



Dynamic Surface Interface Exchanges of Mercury: A Review and Compartmentalized Modeling Framework

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ABSTRACT

This paper presents a review of recent natural surface mercury exchange research in the context of a new modeling framework. The literature indicates that the mercury biogeochemical flux is more dynamic than the current models predict, with interacting multimedia storage and processes. Although several natural mercury emissions models have been created and incorporated into air quality models (AQMs), none are coupled with air quality models on a mass balance basis, and all lack the capacity to explain processes that involve the transport of mercury across atmosphere–surface media concentration gradients. Existing natural mercury emission models treat the surface as both an infinite source and infinite sink for emissions and deposition, respectively, and estimate emissions through the following three pathways: soil, vegetation, and surface waters. The use of these three transport pathways, but with compartmentalized surface storage in a surface–vegetation–atmosphere transport (SVAT) resistance model, is suggested. Surface water fluxes will be modeled using a two-film diffusion model coupled to a surface water photochemical model. This updated framework will allow both the parameterization of the transport of mercury across atmosphere–surface media concentration gradients and the accumulation/depletion of mercury in the surface media. However, several key parameters need further experimental verification before the proposed modeling framework can be implemented in an AQM. These include soil organic mercury interactions, bioavailability, cuticular transport of mercury, atmospheric surface compensation points for different vegetation species, and enhanced soil diffusion resulting from pressure perturbations.

1. Introduction

Current air quality modeling approaches to deposition and natural surface emissions oversimplify the physical, biological, and chemical processes present at the air–surface interface. The separate treatment of deposition and emissions and the omission of pollutant storage in the surface media compromise the current approach to modeling the surface interface (Wesely and Hicks 2000). Resistance models of deposition velocity must be parameterized in a more fundamental physical, chemical, and biological manner (Wesely and Hicks 2000). Emissions must be coupled with deposition to create a more realistic model of the air–surface interface that will remain relevant on surfaces where

the direction and magnitude of the flux depends on the concentration gradient.

In this paper we present a theoretical framework for modeling the flux of mercury (Hg) between the atmosphere and natural surfaces based on a dynamic compartmentalized surface interface (DCSI) approach that provides a more realistic treatment of sources and sinks, and accounts for biological and soil mercury storage and transport processes. The model accommodates the movement between surface media storage and the flux between the atmosphere and surface interface. Transfer velocities are used to describe the atmosphere–surface water flux and atmosphere–vegetation flux for mercury and other volatile species where concentration gradients are applicable. This approach is applied to mercury as well as other volatile and non-volatile species to account for mercury chemistry in the surface media. In this paper we also review and discuss recent mercury flux measurement work, and describe how the new theoretical framework may explain these observations.

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2. Background

a. Environmental flux measurements

Recent natural mercury flux measurements using micrometeorological and flux chamber techniques indicate that storage and flux phenomena in the biogeochemical mercury cycle cannot be explained by the current mercury surface emission models of Lin and Tao (2003), Bash et al. (2004), and Gbor et al. (2006).

Atmosphere–surface water fluxes are a function of the equilibrium between the atmospheric and surface water concentrations of dissolved Hg^0 and a turbulent enhanced transfer velocity (Rolfhus and Fitzgerald 2001). In addition, the aqueous chemistry of mercury in the surface waters indicates that the dissolved elemental mercury primarily comes from the photoreduction of aqueous Hg^{2+} and particulate-bound Hg (Costa and Liss 2000). Currently, either the surface water elemental mercury concentrations are taken to be a constant (Lin and Tao 2003; Bash et al. 2004) or diurnal variations are modeled using empirical equations (Gbor et al. 2006). This treatment of the atmosphere–surface water mercury flux will not capture the impact of surface water concentration enrichments or depletions on the elemental mercury flux, or the surface water photochemistry. Air quality models (AQMs) that parameterize the atmosphere–surface water flux using a transfer velocity and dynamic concentration gradient across the atmosphere–surface water interface would be more physically sound than current uncoupled treatments of emissions and deposition (Wesely and Hicks 2000).

Recent atmosphere–terrestrial flux measurements indicate that mercury is accumulated in the leaves of plants through atmospheric and soil sources (Ericksen et al. 2003; Frescholtz et al. 2003; Rea et al. 2002), and that there is a significant influx of mercury to the soil is through leaf litter fall. Ericksen et al. (2003) found that mercury accumulated in aspen stand foliage for 2–3 months before reaching equilibrium with the environment. Both Ericksen and Gustin (2004) and Hanson et al. (1995) observed compensation points in the vegetative mercury flux. Recent measurements indicate that the atmosphere–vegetation mercury flux is seasonally dynamic and dependent on the atmosphere–leaf intercellular airspace concentration gradient (Ericksen et al. 2003; Ericksen and Gustin 2004). Most recently, Bash and Miller (2007, manuscript submitted to *Appl. Geochem.*) presented terrestrial mercury flux data over a hardwood forest and concluded that foliar accumulation over the growing season apparently reached the foliar storage potential for background concentration levels. This was interpreted as the transition from net deposition to net evasion at mid–growing season. Ex-

isting atmosphere–vegetation mercury emission models do not calculate vegetative concentrations and are unable either to parameterize the buildup of mercury in vegetation or to capture the vegetative compensation point using concentration gradients. These measurements indicate that vegetation is more than just a conduit for the transport of mercury in the soil water solution to the atmosphere.

The atmosphere–soil mercury flux is coupled to the atmosphere–vegetation mercury flux through vegetative uptake of mercury, the evasion of mercury from the soil surface, and leaf litter fall (Rea et al. 2002). Vegetation is also capable of actively removing mercury from soil through the uptake of mercury in the soil water solution (Bishop et al. 1998; Ericksen and Gustin 2004; Hanson et al. 1995). Recent measurements of the atmosphere–soil mercury flux in the absence of vegetation indicates that it is a process involving absorption, desorption, and displacement processes (Johnson et al. 2003). Ravichandran (2004) reviewed the processes that are involved in the desorption of particulate mercury into surface waters and soil water solution, and compiled recent research that indicates the importance of organic matter in the desorption and reduction processes of particulate-bound mercury. Mercury soil evasion models currently treat the processes as either an empirical function of the soil temperature (Lin and Tao 2003; Bash et al. 2004) or a stochastic function of temperature, solar radiation, and the mercury soil water solution concentration (Gbor et al. 2006). These models greatly simplify the atmosphere–soil mercury flux and do not couple the soil mercury reservoir with foliar uptake, deposition, or evasion.

b. Bioremediation research

The bioremediation community has been active in investigating vegetative uptake of mercury in contaminated soils (Heaton et al. 2005; Wang and Greger 2004; Moreno et al. 2005a,b). The results of this research have clarified some of the pathways for vegetative mercury uptake and some of the factors influencing the atmosphere–vegetation exchange of mercury.

Plants have been bioengineered to increase their mercury tolerance and uptake and to increase their ability to reduce ionic mercury bound in the roots and leaves (Heaton et al. 2005). Studies have also focused on spiking contaminated soils with ligands to enhance the vegetative uptake of mercury (Moreno et al. 2005a,b). Mercury appears to pass through the soil root interface much more readily in an ionic ligand complex than other ionic mercury compounds (Moreno et al. 2005a,b). The research of Moreno et al. (2005a) indicates that dissolved elemental mercury also passes

through the soil–root interface but remains much more mobile in the vegetative system. Bioremediation studies, as well as the biogeochemical flux work, have found that mercury concentrations are highest in the roots and that mercury in the leaves likely comes from both atmospheric and soil sources (Heaton et al. 2005; Wang and Greger 2004). Heaton et al. (2005) found that native plants have the ability to reduce ionic mercury bound in foliar cells to elemental mercury, which then escapes into the atmosphere. The reduction of Hg^{2+} in plants needs more investigation, but in highly contaminated sites it appears to be caused by a direct reduction–oxidation (redox) reaction of Hg^{2+} with NADPH, the reduced form of nicotinamide adenine dinucleotide phosphate (NADP) produced by photosynthesis (Lenti et al. 2002; Solymsi et al. 2004).

Existing atmosphere–terrestrial mercury interfaces do not model oxidation, reduction, or mercury–organic matter interactions. The chemical composition of the mercury in the surface media determines its mobility in the environment (Moreno et al. 2005a,b; Ravichandran 2004; Gabriel and Williamson 2004). Research in the bioremediation and mercury biogeochemical cycling indicates that the surface media mercury chemistry must be modeled to parameterize the transport of mercury across the atmosphere–surface interface and the interfaces between heterogeneous surface media.

While bioremediation research can provide valuable insights into the factors affecting mercury movement and storage in natural systems, the high mercury concentrations used may produce physiological and biochemical affects that would not be seen in natural systems with lower mercury concentrations. The objective of much of the bioremediation work is to use vegetation as a means to extract mercury from contaminated soils. The research obtained by such studies may identify potential pathways and mechanisms in the mercury biogeochemical cycle that should be verified experimentally at background concentrations. For example, the NADPH reduction pathway of Hg^{2+} was only observed under either very high soil or foliar mercury concentrations. It is unclear whether this reduction pathway would exist under uncontaminated conditions because of location of Hg^{2+} storages within the plant cells (Solymsi et al. 2004).

c. Related mercury emission modeling work

Several natural mercury emissions models have been developed recently for use with AQMs. A summary of recent natural emissions modeling efforts is presented in Table 1. In these models, natural mercury emissions from vegetation, soil, and surface waters are modeled as lower boundary conditions for the San Joaquin Val-

TABLE 1. A comparison of the conceptual and existing natural surface mercury flux models.

	Proposed model	Gbor et al. (2006)	Bash et al. (2004) (HgSIM)	Lin and Tao (2003)	Xu et al. (1999)
Surface storage	Compartmentalized	None	None	None	None
Transfer model	Two-film resistance	Atmosphere–vegetation interface	Function of transpiration	Function of transpiration	Function of transpiration
Stomatal resistance	Jarvis style	Function of transpiration	Jarvis style	Function of soil moisture	Function of soil moisture
Mesophyll resistance	Included	Included	Neglected	Neglected	Neglected
Wet canopy treatment	Included	Included	Neglected	Neglected	Neglected
Bare soil emissions	Pressure pumping–enhanced two-film resistance model + soil	Function of temperature and concentration	Atmosphere–soil interface	Function of temperature	Function of temperature
Forest soil emissions	photochemical model	Function of solar radiation and concentration	Function of temperature	None	None
Transfer model	Two-film diffusion model	Atmosphere–surface water interface	Two-film diffusion model	Two-film diffusion model	Two-film diffusion model
Schmidt's number	Function of temperature	Wind-enhanced evasion model	Constant	Function of temperature	Constant
Henry's constant	Function of temperature	Constant	Function of temperature	Constant	SAQM
Software interface	Integrated surface layer of an AQM	Stand-alone module + MCIP	Stand-alone module	Stand-alone module + MCIP + CCTM	SAQM
Coupled to AQM	Yes	No	No	No	No

ley Air Quality Study and Atmospheric Utility Signatures, Prediction, and Experiments Regional Modeling Adaptation Project (SARMAP) Air Quality Model (SAQM) and Models-3 frameworks. Vegetative Hg^0 emissions are predicted using a soil water solution concentration and an evasion velocity calculated from modeled transpiration. Soil Hg^0 emissions are predicted using empirical equations derived from measurements. Emissions from surface waters are predicted using a transfer coefficient and an equilibrium concentration of Hg^0 between the atmosphere and the surface water. The modeling framework described below will use these three pathways, but fluxes will be coupled to surface storage through physiochemical relationships taken from recent mercury flux and bioremediation work.

Xu et al. (1999) developed the first natural mercury surface emissions model for the surface boundary conditions of the SAQM. The model of Xu et al. (1999) categorized natural emission into elemental mercury emitted from vegetation, soil, and water. The foliar emission rate was modeled as a function of the soil water elemental mercury concentration and the transpiration rate. Transpiration was modeled using the Penman–Monteith equation (Monteith and Unsworth 1990) with a canopy conductance modeled as a function of soil water content (Raupach 1991). Emissions from the soil were modeled as a function of soil temperature following Carpi and Lindberg (1998). A two-film diffusion model based on Mackay and Yeun (1983) with enhanced diffusion resulting from bubble plumes following Asher and Wanninkhof (1995) and Asher et al. (1996) was used to model both elemental mercury deposition and evasion at the atmosphere–water interface.

