Transport of elemental mercury in the unsaturated zone from a waste disposal site in an arid region

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Abstract

Mercury contained in buried landfill waste may be released via upward emission to the atmosphere or downward leaching to groundwater. Data from the US Geological Survey’s Amargosa Desert Research Site (ADRS) in arid southwestern Nevada reveal another potential pathway of Hg release: long-distance (10–2 m) lateral migration of elemental Hg (Hg0) through the unsaturated zone. Gas collected from multiple depths from two instrumented boreholes that sample the entire 110-m unsaturated zone thickness and are located 100 and 160 m away from the closest waste burial trench exhibit gaseous Hg concentrations of up to 33 and 11 ng m⁻³, respectively. The vertical distribution of gaseous Hg in the borehole closest to the disposal site shows distinct subsurface peaks in concentration at depths of 1.5 and 24 m that cannot be explained by radial diffusive transport through a heterogeneous layered unsaturated zone. The inability of current models to explain gaseous Hg distribution at the ADRS highlights the need to advance the understanding of gas-phase contaminant transport in unsaturated zones to attain a comprehensive model of landfill Hg release.

1. Introduction

Exposure to Hg, a potent neurotoxin, may cause brain, liver, kidney and developmental disorders, particularly in young children and developing fetuses (U.S. EPA, 1997). Mercury fate and transport in the environment is a topic of focused research presently, with particular emphasis on atmospheric emissions. With the promulgation of a Clean Air Act Amendment in 1995 to substantially reduce Hg emissions from medical and municipal waste incinerators, land filling Hg-containing waste has become a more common practice. While there are a number of possible Hg-containing wastes in landfills (e.g., electrical switches, fluorescent bulbs, batteries and thermometers; U.S. EPA, 1992), relatively little research has examined the effectiveness of solid waste disposal landfills in minimizing transport of gaseous Hg (Hg0) or dissolved Hg from burial sites. In addition, what research has been conducted on Hg0 transport from municipal landfills (e.g., Lindberg et al., 2005) or buried cinnabar mine waste (Navarro-Flores et al., 2000) has focused on the vertical migration of Hg gases to the atmosphere within the landfill footprint with...
little consideration for long-distance Hg transport through the unsaturated zone (UZ).

Long-distance, gas-phase transport is especially important in arid regions where depth to the water table may be several tens to hundreds of meters below the bottom of the waste facility. Such thicknesses are commonly presumed to provide an effective barrier to long-distance vertical and lateral Hg contaminant transport over decadal timescales. The Amargosa Desert Research Site (ADRS) in southwestern Nevada, USA (Fig. 1) serves as a field-scale laboratory for investigating complex gas and aqueous flow and transport processes in arid unsaturated soils and sediments. This site has been well characterized over many years of study of gas and aqueous phase subsurface transport (e.g., Fischer, 1992; Striegl et al., 1996; Andraski, 1997; Prudic et al., 1997; Andraski and Stonestrom, 1999; