill and transported through the unsaturated zone.

4 Conclusion

Sources of mercury in soil systems include atmospheric deposition, geogenic sources and anthropogenic contamination. Sites of anthropogenic contamination are characterised by high Hg contamination and the presence of NAPL is even possible. The present literature review indicates that in the case of highly contaminated soils many processes occurring in background soils are altered or influenced by local factors (e.g. the presence of specific species, high Hg concentrations, the presence of a NAPL or co-contaminants).

Mercury sinks include volatilization to the atmosphere, and transport to groundwater or surface water. Mercury is usually characterized by a high affinity for soil mineral and organic particles and long residence time in soils. However, under given conditions transport of dissolved Hg species or colloidal-facilitated transport can pose significant threats of environmental contamination.

Mercury in soils exists in different phases: dissolved or complexed Hg in the aqueous phase, adsorbed to mineral or organic sorbents, in the gas phase or in the form of non-aqueous phase liquid. The present document reviewed factors and processes determining mercury speciation and transformation.

Under oxidized surface soil conditions, Hg and MMHg form almost exclusively complexes with thiols. Common inorganic mercury forms are $Hg(OH)_2$, $HgCl_2$, $HgOH^+$, HgS and Hg^0. In reduced environments common mercury forms are $HgSH^+$, HgOHSH, and HgClSH. These mercury forms are generally bound to organic and mineral ions/molecules.

Sorption capability of Hg^{2+} is highest for organic matter in the particulate and dissolved phases (especially humic and fulvic substances). Adsorption rate depends mainly on initial Hg^{2+} concentration, organic matter content, ions in solution. Hysteresis of mercury adsorption/desorption in soils is generally recognized. Sorption to colloids is very important because colloidal-facilitated transport has been referred to as the main Hg transport process.

Volatilization is a three-step process. Hg^{II} is first reduced to Hg^0. Then, Hg^0 is transported/diffused to the soil surface, and finally volatilized across the soil–air boundary layer into the atmosphere. Sunlight and heat are the main factors driving Hg volatilization.

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6 Annex

6.1 NAPL migration and entrampment

There is no major difference in behaviour between LNAPL and DNAPL in the vadose zone. Modeling NAPL migration usually involves complex multi-phase models, in which relative permeabilities, saturations and pressures determine NAPL movement.

Miller (1998) provided a review of multiphase flow and transport models (of which most were used for studying organic compounds). The standard approach relies on continuum balance equations about a representative elementary volume, empirical equations of state and constitutive relations (pressure-saturation-permeability). In the context of modeling NAPL as a source of contamination in the unsaturated zone, it is important that the constitutive relations account for residual (and entrapped) NAPL[1]. Wipfler and van der Zeze (2001) defined a critical NAPL pressure at the transition between free NAPL and residual NAPL; i.e. all NAPL becomes residual below a critical total liquid saturation. However, Oostrom et al. (2005) found no experimental evidence of such a critical total liquid saturation. Oostrom et al. (2005) found a good agreement with experimental observations using the models of Van Geel and Roy (2002) and of Lenhard et al. (2004). These models stem from an existing hysteretic relative permeability-saturation-capillary pressure model and assume the formation of residual NAPL during NAPL drainage and imbition, respectively.

Very few studies are specific to mercury for NAPL characterization and modeling. A notable exception is the work of Devasena and Nambi (2010). They suggested that mercury migration was influenced only by gravity and capillary forces and not by viscous forces. Following their experiment, the capillary forces dominate and lead to mercury entrapment. They measured Hg residual saturation of 0.04 and 0.08 for coarse and fine sand, respectively. They also estimated capillary forces to be 1.22×10^4 times higher than gravity force for mercury NAPL in saturated soil media (coarse sand). The immobile mercury can then be a persistent source of contamination. However, these findings were obtained in saturated media. Mercer and Cohen (1990) noted that in general, residual saturation in the vadose zone is smaller than in the saturated zone. Moreoever residual saturation in the vadose zone increases with decreasing intrinsic permeability, effective porosity and moisture content (Mercer and Cohen, 1990).

Mercury was suggested to produce lower residual NAPL compared to other DNAPLs (e.g. PCE, TCE) (Devasena and Nambi, 2010). Larger Bond number (Bond number relates gravity and capillary forces) for a mercury-water system than for PCE-water systems reflect larger density differences, which lead to less residual saturation.