Lin and Tao (2003) developed a natural mercury emission model in the Models-3 environment using the newly developed Community Multiscale Air Quality Model (CMAQ) modified to include multiphase mercury chemistry (Bullock and Brehme 2002). Natural emissions of elemental mercury were modeled from vegetation, soil, and water surfaces. Foliar and soil emissions were modeled following Xu et al. (1999). The atmosphere–water interface was modeled using a two-film diffusion model following Poissant et al. (2000). Lin and Tao (2003) modified the CMAQ chemical transport model (CCTM) to include Hg^0 dry deposition and a revised rate of Hg^0 oxidation by OH.

Bash et al. (2004) developed the Mercury Surface Interface Model (HgSIM), which revised the natural mercury emissions model developed by Xu et al. (1999) for use in the Models-3 environment. Foliar emissions were again modeled using the Penman–Monteith equa-

tion (Monteith and Unsworth 1990) but, unlike Xu et al. (1999), with a nonlinear stomatal conductance following Stewart (1988).

Gbor et al. (2006) developed a surface emissions model for the Models-3 framework that predicted natural emissions using the same three pathways as Xu et al. (1999). Gbor et al. (2006) used a modified Jarvis-style stomatal conductance following Noilhan and Planton (1989). The canopy conductance was modified to include reduced transpiration under wet conditions and mesophyll conductance of elemental mercury. Emissions from forest soils were included and modeled as an empirical function of solar radiation. Emissions from surface water were treated using an evasion velocity calculated following Lin and Tao (2003).

All of these previous models treated the atmosphere–surface interface as an infinite sink and source for deposition and emissions, respectively. Recent measurements, noted in the previous section, show that concentrations across and within the surface media contribute to emissions and surface storage. The revised HgSIM modeling framework, described in detail below, will calculate emissions from surface media as a function of a transfer velocities and concentration gradients where applicable, and as physiochemical or absorption–desorption processes where mercury oxidation and reduction are the dominant processes. The transfer of mercury between surface storage contributes to the dynamics of natural mercury cycling and will be modeled where the processes are understood. With the new revisions discussed below, HgSIM will be more capable of capturing the storage and fluxes observed in measurement campaigns.

3. Theoretical modeling framework

A more physically robust model of the air–surface interface can be constructed by coupling the atmospheric deposition with emissions through storage and concentration gradients across the surface media (Wesely and Hicks 2000). The compartmentalized model described below and diagrammed in Figs. 1–3 is better able to represent the dynamics shown in recent mercury flux measurements and mercury bioremediation work. The compartmentalization and coupling of the surface layer introduces fluxes between the surface media and lower atmosphere layer that can be solved numerically. Concentrations can be dynamically calculated in the surface media and the conservation of mass can be extended to the surface media. The surface media chemistry can be solved using available solvers in AQMs, such as CMAQ.

Mercury behaves differently in each of the modeled

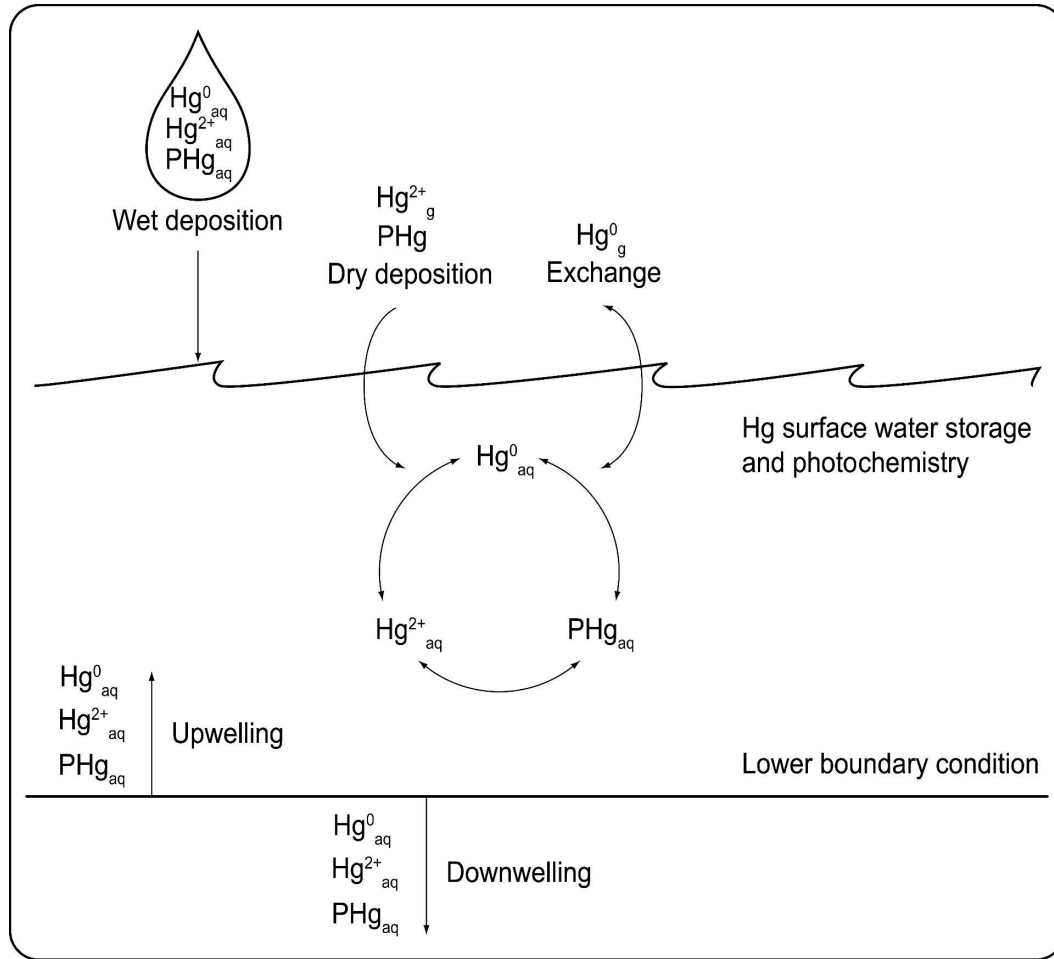


FIG. 1. Illustration of a general conceptual scheme of the mercury flux across the atmosphere–surface–water interface.

surface media. Therefore, the model partitions the surface into water, soil, root, leaf mesophyll, and cuticular storage of elemental, reactive, and particulate mercury. Transport between these media is governed by multiphase mercury chemistry, physical diffusive processes, and biological processes.

