The dry-deposition of speciated mercury to the Florida Everglades: Measurements and modeling

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Received 6 April 2006; received in revised form 16 July 2006; accepted 24 July 2006

Abstract

The Florida Everglades Dry-Deposition Study (FEDDS) was designed to test the viability of using new and existing measurement techniques in the estimation of the dry-depositional loading of speciated mercury (elemental gaseous, reactive gaseous and particulate) to a mixed sawgrass (Cladium jamaicense) and cattail (Typha domingensis) stand within the Florida Everglades. Measurement intensives were performed during 24 February–04 March 1999 and 05–21 June 2000, which corresponded to the climatological dry and wet seasons in South Florida, respectively. During these intensives, direct measurements of mercury dry-deposition were made using a newly developed surrogate water surface technique. These direct measurements were compared with modeled estimates of mercury dry-deposition to the site that were obtained through the use of an inferential or “bigleaf” model that was modified for use with speciated mercury. On-site measurements of ambient speciated mercury concentrations and numerous micrometeorological variables were used as input to the model.

The average mercury dry-deposition measured during the 1999 FEDDS measurement intensive was $13.3 \pm 4.0$ ng m$^{-2}$ day$^{-1}$, while the modeled deposition for this period was $3.4 \pm 2.3$ ng m$^{-2}$ day$^{-1}$. The average mercury dry-deposition measured during the 2000 FEDDS measurement intensive was lower, $5.9 \pm 2.8$ ng m$^{-2}$ day$^{-1}$, while the average modeled deposition for this period was $1.8 \pm 0.6$ ng m$^{-2}$ day$^{-1}$. A least-squares linear regression suggests that the model was able to explain 74% and 73% of the variability in the datasets for the 1999 and 2000 FEDDS intensives, respectively. While reported reductions in total mercury emissions across South Florida between study periods could explain the reductions in both the measured and predicted mercury dry-deposition estimates, the increased presence of cumulus convection during the summer-intensive could have also resulted in a removal of reactive and particulate mercury species within the atmosphere of South Florida.

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Keywords: Mercury; Dry-deposition; Modeling; Florida Everglades

1. Introduction

The accumulation of toxic methylmercury in fish and other aquatic wildlife within the Florida Everglades has prompted the Florida Department of Health to recommend limited consumption of...
several species of sport fish due to potential health risks to consumers (State of Florida Department of Health, 1989, 2005). The atmosphere has been found to be a significant pathway for the transport and deposition of mercury in South Florida (Guentzel et al., 1995; Dvonch et al., 1995, 1998), as well as North American and Europe (Sorensen et al., 1994; Hoyer et al., 1995; Munthe et al., 1995; Lorey and Driscoll, 1999). Atmospheric mercury has both natural and anthropogenic sources and is predominantly found within the atmosphere in three forms: elemental gaseous mercury (Hg(0), believed to be >95% of total gaseous mercury), divalent reactive gaseous mercury (RGM, believed to be primarily HgCl₂) and particulate mercury (Hg(p)) (Pleijel and Munthe, 1995; Schroeder and Munthe, 1998). Due to its relatively low solubility and high vapor pressure, Hg(0) can be transported and deposited far from its original source (Hall, 1995). In contrast, RGM and Hg(p) are believed to be efficiently removed via wet- and dry-deposition, resulting in atmospheric removal relatively close to their respective emission sources or areas of formation (Schroeder and Munthe, 1998).

The relative importance of the wet- and dry-deposition pathways varies considerably depending upon location (Lindberg et al., 1992; Munthe et al., 1995; Rea et al., 1996). In South Florida, it has been suggested that wet-deposition is an important pathway for mercury loading during the summer season due to the high frequency of convective storms (Guentzel et al., 1995). However, the dry-deposition of mercury is also likely to be important across South Florida during the months of October–May, when precipitation is relatively infrequent.

Numerous regional and global scale modeling studies have been conducted to obtain a better understanding of the relationships between the sources, transport, transformation and fate of the important mercury species (e.g., Shannon and Voldner, 1995; Pai et al., 1997; Bullock, 2000; Petersen et al., 2001; Seigneur et al., 2001; Bullock and Brehme, 2002; Ryaboshapko et al., 2002; Cohen et al., 2004; Dastoor and Larocque, 2004; Travnikov, 2005; Gbor et al., 2006). While most of these modeling studies describe the dry-deposition of speciated mercury in terms of the product of species concentration and species-specific dry-deposition velocity, the manner in which the dry-deposition velocities are obtained varies. While some models use explicit values (e.g. lookup tables) for these dry-deposition velocities, others employ a resistance analog approach that allows for the determination of time-varying dry-deposition velocities as a function the chemical nature of the species of interest, the observed meteorology and the physical/biological characteristics of the surface to which the mercury species in question is depositing (water, soil and/or vegetation).

The ability to place bounds on the estimated rates of speciated mercury dry-deposition within South Florida has been hampered by the lack of direct measurement of these dry-deposition fluxes. The Florida Everglades Dry-Deposition Study (FEDDS) provided an opportunity for direct mercury flux measurements over a mixed sawgrass (Cladium jamaicense) and cattail (Typha domingensis) stand during two seasonal intensives: 24 February–04 March 1999 (dry season) and 05–21 June 2000 (wet season), within the Florida Everglades. During these studies, direct measurements of Hg(0) fluxes were performed using a micrometeorological technique, while direct measurements of RGM and Hg(p) dry-deposition were performed using a surrogate water surface technique.

Study results pertaining to the air–surface exchange of Hg(0) have been reported previously (Marsik et al., 2005). This paper primarily focuses on the comparison of surrogate water surface estimates of RGM and Hg(p) dry-deposition to the canopy with modeled estimates of these fluxes obtained using a single-layer inferential model that was modified for use in calculating the dry-deposition velocities of speciated mercury. Measured ambient concentrations RGM and Hg(p) were combined with their respective modeled dry-deposition velocities to obtain estimates of the dry-depositional fluxes of these species for comparison with our directly measured fluxes using the surrogate surfaces, to obtain a better understanding of the processes controlling these dry-deposition fluxes, and to determine the ability of our inferential model to accurately describe the magnitudes and time-varying nature of these fluxes.

2. Methodology

2.1. Field-sampling site

The Florida Everglades, the largest subtropical wetland in the USA, consist of the Everglades National Park, the Big Cypress National Preserve and a series of Water Conservation Areas (WCAs).
WCA-3, the largest of the WCAs, covers an area of 234,913 ha in western Broward and Dade counties and is primarily comprised of sawgrass marshes (141,095 ha, 60%), with smaller but significant fractions of wetland prairies (64,470 ha, 28%) and cattail marshes (11,750 ha, 5%) (Kenneth Rutchey, personal communication). The FEDDS measurement site was located in the eastern portion of WCA-3, near the South Florida Water Management District’s S-151 pumping station. The measurements reported here were conducted from a 4 × 4 m wooden platform that extended ~30 m into the marsh from the canal road. The vegetation surrounding the platform was primarily sawgrass with an intrusion of cattail in the immediate vicinity of the platform.

2.2. Chemical measurements

2.2.1. Automated Hg sampling

Collection and analysis of Hg(0) and RGM was accomplished using an automated system combining the analytical capability of the Tekran Instruments Corporation (Knoxville, Tennessee) Model 2537A cold vapor atomic fluorescence spectrometer (CVAFS) and a prototype Model 1130 speciation unit (Landis et al., 2002b). The 1130 system was configured to collect 2-h integrated RGM samples onto a KCl-coated quartz annular denuder at 10 l min⁻¹. During the 2-h RGM sampling period, 5-min Hg(0) samples were continuously quantified by the 2537A analyzer. After the 2-h sampling period, the 1130 system was flushed with Hg free air, and the quartz annular denuder was heated to 500 °C. The RGM collected on the denuder was thermally decomposed into the Hg free air stream and subsequently quantified as Hg(0). The Tekran 2537A analyzer was calibrated at the field site using the internal permeation tube calibration system. The Tekran 2537A internal permeation tube was calibrated just prior to each deployment as described in Landis et al. (2002b) and post verified after the study using a Tekran Instruments Corporation Model 2505 primary calibration unit. Manual injections performed in the laboratory also suggest a relative uncertainty in the 5-min average Hg(0) concentrations on the order of 1–3%.

2.2.2. Hg(p) sampling and analysis

Hg(p) samples were manually collected and analyzed in a manner previously described by Landis et al. (2002a). Briefly, total Hg(p) samples were collected using 47 mm open-faced Teflon filter packs and fine fraction (<2.5 μm) Hg(p) samples were collected in a Teflon filter pack attached to a Teflon-coated aluminum cyclone (URG Corporation, Chapel Hill, NC). Total and fine Hg(p) were collected at 30 and 16.71 min⁻¹ nominal flow rates, respectively. Sample flows were checked at the start and end of every sample period with calibrated rotameters to insure proper flows and size fractionation. Hg(p) filter packs were inserted into a custom-made fiberglass sampling enclosure mounted 2 m above water level.

All analytical procedures for determination of Hg(p) were carried out in a Class 100 clean room. Hg(p) filters were microwave digested in HNO₃ and subsequently analyzed using a dual amalgamation CVAFS technique. The performance characteristics of this technique were previously reported by Landis et al. (2002a), where the system detection limit (SDL) for Hg(p) was determined to be 1 pg m⁻³, calculated using 3σ of the field blanks. The precision of collocated samples was 91% and the analytical precision was 97%. The potential for collecting RGM artifact on the Hg(p) samples using this method has been previously reported (Landis et al., 2002b). We feel that RGM artifact was not a significant problem, since the RGM levels observed during this study at our remote Everglades location were below the reported RGM threshold of 15 pg m⁻³ where artifacts were observed.

All particulate measurements were performed using separate daytime (approximately 0900 am–1800 pm local time) and nighttime (approximately 1900 pm–0800 am local time) sample periods in order to determine potential differences in the chemical characteristics of the daytime and nighttime atmospheric surface layers.

2.3. Direct measurement of mercury dry-deposition

A number of studies have utilized surrogate surface techniques to quantify the dry-deposition of gaseous and particulate species (Yi et al., 1997; Shahin et al., 1999; Sakata and Marumoto, 2005). During 1999 and 2000 FEDDS measurement intensives, direct measurements of mercury dry-deposition were obtained using a surrogate water surface technique developed by the University of Michigan Air Quality Laboratory (Keeler and Dvonch, 2005). These surfaces consisted of frisbee-shaped airfoils designed to collect dry-depositing gases and particles without altering the existing
turbulent flow field. These surrogate water surfaces were deployed at a height approximately 40 cm above the average height of the vegetation canopy. Collocated plates were used to estimate the uncertainty of the technique. The differences in fluxes measured by the collocated plates resulted in an estimated uncertainty of approximately 20% and 30% during the 1999 and 2000 studies, respectively. The elevated uncertainty during the 2000 study was primarily due to discrepancies in the overnight samples. Each deposition plate, made of PFA Teflon, contained a removable Teflon well that held 300 ml of Milli-Q (Millipore Corp, Bedford, MA) ultra-pure water (18.2 MΩ cm). Sample wells were replaced at the start of each sampling period, with Milli-Q water poured into the well from previously filled 500 ml Teflon bottles. The Milli-Q water-filled deposition plates were then left exposed to the atmosphere for the entire sample period (either daytime or nighttime). In the event of rainfall, deposition plates were manually covered with snugly fitting plastic covers to prevent potential contamination from rainfall. These covers were removed immediately following the completion of the rain threat. At the end of each ~12-h sampling period, the exposed water was drained into its original bottle. Samples were analyzed for total mercury using a previously established technique (Landis and Keeler, 1997). Earlier chamber-based tests found that the surrogate water surfaces did not collect quantifiable levels of gaseous Hg(0) over extended measurement periods (Keeler and Dvovich, 2005), thus it is assumed that the surrogate water samplers measure only RGM and Hg(p) deposition and these fluxes are modeled accordingly.

2.4. Meteorological measurements

Micrometeorological measurements were made within the atmospheric surface layer above the canopy to characterize energy exchanges and the resulting turbulent transfer environment over the canopy. These measurements included temperature and relative humidity (Campbell Scientific, Inc. CS500 Temp/RH probe), wind direction and wind speed (RM Young Co. Wind Monitor-RE), global radiation (Li-Cor 200-X Pyranometer), surface wetness (Campbell Scientific, Inc. 237-L Wetness Sensing Grid) and turbulent fluxes of momentum, sensible heat and latent heat (Gill Instruments Solent Ultrasonic Anemometer and NOAA Infrared Gas Analyzer). These measurements were made continuously during the course of the study and archived as 30-min average quantities using a Campbell Scientific, Inc. 21X Micrologger and a laptop computer. This data was used in both the overall interpretation of the chemical data collected during the two measurement intensives and as input for the inferential dry-deposition model.

2.5. Inferential dry-deposition model

Model estimates of the dry-deposition of mercury to our site were calculated as the product of the ambient concentration of the mercury species in question and its respective dry-deposition velocity:

\[ F_i = V_{d,i} C_i, \]

where \( F_i \) is the dry-deposition flux a given species (\( i \)), \( C_i \) is the concentration of the species and \( V_{d,i} \) is the dry-deposition velocity for the species.

For Hg(0) and RGM, the determination of the species-specific dry-deposition velocities was accomplished using a single-layer, inferential modeling approach suggested by Wesely and Hicks (1977). This approach is based upon an electrical resistance analogy whereby the delivery of a chemical species from the atmosphere to a given surface is described in terms of a series of “resistances to deposition” which arise due to meteorological, chemical and biological processes that control pollutant delivery and capture at natural surfaces. Mathematically, this is described by:

\[ V_d = 1/(R_a + R_b + R_c), \]

where \( R_a \) is the the aerodynamic resistance to transfer (related to atmospheric turbulence), \( R_b \) is the near-surface boundary-layer resistance (related to the molecular diffusivity of the depositing species) and \( R_c \) is the canopy resistance (related to the various chemical and biological processes associated with the depositing species and the surface to which the species is being delivered). Typically, the canopy resistance, \( R_c \), is first calculated on a “per leaf” basis and then divided by the canopy leaf area index (LAI) to scale the “per leaf” resistances up to the canopy level.

For our base model, we started with the single-layer inferential model of Hicks et al. (1987), which was further reported by Baldocchi et al. (1987). This model was originally implemented as part of a National Oceanic and Atmospheric Administration (NOAA) research dry-deposition network and
subsequently used in a number of other dry-deposition networks, including the US Environmental Protection Agency’s Clean Air and Status Trends Network (CASTNet) (Hicks et al., 1991; Meyers et al., 1998). This model has previously been used to model the dry-deposition of Hg(0) to a hardwood forest in the Walker Branch Watershed, Oak Ridge, TN (Lindberg et al., 1992). While more detailed, multi-level dry-deposition models are now frequently used in such applications (Meyers et al., 1998), the existing uncertainties related to both the mercury species and vegetation types associated with this study lead us to choose the more basic single-level model for this application to the Florida Everglades.

We maintained the NOAA model’s original parameterizations for determination of the aerodynamic and boundary layer resistances (Hicks et al., 1987), while modifying the model’s description of interception of solar radiation by the canopy (Weiss and Norman, 1985; Campbell and Norman, 1998) and the canopy resistance term (Zhang et al., 2002, 2003).

2.5.1. \( R_a \), aerodynamic resistance

The model of Hicks et al. (1987) was developed primarily for use in monitoring networks and thus the aerodynamic resistance was parameterized to the allow use of easily measured meteorological quantities. The model computes the aerodynamic resistance using the following relation:

\[
R_a = \frac{(\sigma_V \cdot u_*)^2}{(U \cdot \sigma_b^2)},
\]

where \( \sigma_V \) is the standard deviation of the crosswind component of the wind (perpendicular to the mean wind vector), \( u_* \) is the friction velocity, \( \sigma_b \) is the time-average standard deviation (degrees) of the horizontal wind direction and \( U \) is the time-average horizontal wind speed (m s\(^{-1}\)). Hicks (1981) found that the value of \( \sigma_V \) \( u_* \) approached asymptotic limits under both stable/near neutral conditions (\( \sigma_V \) \( u_* \approx 2 \)) and unstable conditions (\( \sigma_V \) \( u_* \approx 3 \)). A review of data collected during the 1999 and 2000 FEDDS studies suggested that due to the aquatic nature of our Everglades site, strongly unstable conditions were rarely observed and a value of \( \sigma_V \) \( u_* \approx 3 \) was typically not attained. As a result, a value of \( \sigma_V \) \( u_* \approx 2 \) was used for all of our model simulations.

2.5.2. Boundary layer resistance, \( R_b \)

The boundary layer resistance is associated with the transfer of the chemical species in question through the quasi-laminar layer of air close to the natural surface and it is strongly related to the diffusivity of the pollutant in question. Mathematically, this is described as

\[
R_b = \frac{2}{ku_*}(\kappa_T/D_I)^{2/3},
\]

where \( k \) is the von Karman constant (0.4), \( \kappa_T \) is the thermal diffusivity of dry air (0.22 cm\(^2\) s\(^{-1}\) at \( T = 20^\circ C \)) and \( D_I \) is diffusivity of the gaseous chemical species in question. Massman (1999) determined a theoretical value for \( D_{Hg(0)} \) (0.12 cm\(^2\) s\(^{-1}\)) using Chapman–Enskog Leonard–Jones (CELJ) potentials (Reid et al., 1977), which agreed well with measurements by the same author. As noted earlier, it is generally believed that RGM is found in the atmosphere primarily as gaseous HgCl\(_2\). Given the lack of information regarding the diffusivity of gaseous HgCl\(_2\), we used the CELJ approach to calculate the molecular diffusivity for gaseous HgCl\(_2\) in air and obtained an estimated value of \( D_{RGM} = 0.09 \text{ cm}^2 \text{s}^{-1} \).

2.5.3. Canopy resistance, \( R_c \)

For our description of the canopy resistance to deposition, we incorporated the formulation suggested by Zhang et al. (2003):

\[
R_c = 1/[1 - W_{st}]/(R_{st} + R_m + 1/R_{cut} + 1/(R_{ac} + R_g)),
\]

where \( R_{st}, R_m, R_{cut}, R_{ac} \) and \( R_g \) are the canopy stomatal, mesophyll, cuticular, within-canopy aerodynamic and ground resistances, respectively. \( W_{st} \) represents the fraction of stomatal blocking when the leaves are wet. The value of \( W_{st} \) ranges from 0.0 to 0.5 for dry to wetted (rain or dew) leaf conditions and its formulation, as well as those used for \( R_{st}, R_{cut}, R_{ac} \) and \( R_g \), can be found in Zhang et al. (2003). These latter formulations require plant-specific information for the given land-use category (LUC) under consideration. Plant-specific information was not available for sawgrass which was chosen as the model canopy given its predominance. Thus, we assumed our canopy to be similar to Zhang et al. (2003) LUC# 14 (tall grass), with wet soil and a minimum stomatal resistance of sawgrass of 109 s m\(^{-1} \), the latter based upon a study of the transpiration rates of sawgrass within the Florida Everglades (Koch and Rawlik, 1993).

Given the assumption that our surrogate water surfaces do not take up quantifiable amounts of Hg(0), the modeled dry-deposition fluxes presented in this manuscript assume that dry-deposition is
limited to RGM and Hg(p). In reality, while the dry-deposition velocities of the weakly soluble Hg(0) are relatively small, the magnitude of the available pool of Hg(0) suggests that it could still provide an important component of the total Hg uptake by vegetation, as has been suggested by the measurements of Rea et al. (2002), among others. For this reason, we have computed the dry-deposition velocity of Hg(0) for completeness. Only limited measurements were available for use in specifying values of the canopy resistance terms for Hg(0) within the model. Lindberg et al. (1992) inferred values of 33 400 s m\(^{-1}\) for \(R_{cut}\) based on a study of Hg(0) uptake by wheat conducted by Browne and Fang (1978), and a value of 21 400 s m\(^{-1}\) for \(R_g\) based upon a study by Xiao et al. (1990). Some previous studies which have modeled Hg(0) dry-deposition have characterized the resistance to uptake of Hg(0) by leaf mesophyll tissue, \(R_m\), using a temperature-dependent relationship suggested by Du and Fang (1982). This relationship was determined as a residual of the difference between the total leaf resistance and the mesophyll resistance and thus cannot be simply inferred values of 33 400 s m\(^{-1}\) for \(R_{cut}\) based on a study by Xiao et al. (1990). Some previous studies which have modeled Hg(0) dry-deposition have characterized the resistance to uptake of Hg(0) by leaf mesophyll tissue, \(R_m\), using a temperature-dependent relationship suggested by Du and Fang (1982). This relationship was determined as a residual of the difference between the total leaf resistance and the mesophyll resistance and thus cannot be simply used as determinant of the mesophyll resistance alone. In our base case model, we chose to use the value suggested by Zhang et al. (2002) for weakly soluble species, \(R_m = 100\ \text{s m}^{-1}\).

Estimates for the values of \(R_m\), \(R_{cut}\), and \(R_g\) with respect to the uptake of RGM have not been presented in literature. Zhang et al. (2003) suggest a value of \(R_m = 0\) for highly soluble species and thus this value is adopted for the base case in our study. For \(R_{cut}\) and \(R_g\), values were estimated using the relationship suggested by Zhang et al. (2003):

\[
1/R_s(i) = \alpha(i)/R_s(SO_2) + \beta(i)/R_s(O_3),
\]

where “\(\alpha\)” represents either the cuticular and ground resistances to uptake for species “\(i\)”.

Using this relation, Zhang et al. (2003) scale the resistances to deposition for poorly characterized species according to their relative solubility and reactivity compared to that of the highly soluble species SO\(_2\) and the highly reactive species O\(_3\), two species whose dry-deposition has been studied extensively. This approach is similar to that of Wesely (1989) and Walmsley and Wesely (1996), but has the advantage that it does not require specification of exact values of the effective Henry’s Law Coefficient, which have not reported for Hg(0) and RGM.

Given that chemical properties of RGM are not well-known, we were not able to use the methodology of Zhang et al. (2002) to obtain estimates for the scaling parameters, \(\alpha(i)\) and \(\beta(i)\). A common assumption that is made in mercury dry-deposition modeling is that RGM is expected to behave in a manner similar to HNO\(_3\), which would suggest the use of values \(\alpha = 10\) and \(\beta = 10\) based upon the values successfully used for HNO\(_3\) in the work of Zhang et al. (2002). We feel that this choice is justified for the following reasons: (1) RGM has a solubility on the order of that for HNO\(_3\) and (2) while the redox-chemistry of RGM is not well characterized, we feel that a using a value for \(\beta = 10\) with RGM is supported given the affinity of RGM for organic matter in soils (Kordel et. al., 1997; Grigal, 2003) and thus efficient uptake by such soils. Additionally, Morel et al. (1998) report that RGM is lipid-soluble \((K_{ow} \sim 3)\). Barber et al. (2004) note that while the morphology of leaf cuticles vary tremendously between plant species, and thus greatly impact gas-cuticle exchange, some researchers have suggested that the ability of some gases to be adsorbed onto and/or pass through leaf cuticular surfaces increases with lipid solubility. Potential limitations associated with the use of HNO\(_3\) coefficients as surrogates for those of RGM include likely differences in the actual lipid solubility of the two species, as well as differences in the pH-dependent solubility within leaf apoplastic waters.

2.5.4. Particle dry-deposition

Finally, particle dry-deposition within our model followed the formulation presented in Seinfeld and Pandis (1998):

\[
V_d(Hg(p)) = V_s + 1/(r_a + r_b + r_ar_b V_s),
\]

(7)

where \(V_s\) is the particle settling velocity, \(r_a\) is the aerodynamic resistance and \(r_b\) is the quasi-laminar sublayer resistance. This relation considers the effects of both gravitational settling and Brownian diffusion. The equations used to obtain \(V_s\), \(r_a\) and \(r_b\) can be found in Seinfeld and Pandis (1998).

The parameterizations for \(V_s\) and \(r_b\) require knowledge of the diameter of the particle being characterized. Limited size distribution data is available for Hg(p) (e.g., Duce et al., 1976; Keeler et al., 1995), but these studies suggest that this size distribution is bimodal. Keeler et al. (1995) made a series of measurements in Detroit, Michigan and
found that Hg(p) size distributions had distinct peaks in both the fine (\(D_p\leq 2.5 \mu m\)) and course (\(D_p > 2.5 \mu m\)) fractions, with the mass median diameters in these fractions equal to 0.68 \(\mu m\) and 3.78 \(\mu m\), respectively. While detailed measurements of Hg(p) size distributions were not performed during the two FEDDS intensives, measurements of PM_{2.5} and TPM were performed and it was found that a significant amount of mass was observed in both fractions. As a result, dry-deposition velocities for both size fractions were obtained and used to determine to total Hg(p) loading to the site:

\[
\text{Flux}_{\text{Hg(p)}} = V_{d,\text{fine}}C_{\text{Hg(p)},\text{fine}} + V_{d,\text{coarse}}C_{\text{Hg(p)},\text{coarse}},
\]

where \(V_{d,\text{fine}}\) and \(V_{d,\text{coarse}}\) represent the fine and coarse fraction dry-deposition velocities and \(C_{\text{Hg(p)},\text{fine}}\) and \(C_{\text{Hg(p)},\text{coarse}}\) represent the Hg(p) concentrations for the fine and coarse fractions.

Based upon the uncertainties associated with measured gaseous and particulate species concentrations, an assumed uncertainty in the calculated dry-deposition velocities of 30% (Hicks et al., 1991), and the assumption that these uncertainties are independent, the estimated uncertainty in the modeled dry-deposition flux of RGM plus Hg(p) is approximately 60%.

2.6. Statistical analysis

All statistical analyses presented within this manuscript (descriptive statistics, tests of normality and tests of significance where noted) were performed using SPSS Statistical Analysis Package, V11.0.

3. Presentation of results

3.1. Inferential dry-deposition model sensitivities

Model sensitivity to several parameters was quantified in order to obtain a better understanding of the potential uncertainties in the model results. In particular, it was felt that our model would be sensitive to uncertainties in: (i) the magnitude of the resistance to uptake of Hg(0) by leaf mesophyll tissue, (ii) the reactivity scaling parameter (\(\beta\)) used for RGM, and (iii) the description of the vegetation canopy architecture: cylindrical or spherical leaf distribution.

3.1.1. Uptake of Hg(0) by leaf mesophyll tissue

Considerable uncertainty exists regarding the potential magnitude of the mesophyll resistance to the uptake of Hg(0). We chose to determine the impact of three potential values of \(R_m\) for Hg(0) uptake: 100 \(s\ m^{-1}\) (our base case and the value suggested by Zhang et al. (2003) for weakly soluble species), an intermediate value of 1000 and 10 000 \(s\ m^{-1}\) (the general magnitude of values obtained if one used the temperature-dependent relationship of Du and Fang (1982)). Using our base case model for the FEDDS 2000 measurement period, we obtained the following predicted dry-deposition velocities for Hg(0) for day and night periods, respectively: \(R_m = 100 \text{ s m}^{-1}\) (day: 0.46 \(\pm\) 0.08 \(\text{cm s}^{-1}\); night: 0.08 \(\pm\) 0.12 \(\text{cm s}^{-1}\)), \(R_m = 1000 \text{ s m}^{-1}\) (day: 0.10 \(\pm\) 0.01 \(\text{cm s}^{-1}\); night: 0.03 \(\pm\) 0.03 \(\text{cm s}^{-1}\)) and \(R_m = 10000 \text{ s m}^{-1}\) (day: 0.02 \(\pm\) 0.02 \(\text{cm s}^{-1}\); night: 0.02 \(\pm\) 0.02 \(\text{cm s}^{-1}\)). The predicted uptake of Hg(0) by plant canopies is highly sensitive to the assumed value of \(R_m\) during the daytime, though the impact during the nighttime periods is negligible given the assumption that the leaf stomata are mostly closed during the night. These results underscore the fact that the accurate characterization of this resistance component should be a high research priority with respect to the development of improved process-based modeling of Hg(0) dry-deposition to vegetation.

3.1.2. Reactivity scaling parameter (\(\beta\)) used for RGM

While the assumed chemical similarities between RGM and HNO_3 support the use of the value \(\beta = 10\), the reactivity/interaction of RGM with plant elements or within apoplastic waters is highly uncertain and may be quite different than HNO_3. For this reason, we felt it necessary to determine whether the modeled dry-deposition velocity of RGM was significantly impacted by our choice of this parameter and thus performed sensitivity tests using values of \(\beta = 1\) and 10. The results were: \(\beta = 1\) (day: 1.99 \(\pm\) 0.44 \(\text{cm s}^{-1}\); night: 0.63 \(\pm\) 0.28 \(\text{cm s}^{-1}\)) and \(\beta = 10\) (day: 2.10 \(\pm\) 0.46 \(\text{cm s}^{-1}\); night: 0.67 \(\pm\) 0.48 \(\text{cm s}^{-1}\)). This result suggests an uncertainty of approximately 5% in the modeled dry-deposition velocity of RGM due to the uncertainty in the appropriate value for the "reactivity" parameter, \(\beta\).

3.1.3. Vegetation canopy architecture

The vegetation canopy architecture (leaf orientation and distribution) directly impacts the model's
calculation of the penetration and partitioning (direct beam versus diffuse) of photosynthetically active radiation (PAR) through the canopy. The accurate description of this process is vital to an accurate determination of the stomatal resistance to gaseous species uptake by the vegetation canopy. The canopy architecture for sawgrass (our modeled canopy) is not well characterized, but likely combines the characteristics of both cylindrical and spherical leaf distributions. Therefore, we chose to look at the sensitivity of our model results to the choice of these two canopy architectures. For Hg(0), the model estimated dry-deposition velocities for both cylindrical (our base case) and spherical leaf distributions were: day (0.46 ± 0.08 cm s\(^{-1}\)) and night (0.08 ± 0.12 cm s\(^{-1}\)). For RGM, the model estimated dry-deposition velocities were: cylindrical (day: 2.10 ± 0.46 cm s\(^{-1}\); night: 0.67 ± 0.48 cm s\(^{-1}\)) and spherical (day: 1.61 ± 0.37 cm s\(^{-1}\); night: 0.54 ± 0.36 cm s\(^{-1}\)). Given the relatively high mesophyll resistance associated with Hg(0), differences in the stomatal resistance (resulting from modeled differences in the light interception by the canopy) had a minimal affect for this species. In contrast, the uncertainty regarding canopy architecture resulted in an average difference (cylindrical minus spherical deposition velocity) in the modeled RGM dry-deposition velocity of 0.49 cm s\(^{-1}\) (day) and 0.13 cm s\(^{-1}\) (night), for an uncertainty on the order of 20–26%.

### 3.2. Modeled deposition velocities

A summary of the dry-deposition velocity modeling results for our base case simulations over vegetation are presented in Table 1 and are specific to his ecosystem. On average, the modeled dry-deposition velocities for the 2000 FEDDS intensive were greater than those for the 1999 FEDDS study for all three species. One potential reason for this difference is that turbulence levels (as represented by direct measurements of the friction velocity with our sonic anemometer) were greater during the 2000 FEDDS study period. The distributions of observed friction velocity values were found to approximate the normal distribution during both study periods and a \(t\)-test for independent samples suggested that the difference in this parameter during the two studies was statistically significant (\(z = 0.05\)). Due to its relatively low solubility and reactivity, the limiting resistance to uptake for Hg(0) is the canopy resistance, and thus the difference in turbulence levels between the 1999 and 2000 measurement intensives would not be expected to result in a large difference modeled deposition velocities for this species. In contrast, the relatively high solubility and reactivity that have been assumed for RGM result in a relatively low canopy resistance, with the aerodynamic and boundary layer resistances being the limiting resistances. Given that these latter resistances are inverse functions of the turbulence levels, the higher turbulence levels in 2000 had a larger impact on the dry-deposition velocities of RGM compared to those of Hg(0). The limited increase in the course fraction Hg(p) dry-deposition velocity was likely due to the fact that this fraction is dominated by gravitational settling, while the fine fraction Hg(p) dry-deposition remained unchanged due to the general removal inefficiency for PM\(_{2.5}\).

Examples of the diurnal variation in the modeled dry-deposition velocity \((V_{d,Hg(0)}^d, V_{d,RGM}^d and V_{d,Hg(p)}^d)\) for the 2000 FEDDS study period are presented in Figs. 1 and 2. A diurnal influence is observed for all species, due primarily to the effects of solar radiation levels on the stomatal resistance and atmospheric stability/turbulence levels. The modeled estimates of \(V_{d,Hg(0)}\) range from near zero at night to near 0.5 cm s\(^{-1}\) at midday. On average, these values are consistent with those obtained by Poissant et al. (2004), who observed a median value of 0.19 cm s\(^{-1}\) over two-week period at a wetland site in Canada. Our calculated values are greater than those typically assumed for Hg(0), reflecting our choice of a lower mesophyll resistance for our base case simulation.

The modeled estimates of \(V_{d,RGM}\) range from near 0.5 cm s\(^{-1}\) during the relatively quiescent nighttime periods to approximately 2.5 cm s\(^{-1}\) at

### Table 1

<table>
<thead>
<tr>
<th>Period</th>
<th>n</th>
<th>Hg(0)</th>
<th>RGM</th>
<th>Hg(p) fine</th>
<th>Hg(p) course</th>
</tr>
</thead>
<tbody>
<tr>
<td>1999 Study period</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Day</td>
<td>137</td>
<td>0.42 ± 0.09</td>
<td>1.27 ± 0.44</td>
<td>0.01 ± 0.00</td>
<td>0.13 ± 0.05</td>
</tr>
<tr>
<td>Night</td>
<td>320</td>
<td>0.06 ± 0.07</td>
<td>0.47 ± 0.32</td>
<td>0.01 ± 0.00</td>
<td>0.09 ± 0.01</td>
</tr>
<tr>
<td>2000 Study period</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Day</td>
<td>303</td>
<td>0.46 ± 0.08</td>
<td>2.10 ± 0.46</td>
<td>0.01 ± 0.00</td>
<td>0.15 ± 0.05</td>
</tr>
<tr>
<td>Night</td>
<td>435</td>
<td>0.08 ± 0.12</td>
<td>0.67 ± 0.48</td>
<td>0.01 ± 0.00</td>
<td>0.09 ± 0.02</td>
</tr>
</tbody>
</table>

Values in the table represent study mean ± standard deviation.
midday. These values are consistent with those calculated by Malcolm and Keeler (2002) for deposition to dew covered surfaces at our measurement site during the same time period, as well as those observed by Poissant et al. (2004) at the aforementioned Canadian wetland site. However, Poissant et al. (2004) reported a median value for $V_{d,RGM}$ of 7.6 cm s$^{-1}$, compared to median values of 2.1 and 0.6 cm s$^{-1}$ estimated with our model for daytime and nighttime periods, respectively.

Finally, our modeled values of $V_{d,Hg(p)}$ for the fine particulate (represented here by $D_p = 0.68 \mu m$) and coarse particulate (represented here by $D_p = 3.78 \mu m$) fractions are presented in Table 1 and Fig. 2. The model suggested a diurnal variation in the estimated values of both the fine and coarse fractions, due primarily to the effects of wind speed and turbulence. The constant offset in the coarse fraction dry-deposition velocity as shown in Fig. 2 is a result of the settling velocity associated with larger particles. In general, the predicted values of
$V_{d,Hg(p)\text{fine}}$ were consistent diurnally and between studies (approximately $0.01 \text{ cm s}^{-1}$), while the predicted values of $V_{d,Hg(p)\text{course}}$ varied from 0.09 to $0.15 \text{ cm s}^{-1}$. These values are lower than those suggested by Poissant et al. (2004) who obtained a median $V_{d,Hg(p)}$ of $2.1 \text{ cm s}^{-1}$ for PM$_{2.5}$. This difference is not unlike observed differences between theoretical and measured values observed by other investigators (Allen et al., 1991), and suggests that Hg(p) dry-deposition is an area in which additional observations are needed.

### 3.3. Measured total Hg dry-deposition

While it is understood that our surrogate water surfaces cannot mimic the physical and chemical nature of the surfaces of vegetation exactly, we believe that our surfaces should provide reasonable estimates of the dry-deposition of Hg to the canopy environment for the following reasons. First, the rate of dry-deposition flux toward the vegetation is being controlled by the vegetation canopy itself. By placing our small surrogate water deposition surfaces within this dry-deposition field, we feel these surfaces are measuring the rate of dry-deposition resulting from vegetation influenced processes by “intercepting” the depositing gases and particulate matter. Second, surfaces that control air–vegetation exchange often have aqueous characteristics due to: (i) the potential presence of a thin-film of water on leaf surfaces during high humidity conditions (Wu et al., 2003), (ii) the existence of apoplastic water surrounding mesophyll tissues within the leaf cavities and (iii) the presence of significant amounts of dew on Everglades vegetation during the nighttime periods.

For the 1999 and 2000 FEDDS intensives, the average daily Hg dry-deposition estimates obtained using our surrogate water surfaces were $13 \pm 4$ and $6 \pm 3 \text{ ng m}^{-2} \text{ d}^{-1}$, respectively. These values are somewhat lower than those reported by Sakata and Marumoto (2005), who used surrogate water surfaces to obtain estimates of annual Hg dry-deposition from 4.4 to $13.2 \mu \text{g m}^{-2} \text{ yr}^{-1}$ (roughly $12-36 \text{ ng m}^{-2} \text{ d}^{-1}$) for a 1 year study across nine sites within Japan. The lower Hg dry-deposition fluxes measured during our two study periods could be related to the fact that on several occasions, a loss of water (sample solution) from the surrogate surfaces was observed during periods of strong, gusty winds. While lost sample solution water was replaced with clean Milli-Q water in an effort to maintain the smooth aerodynamic nature of our surrogate surfaces, quantifiable levels of Hg may have been lost. Also, due to occasional thunderstorm activity, there were several occasions for which the surrogate water surfaces needed to be covered to insure that the samples were not contaminated by potential rainfall. During these instances, the surrogate water surfaces were covered for periods of multiple hours, potentially resulting in an underestimate of the actual amount of Hg depositing to the surface for the given period.