1) Nambi [AGU abstract] "*Mercury-water systems exhibited a low residual saturation of 0.02 and 0.07 as compared to 0.16 and 0.27 for PCE-water systems. Less residual mercury saturation, lack of apparent hysteresis in capillary pressure saturation curves and large variation in van Genuchten's parameters 'α' (inverse of displacement pressure) and 'n' (pore size distribution index) for mercury-water systems compared to PCE-water*

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[1] Lenhard et al. (2004) make the distinction between residual, entrapped and free NAPL. Residual NAPL is immobile NAPL in small pores and pore wedges (i.e. can be continuous), formed during imbibition. Entrapped NAPL is immobile NAPL occluded by water (i.e. discontinuous). Free NAPL is mobile NAPL, moving in larger pores.

systems were observed. These anomalies between the two systems elucidate that the capillary trapping is equally dependent on the fluid characteristics especially for high density immiscible fluids. Gravity force nevertheless a predominant controlling factor in the migration of highly dense mercury, is counteracted by not less trivial capillary force which was 1.22×10^4 times higher than gravity force. The capillary forces thus surmount the gravity forces and cause entrapment of mercury in the soil pores even in homogeneous porous medium system. Bond number (Bond number relates gravity and capillary forces) for mercury-water system was found to 2.5 times higher than PCE-water systems. Large density differences between mercury and water lead to high Bond number and thus less residual saturation. Capillary number (Capillary number relates viscous and capillary forces) was found to be less for mercury-water systems. Literature review unveils that low Capillary number does not influence non wetting residual saturation. But for high density mercury with natural infiltration, even low Capillary number influences residual saturation. With the alarming increase in number of mercury spill sites, results of this study showed a better understanding of the capillary entrapment phenomena and the extent of influence of each predominant force during displacement of highly dense mercury. The fundamental inputs to NAPL entrapment models were generated in this study for mercury for the first time."

It may be interesting to have an idea of the travel time needed for Hg NAPL to migrate in the subsurface. Gerhard et al. (2007) numerically studied DNAPL mobility in a sandy aquifer. They simulated DNAPL migration in aquifer for the following compounds: TCE, PCE, 1,1 DCE, chlorobenzene, PCB and coal tar. DNAPL density and viscosity were identified as parameters having a significant influence on time scales of migration. Gerhard et al. (2007) showed that DNAPL migration (infiltration rate in saturated zone, in $m^3 \, y^{-1}$) could be plotted as a function of DNAPL mobility M_D (s m^{-3}), defined as $M_D = \frac{\Delta\rho}{\mu_D}$, where $\Delta\rho$ is the difference between DNAPL and water densities (kg m^{-3}) and μ_D is DNAPL viscosity (Pa s). If the properties of mercury (ρ_{Hg} = 13546 kg m^{-3} at 20°C and μ_{Hg} = 1.526×10^{-3} Pa s; M_D = 8.24×10^6 s m^{-3}) are compared to those of the DNAPLs analysed by Gerhard et al. (2007), mercury would be classified as a highly mobile compound; i.e. having relatively short time scales for "subsurface invasion". However, this extrapolation has to be considered with caution because the behaviour of Hg NAPL in the subsurface may not be directly comparable to other DNAPLs, due to the unique properties of mercury[2] (Devasena and Nambi, 2010).

Given that the parameterisation of permeability-saturation-capillary relations seems problematic for Hg NAPLs, one could use simpler models of NAPL migration in the vadose zone. For example, the KOPT module of the HSSM model (Weaver et al., 1994) can simulate the migration of a NAPL front in the vadose zone. To investigate the rate of downward migration of a Hg NAPL in a soil of texture "light sand loam", HSSM was run with the parameterization presented in Table 1. Figure 4 shows the NAPL migration front at different time steps. It can be seen that, starting from a depth of 0.5 m, the front migration reaches 1 m after 2 days; and about 3.3 m (i.e. a 2.8 m downward migration) after 1 year. The downward migration rate is of course highly sensitive to the NAPL release conditions. In a simulation with a 0.1 m ponding depth, it takes ~40 days for Hg NAPL to migrate 0.5 m downwards, and the migration front is ~0.77 m deep after 1 year (i.e. 0.67 m migration). In a simulation with 1 m ponding depth, it takes only ~30 days for the NAPL front to migrate 2.8 m downward (results not shown).

Similar simulations were performed by Marsman et al. (2012), who tested different infiltration scenarios of Hg DNAPL using the model STOMP.

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[2] For example, mercury is the only NAPL which does not preferentially wet solid particles.

Table 1 – Parameters of the HSSM model for simulating a test case of Hg NAPL migration in the vadose zone.

Parameter	Unit	Value	Comment
Water infiltration	m/d	0.001096	Equivalent to 400 mm/y
θ_r	-	0.034	Soil parameters derived for a light sand loam
van Genuchten α	1/m	2.21	
van Genuchten n	-	1.423	
K_{sat}	m/d	0.49	
Max. relative permeability	-	0.5	Default; ensures that the soil is never saturated
Hg NAPL density	g/cm³	13.546	At 20°C (Ebadian et al., 2001)
Hg dynamic viscosity	cP	1.554	At 20°C (Ebadian et al., 2001)
Hg NAPL solubility	mg/L	0.0662	(Clever, 1985)
Hg NAPL surface tension	dyn/cm	436	At 20°C (Ebadian et al., 2001)
Hg NAPL residual saturation in vadose zone	-	0.05	Chosen lower than values for saturated zone in (Devasena and Nambi, 2010); accounting for lower residual saturation in vadose zone than in aquifer (Mercer and Cohen, 1990)
NAPL ponding depth	m	0.5	NAPL release is simulated as a 0.5 m "landfill" at the soil surface
Lower depth of NAPL zone	m	0.5	
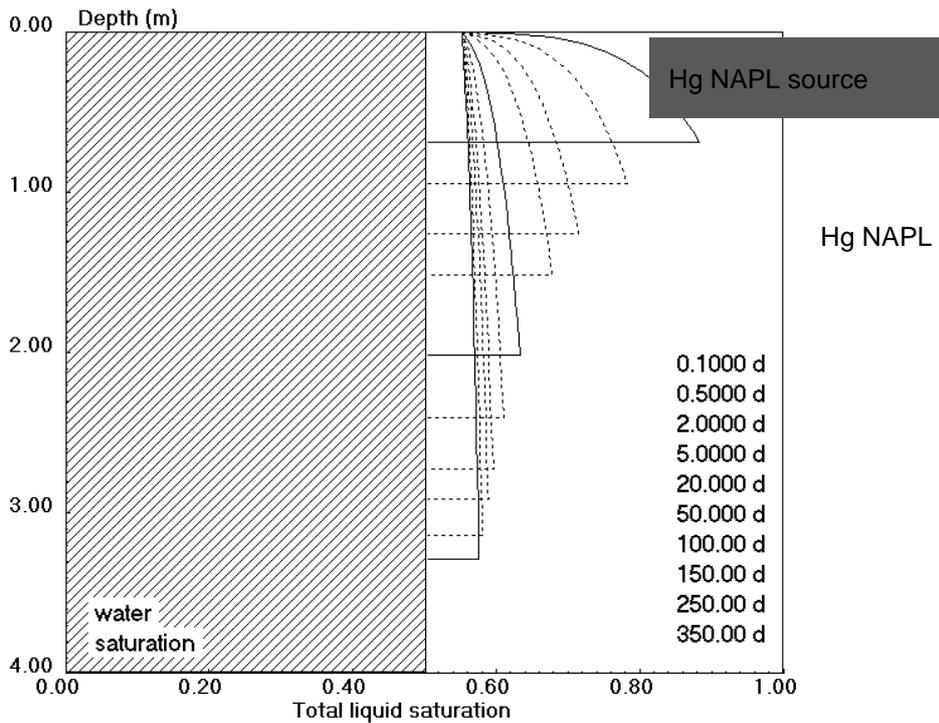
Figure 4 – Hg NAPL saturation profile at different time steps, for an illustrative simulation with parameters given in Table 1.

In practical applications, if Hg contamination in the vadose zone can be assumed to be historical (i.e. only immobile Hg is left), NAPL residual saturation is the main parameter to estimate. Residual saturation can then be used as input to parameterize Hg release to the aqueous and gas phases.