The current representation of the atmosphere–surface exchange of mercury in most AQMs is expressed using separate deposition velocities for gaseous deposition [Eq. (1)] and evasion velocities for emissions [Eq. (2)],

$$F_{d,\text{Hg}^x} = V_{d,\text{Hg}^x} C_{a,\text{Hg}^x}, \quad (1)$$

where F_{d,Hg^x} is the dry deposition flux, V_{d,Hg^x} is the dry deposition velocity, and C_{a,Hg^x} is the atmospheric concentration of mercury species x . The dry deposition velocity is often represented using either a series of boundary layer and surface layer resistance models

(Wesely and Hicks 2000) or a constant value for dry deposition (Lee et al. 2001).

Evasion from natural surfaces can be generalized as follows:

$$F_{e,\text{Hg}^x} = V_{e,\text{Hg}^x} C_{s,\text{Hg}^x}, \quad (2)$$

where F_{e,Hg^x} is the surface evasive flux, V_{e,Hg^x} is the evasion velocity, and C_{s,Hg^x} is the surface media concentration of mercury species x . The evasion velocity, much like the dry deposition velocity, can be parameterized using a resistance model.

Flux measurements and modeling studies indicate that Hg^0 dry deposition is an increasingly important process in the mercury geochemical cycle, and ionic mercury can be readily reduced in surface media (Lee et al. 2001; Lin et al. 2006). The evasion and deposition velocities are physically similar and Eqs. (1) and (2) can be combined using a two-film resistance parameterization for a more physically sound surface exchange

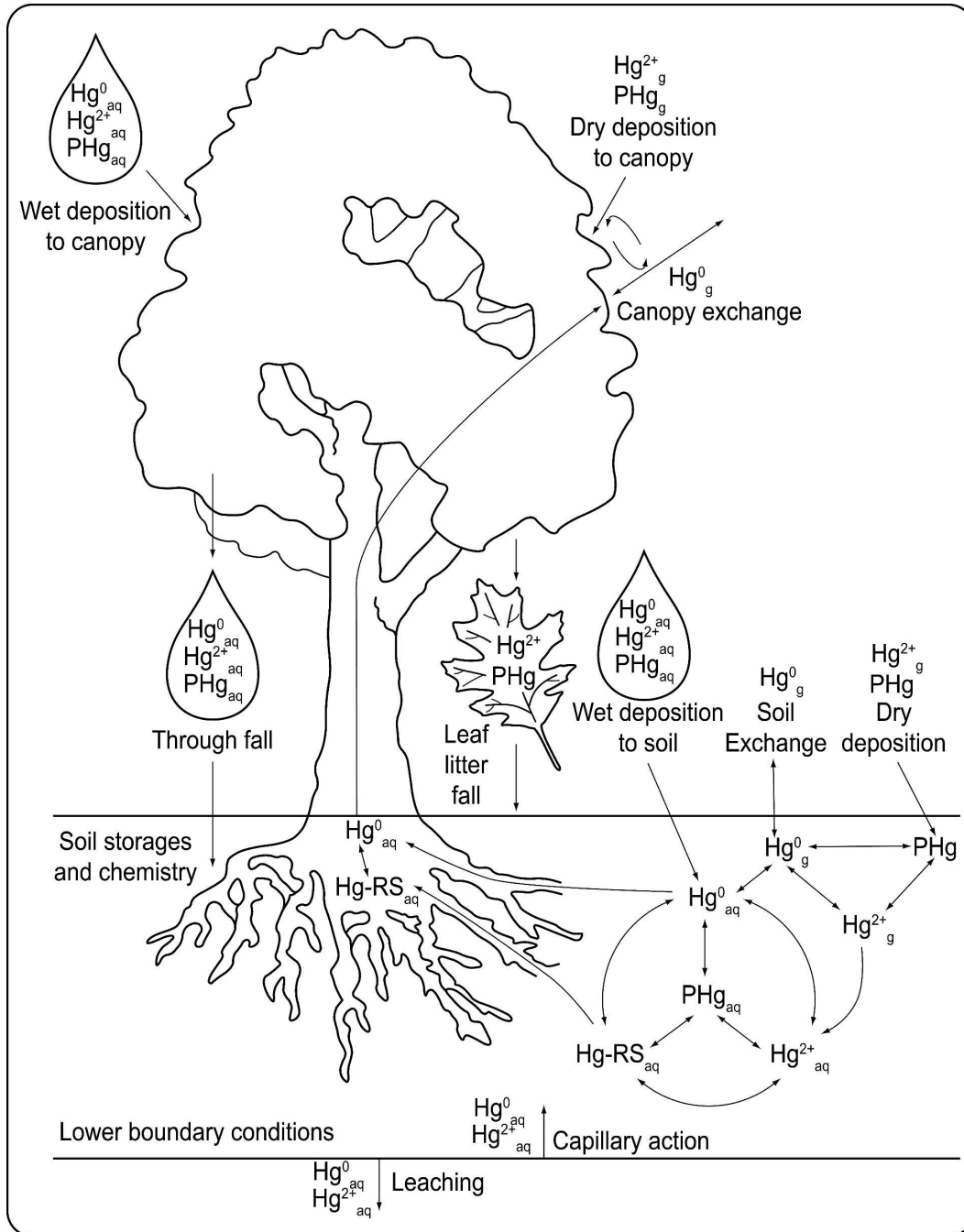


FIG. 2. Illustration of the general conceptual scheme of atmosphere-terrestrial-mercury cycling.

model with the potential to capture gradient-dependent fluxes or “compensation points,”

$$F_{Hg^x} = V_{Hg^x} \Delta C_{Hg^x}, \quad (3)$$

where F is the atmosphere-surface flux of mercury species x , V is the exchange velocity across the atmosphere-surface media interface, and ΔC_{Hg^x} is the con-

centration gradient of mercury species x across the atmosphere-surface media interface. Atmosphere-surface media concentration gradients can be modeled using partitioning coefficients. Equation (3) can be generalized for exchanges across atmospheric-vegetation, -soil, and -surface waters. Examples of atmosphere-surface layer exchanges are given below.

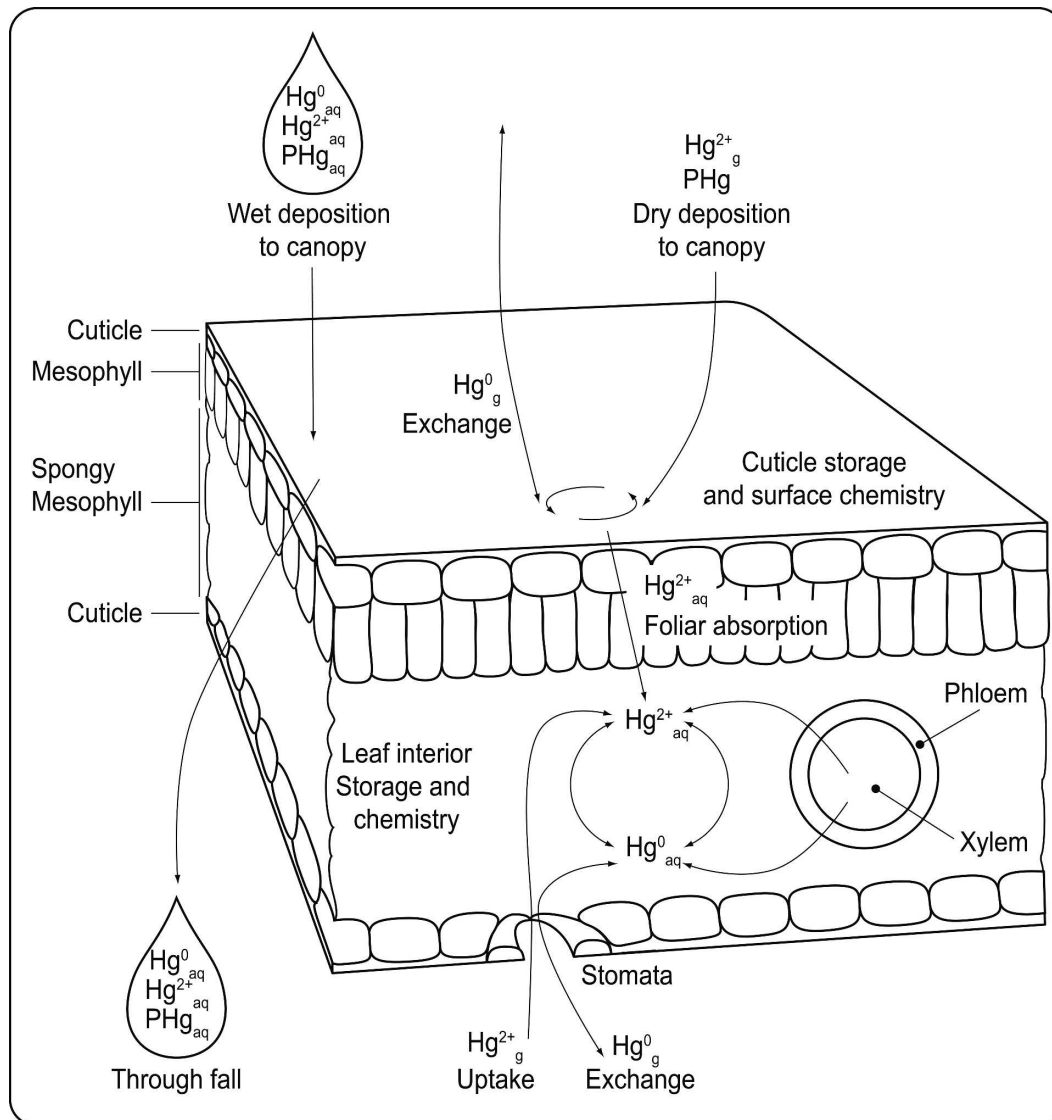


FIG. 3. Illustration of a general conceptual scheme of atmosphere–foliar–mercury cycling.

a. Atmosphere–surface water interface

The direction of the surface flux over water bodies is dependent on the atmospheric mercury concentration, the surface water mercury concentration, and Henry's constant (Rolfhus and Fitzgerald 2001). The magnitude of the flux depends on the concentration gradient between the atmosphere and the water, and the turbulent transfer velocity. The traditional method of separately modeling emissions from and deposition to surface waters is unsatisfactory because of the air–surface water gradient dependence on the direction of the flux (Wesely and Hicks 2000). Dynamic surface conditions over water bodies can be modeled by using a two-film diffusion model to couple the AQM atmospheric chem-

istry model with a surface water chemistry model, as described in Fig. 1.

A two-film model can be used to couple atmospheric–surface water mercury flux by incorporating surface storage and surface water aqueous chemistry (Fig. 1) to provide a dynamic surface water concentration [Eq. (3)]. Disequilibrium between the surface water and atmospheric concentrations can occur because of chemical consumption or production of a pollutant, shifts in concentrations resulting from atmospheric advection, or the up- or downwelling of surface water. Surface water–dissolved elemental mercury concentrations are often above the atmospheric equilibrium, suggesting that mercury bound to particles and dissolved reactive mercury is being reduced to dissolved elemental mer-

cury (Rolfhus and Fitzgerald 2001; Costa and Liss 2000; Costa and Liss 1999). Surface water inputs of mercury resulting from wet and dry deposition can be coupled with the photochemistry and evasion of elemental mercury in the surface water across the atmosphere–surface water interface using a two-film diffusion model.