Finally, the average daily Hg dry-deposition estimates obtained with our surrogate water surfaces suggested that the dry-deposition flux was lower during the 2000 FEDDS intensive, compared with that observed during our 1999 FEDDS intensive. One potential explanation for this observation is the reported reductions in mercury emissions within South Florida during the period between the two FEDDS intensives. The 2003 Florida Everglades TMDL Pilot Study Report (Florida Department of Environmental Protection, 2003) noted that emissions from South Florida mercury sources decreased from approximately $600 \text{ kg yr}^{-1}$ in 1999 to approximately $250 \text{ kg yr}^{-1}$ in 2000, with a substantial fraction of the emissions reductions attributed to the medical and municipal waste incineration sectors. Due to variations in wind patterns, we would not expect the impact of reduced emissions on any given location to be linear. However, during the 2000 FEDDS intensive, winds were predominantly from the east to southeast ($90-150^\circ$), corresponding to the urban/industrial regions along the south Florida coast. Thus, reductions in Hg emissions likely led to the observed reduction in measured Hg dry-deposition from the 1999 to 2000 studies. Additionally, the increased presence of cumulus convection during the summer intensive could have also resulted in a removal of reactive and particulate mercury species within the atmosphere of South Florida.

### 3.4. Modeled Hg dry-deposition

The modeled estimates of Hg dry-deposition are based upon the modeled dry-deposition of gaseous RGM and Hg(p) only, since insignificant amounts of Hg(0) are taken up by our surrogate water surfaces. The model-predicted Hg dry-deposition fluxes for the 1999 and 2000 FEDDS measurement intensives are presented in Figs. 3 and 4, respectively. The model does a reasonable job of
explaining the variance in the 1999 FEDDS data set ($r^2 = 0.74, p < 0.05$), though the model under-predicts the magnitude of the dry-deposition flux and there is a significant zero offset. Similarly, the model does a reasonable job of explaining the variance in the 2000 FEDDS data set ($r^2 = 0.73, p < 0.05$), though it again under-predicts the magnitude of the dry-deposition flux.

The ability of our model to explain a significant fraction of the variability of the observed Hg dry-deposition in both the 1999 and 2000 measurement studies is likely due to the fact that the limiting resistances to the dry-deposition for the primary depositing species, RGM and Hg(p), are the aerodynamic and boundary layer resistance terms. These resistances are fairly well characterized by the model relations and our on-site measurements of pertinent wind variables. The remaining unexplained variability between measured and modeled estimates of Hg dry-deposition could be explained by: (i) the potential under-quantification of ambient concentrations of RGM and Hg(p) by our measurement systems, (ii) the method employed to directly measure the Hg dry-deposition (surrogate water surface), (iii) inaccuracies in our description of the resistances to uptake of RGM and Hg(p) by the canopy and (iv) random error. While we do not have the ability to address the potential under-quantification of ambient concentrations of RGM and Hg(p) by our measurement systems, a brief discussion of the other potential sources of uncertainty is given below.

Surrogate water surface designs make this method susceptible to loss of sample solution during periods characterized by strong and/or gusty surface winds. Aqueous phase chemical reactions within the sample solution may also impact measured fluxes. While our previous laboratory studies suggested that quantifiable levels of Hg(0) are not taken up by the surrogate water surfaces, within the ambient environment the uptake of Hg(0) by the surrogate water surfaces could be enhanced by co-depositing gaseous species. The presence of dissolved O$_3$ or other oxidant species within the sample solution could lead to the oxidation of Hg(0) and subsequent attachment of newly formed dissolved RGM onto particulate matter which previously had been collected by the water surfaces, leading to an overestimation of Hg dry-deposition. We also cannot rule out the potential aqueous phase reduction of RGM to Hg(0), which could then be subsequently lost from the surrogate water surfaces via evasion leading to an underestimation of Hg dry-deposition.

Second, the ultimate endpoints for RGM and Hg(p) within the physical vegetation canopy are not well-known and thus our understanding of the processes and rates of delivery of these species to the canopy may not have been adequately characterized in our model. RGM, assumed to be removed efficiently given its high solubility and reactivity, likely adsorbs onto previously deposited particulate matter or other physical structures on leaf surfaces. Little is known as to the fate of RGM within leaf interiors. Experimental studies regarding the interaction of HgCl$_2$ with various biological cellular membranes suggest differing endpoints, in part depending upon whether HgCl$_2$ remains in its neutral state or whether it dissociates within solution (Gutknecht, 1981; Mason et al., 1995;
Morel et al., 1998; Suwalsky et al., 2000). Our description of Hg(p) deposition does not specifically consider the interaction of Hg(p) with the uneven structure of leaf cuticular surfaces and other plant structures. Additionally, our estimations of Hg(p) deposition are function of assumed particle diameters. If the mass median diameter of the course particle fraction was larger than that assumed, our model would have underestimated this component of the deposition.

Acknowledgments

The authors would like to thank Dr. Thomas Atkeson, Mr. Robert K. Stevens, Mr. Douglas Boyer and Dr. Elizabeth Malcolm for their assistance in all aspects of this work. We would also like to thank Dr. Steve Lindberg and Dr. Tilden Meyers for sharing their expertise on Hg air–surface exchange processes. Finally, this project would not have been possible without the generous efforts of Mr. Larry Fink and the South Florida Water Management District. This research was funded by the Florida Department of Environmental Protection and the US Environmental Protection Agency Office of Research and Development. It has been subjected to Agency review and approved for publication. Mention of trade names or commercial products does not constitute an endorsement or recommendation for use.

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