Turbulence-enhanced emissions from surface waters will be modeled using a two-film diffusion model with a turbulent transfer coefficient calculated according to Wanninkhof (1992),

$$F_{\text{SwAqHg}^x} = k_l(C_{\text{SwAqHg}^x} - C_{\text{AtmGHg}^x}/H), \quad (4)$$

where $F_{\text{SwAqHg}^x} \lim_{x \rightarrow \infty}$ is the net elemental mercury flux from the surface water, k_l is the two-film diffusion coefficient, C_{AtmGHg^x} is the atmospheric concentration of Hg^0 , C_{SwAqHg^x} is the aqueous Hg^0 concentration, and H is Henry's constant for an air–water mercury equilibrium.

A sink term representing the up- and downwelling of deep-water areas in modeling domains will be necessary to more realistically portray the oceanic system.

b. Atmosphere–soil interface

Recent experimental evidence indicates that the transport between the soil particles and the soil water solution is mediated by chemical sorption and desorption processes (Ravichandran 2004; Moreno et al. 2005a; Johnson et al. 2003) governed by soil redox potential, pH, dissolved ions, and sunlight (Gabriel and Williamson 2004). Reduction of ionic mercury compounds in soil is dominated by available electron donors, low redox potential, and sunlight intensity (Ravichandran 2004; Gabriel and Williamson 2004). The dissolved elemental mercury pool in the soil water solution is then available for evasion into the atmosphere or uptake by plants (Moreno et al. 2005a). A multiphase physiochemical model similar to Zhang and Lindberg (1999) with the addition of the ligand and dissolved organic matter reactions described by Ravichandran (2004) and Gabriel and Williamson (2004) should be used to partition the mercury into solid, gaseous, and liquid phases in the soil media (Fig. 2). The addition of ligand–mercury reactions is included because recent research indicates that other ionic forms of mercury, HgCl_2 , in particular, physically block root aquaporin water channels and do not cross the soil solution–root barrier (Hukin et al. 2002).

Adsorption/desorption physiochemical models have underpredicted mercury fluxes when compared with soil flux measurements (Johnson et al. 2003). We hypothesize that the diffusive transfer coefficient in these

models may be underpredicted because they do not take into account pressure perturbations from air motion above the soil surface that enhances mixing in the porous soil media. Takle et al. (2004) observed that measured CO_2 fluxes were 5–10 times higher than the predicted diffusional fluxes predicted by Fick's law and the vertical concentration gradient under conditions conducive to pressure pumping. Enhanced diffusion through the soil pore spaces resulting from pressure perturbations reported by Takle et al. (2004) are apparently large enough to rectify the underprediction of the physiochemical model proposed by Zhang and Lindberg (1999). A more physical description of the atmosphere–soil flux of mercury should be modeled using Fick's law with an exchange coefficient, which is enhanced by pressure pumping and the concentration gradient between the atmosphere and soil airspace concentrations.

Two-film modes of the atmosphere soil exchange of mercury have been successfully applied to describe mercury fluxes measured using the dynamic flux chamber (DFC) technique (Zhang et al. 2002; Lindberg et al. 2002). The two-film resistance model can be applied to the soil–atmosphere flux similarly by applying the atmospheric boundary layer resistance to the model presented by Zhang et al. (2002),

$$F_{\text{Sl,Hg}^x} = \frac{1}{R_{\text{Sl}}} (C_{\text{SlG,Hg}^x} - C_{\text{AtmG,Hg}^x}), \quad (5)$$

where $F_{\text{Sl,Hg}^x}$ is the flux of mercury species x across the air–soil interface, R_{Sl} is the sum of the atmospheric boundary layer and soil resistances accounting for pressure pumping, and $C_{\text{SlG,Hg}^x}$ and $C_{\text{AtmG,Hg}^x}$ are the soil and atmospheric concentrations of mercury species x . The multiphase soil aqueous–gaseous–solid concentrations will be modeled using sorption coefficients similar to Bullock and Brehme (2002).

c. Soil–vegetation interface

Plant roots are highly specific about what minerals and nutrients that they take up, and recent experiments suggests that ionic divalent mercury bound to ligands and elemental mercury are the most mobile species to be transported from the soil to the leaves (Moreno et al. 2005b). Plants have the ability to modify their local environment in response to nutrient demands. Enzymes and small molecules are released to acidify the plant's rhizosphere and mobilize trace metals that are typically bound to soil particles (Meagher and Heaton 2005). Recent experiments have shown that divalent ionic mercury bound to organic thiols and sulfur-

containing ligands are more readily taken up by the root system than other divalent mercury compounds (Meagher and Heaton 2005; Moreno et al. 2005b). Recent measurements have also suggested that the binding constants for organic ligands can compete with inorganic sulfides in the soil matrix (Ravichandran 2004).

The theoretical compartmentalized model presented in Fig. 2 represents a multipathway exchange process between the soil, root, and foliar compartments. Root uptake of mercury is a selective process where ionic mercury is most likely to be transported through the soil–root barrier when it is bound to sulfur sites of organic thiols, similar to the uptake of iron, copper, and zinc (Meagher and Heaton 2005). Once in the transpiration stream, mercury can be stored in the roots or translocated to the stems and leaves (Ericksen and Gustin 2004; Meagher and Heaton 2005).

Inputs of mercury into the soil matrix are assumed to be from wet and dry deposition and leaf litter fall, while outputs are assumed to be due to evasion from the soil surface, plant uptake, and leeching, Fig. 2. Mercury uptake in the soil water solution can be parameterized as a function of plant transpiration. Transpiration can be modeled assuming that the total root water uptake is equal to the total amount of canopy transpiration neglecting the plants water storage capacity (Chen and Coughenour 1994). This assumption neglects seasonal and diurnal lags between root uptake and transpiration, as well as events that may dry or moisten the aboveground biomass. Concentrations of sulfur-containing ligands are assumed to be a fraction of the soil organic matter content as described by Ravichandran (2004).

The soil–vegetation flux can be modeled by combining the multimedia fugacity model of Trapp and Matthies (1995) with a foliar resistance model. Assuming a bidirectional diffusion between the roots and the soil water solution where a positive flux is from the roots to the soil,

$$F_{SR,Hg^x} = D_w \left[C_{SIAq,Hg^x} - \frac{C_{R,Hg^x}}{\left(\frac{K_{RW,Hg^x}}{K_{d,Hg^x} Q_b + \theta} \right)} \right], \quad (6)$$

where F_{RB,Hg^x} is the flux of mercury species x across the soil–root interface, D_w is the diffusivity of mercury in water, C_{SB,Hg^x} and C_{R,Hg^x} are the concentrations of mercury species x in the bulk soil matrix and the root tissue, respectively, K_{RW,Hg^x} is the partitioning coefficient for mercury species x between root tissue and water media, K_{d,Hg^x} is the distribution coefficient between the soil matrix and water for mercury species x , and Q_b is the bulk density of the soil.

d. Translocation from roots to leaves

There has been abundant recent research in both bioremediation and biogeochemical cycling to determine the source of mercury measured in foliar tissue (Ericksen and Gustin 2004; Rea et al. 2002; Moreno et al. 2005a,b). Currently, annual mercury accumulation in foliage has been published for aspen seedlings in sandy loam soils, amended with mine tailings (Ericksen and Gustin 2004) and mature aspen, beech, birch, maple, and oak at mixed hardwood sites in Vermont and Michigan (Rea et al. 2002). The model is generalized using the available data; however, other species of plants likely exhibit different dynamics when exposed to atmospheric and soil mercury. Mercury accumulation in roots has been determined to originate from the soil mercury pool (Ericksen and Gustin 2004; Moreno et al. 2005a,b). Foliar mercury concentrations are much lower than soil mercury concentrations and measured root concentrations (Ericksen and Gustin 2004; Moreno et al. 2005a,b). Once in the transpiration stream, mercury is primarily accumulated in the roots (Moreno et al. 2005b; Greger et al. 2005; Frescholtz et al. 2003). The research of Moreno et al. (2005b) suggests that mercury bound to ligands passes through the soil root interface but is stored in plant tissue and not volatilized to the atmosphere. Moreno et al. (2005a) indicates that Hg^0 is present in the soil water solution and speculates that it is available for uptake into the transpiration stream and is subsequently released into the atmosphere.

Translocation from roots to foliar tissue in the model is considered a single direction phenomenon and parameterized as follows;

$$F_{Tr,Hg^x} = Q_t \frac{C_{R,Hg^x}}{K_{RL,Hg^x}}, \quad (7)$$

where F_{Tr,Hg^x} is the translocation flux of mercury species x from the roots to foliar tissue, Q_t is the rate of transpiration, C_{R,Hg^x} is the concentration of mercury x in the roots, and K_{RL,Hg^x} is the partitioning coefficient of mercury species x between the roots and leaves

e. Leaf–atmosphere interface

Aboveground accumulation of mercury in plant biomass is believed to originate from both atmospheric and soil sources (Frescholtz et al. 2003; Hanson et al. 1995; Ericksen and Gustin 2004; Meagher and Heaton 2005). The foliar tissue can accumulate mercury from the atmosphere through cuticular deposition or stomatal uptake or from the soil because of transport through the transpiration stream (Leonard et al. 1998;

Moreno et al. 2005a, Rea et al. 2000; Fig. 3). Mercury bound to foliar tissue is reduced to elemental mercury by the plant (Heaton et al. 2005). Because of elemental mercury's low solubility and high vapor pressure, we assume that the reduced elemental mercury is quickly diffused from the mesophyll to the leaf intercellular airspace. The atmosphere–biosphere continuum described by Campbell and Norman (1998) and Niyogi et al. (2003) will be described by modeling fluxes across the stomata and storage within the leaves. This bidirectional diffusion process is assumed to enrich the interstitial gaseous elemental mercury concentration; and if the interstitial concentration is greater than the atmospheric concentration, then mercury will diffuse from the leaf intercellular spaces to the atmosphere through the stomata. If the atmospheric concentration is greater than the leaf intercellular space concentration, then mercury would diffuse from the atmosphere to the leaves (Fig. 3). Reactive ionic and elemental mercury can enter the foliar system through stomatal uptake where it likely is absorbed by the leaf mesophyll (Hanson et al. 1995).

An alternative pathway of accumulation of mercury in leaves is of dry deposition to the leaf surface and foliar absorption of reactive gaseous mercury through the leaf cuticle (Rea et al. 2000). Zhang et al. (2003) have developed a dry deposition and foliar absorption resistance model for ozone and sulfur dioxide (O_3 and SO_2) that could be expanded to mercury. Reactive gaseous mercury deposited onto the leaf surfaces follows this pathway into the leaf interior where it is likely is reduced and evades back into the atmosphere or is absorbed into the foliar system. Measurements by Rea et al. (2000) and Ericksen et al. (2003) reported that the majority of the mercury in the leaves is located within the leaves and not on the surface. Rea et al. (2000) speculated that mercury deposited to the leaves was either revolatilized, washed off in precipitation events, or absorbed through the leaf cuticle. Rea et al. (2000) hypothesize that the multiphase atmosphere–leaf cuticle flux can be treated similarly to mercury–aerosol chemistry. For a complete atmosphere–foliar model, mercury deposited to leaf surfaces could be reduced through photogenic or chemical processes and reemitted into the atmosphere, it could be washed off by precipitation events, or it could be absorbed into the leaf and stored in leaf mesophyll, Fig. 3.

Deposition of Hg^{2+} to the canopy can be treated using the traditional deposition velocity because of its low volatility and high solubility. Nonstomatal deposition of Hg^{2+} can also be treated as resistance following Zhang et al. (2003) and scaled from the cuticular resistances of O_3 and SO_2 from the solubility and half-redox

reactivity of Hg^{2+} following Wesely (1989). Reduction and evasion processes from the cuticle surface should be modeled as a desorption process.

The atmosphere–vegetation flux at the canopy level can be described by adapting a big leaf model and applying compartments to cuticular and stomatal storage.

Exchange between leaf cuticles and atmosphere, where foliar uptake of atmospheric mercury is designated with a negative flux value,

$$F_{C,Hg^x} = \frac{LAI}{r_c} \left(\frac{C_{C,Hg^x}}{K_{CA,Hg^x}} - C_{AtmG,Hg^x} \right), \quad (8)$$

where F_{C,Hg^x} is the flux of mercury species x to and from the leaf cuticles, LAI is the leaf area index, r_c is the sum of the cuticular and boundary layer resistances, C_{AtmG,Hg^x} is the atmospheric concentration of gaseous mercury species x , C_{C,Hg^x} is the concentration of mercury species x on the cuticle, and K_{CA,Hg^x} is the partitioning coefficient of mercury species x between the leaf cuticle and atmosphere.

Similarly, exchange across the leaf stoma and atmosphere can be modeled as follows;

$$F_{St,Hg^x} = \frac{LAI}{r_{St}} \left(\frac{C_{M,Hg^x}}{K_{LA,Hg^x}} - C_{AtmG,Hg^x} \right), \quad (9)$$

where F_{St,Hg^x} is the flux of mercury species x across the stoma, LAI is the leaf area index, r_{St} is the sum of stomatal, mesophyll, and boundary layer resistances, C_{M,Hg^x} is the concentration of mercury species x in the leaf mesophyll, and K_{LA,Hg^x} is the partitioning coefficient of mercury species x between the foliar tissue and atmosphere.

4. Future directions

Currently there are several key parameters that need further work before the proposed modeling framework can be implemented into an AQM. The role of ligands on vegetative mercury uptake and the natural redox properties in plants need to be investigated at background concentrations. Rea et al. (2000) have indicated that foliar leaching of mercury through the cuticle of leaves takes place, but more work needs to be done to determine transfer rates and differences between tree species. Pressure perturbations have been shown to enhance diffusion from soils, but a computationally efficient model of this phenomenon that agrees with recent measurements has yet to be developed. Last, further measurements are needed to determine the rate of partitioning of elemental and ionic mercury between different soil media components (organic matter, minerals, etc.), soil and rainwater pH, and vegetation surfaces.

Potential Models-3 integration

This conceptual model can be integrated into the Environmental Protection Agency's Models-3 framework by creating a surface media compartment with stomatal, cuticular, soil, and water storage. These storages will be coupled to one another and the atmosphere via the mass balance and the transfer of pollutants there between. A two-film resistance and partitioning model appears to be the most promising existing multimedia modeling framework that can be adapted to describe these mass transfers. The use of a two-film fugacity model has been used in the past on hourly time intervals to parameterize the atmosphere-surface water flux of mercury (Wanninkhof 1992; Bash et al. 2004) and to partition Hg^0 and Hg^{2+} to multiphase atmospheric particles in CMAQ-Hg (Bullock and Brehme 2002). Transfer velocities between surface media should be modeled in the Meteorology-Chemistry Interface Processor (MCIP) using updated canopy, soil, and surface water resistance models. Different chemical species will be coupled by atmospheric chemical kinetics of the AQM and assumed surface transformations, that is, Hg^0 adsorbed onto particles, and foliar tissue is transformed into Hg^{2+} . Current knowledge of mercury soil and vegetative surface chemistry is in its infancy. The use of partitioning coefficients appears to be the most promising approach at this moment until the kinetics of the soil and vegetation systems are better understood (Macleod et al. 2005). However, to model fluxes, the assumption must be made that the reactions governing adsorption and volatilization of mercury from the surface media is more rapid than the transport processes across the media (Macleod et al. 2005). The chemical kinetics of the reactions between species bound to the surface media and volatile species must be parameterized in cases where the above assumption is not valid, Macleod et al. (2005). In cases where the kinetics are unclear, kinetic processes can be estimated from the sorption constants (Bullock and Brehme 2002; Lin et al. 2006).

An assimilation model may be a better method for calculating transfer velocities between the atmosphere-vegetation interface because of possible mercury interactions with biological processes (Niyogi et al. 2003). An assimilation model may make a better foundation for the possible foliar reduction of Hg^{2+} in the NADPH cycle than an environmentally driven evapotranspiration model. The use of an assimilation model better represents nonlinearities in stomatal behavior and may require less tuning than an evapotranspiration model (Niyogi et al. 2003).

The model framework is governed by a series of

coupled differential equations by assuming a dynamic system in disequilibrium (Wania and Mackay 1999). The coupling of a single species of mercury occurs between the equations via applying mass balance to the transport between the surface media and across the surface media and the atmosphere. The coupling of surface models between mercury species occurs by applying mass balance of the total mercury concentration to reactions within the surface media and the atmosphere.

5. Conclusions

A review of recent research has shown that vegetation is a sink of atmospheric mercury (Lee et al. 2000; Erickson et al. 2003), a means of transportation between soil mercury reservoirs and the atmosphere (Lindberg et al. 1998; Bishop et al. 1998), and a storage location for mercury originating from both the soil and the atmosphere (Hanson et al. 1995; Erickson and Gustin 2004; Meagher and Heaton 2005). The current treatment of the air-surface interface in most air quality models treats vegetation as a simple means of transport of mercury from the soil compartment to the atmosphere (Bash et al. 2004; Xu et al. 1999), and the dry and wet deposition to the surface interface is modeled uncoupled to the emissions. Existing models cannot account for mercury flux and storage phenomena reported in recent research. The surface emissions of mercury are modeled separately, if at all, and dry deposition is modeled separately. This framework assumes that the surface is both an infinite sink and source for mercury and neglects accumulation (Wesely and Hicks 2000).

The theoretical modeling framework presented here has the potential to reconcile recent measurement and modeling results by coupling atmospheric and surface cycling processes through storage and multimedia transport of mercury in a dynamic compartmentalized surface interface (DCSI). A DCSI provides the framework to model gradient and known surface chemistry phenomena for mercury and can be extended to the treatment of the surface fluxes of other atmospheric pollutants. Further research must be conducted to determine the most important aspects of the mercury flux at the air-surface interface, and clever parameterizations of the surface processes must be made to prevent the addition of a DCSI from rendering the AQM too computationally expensive to be useful. The use of a fugacity model requires extensive use of sorption coefficients to parameterize absorption and desorption kinetics that are currently not well understood. Furthermore, many of the existing sorption coefficients for mercury species are either calculated from a very limited

number of studies or estimated from the thermodynamic properties of mercury. Further research is needed to verify and identify mercury sorption coefficients for natural media.

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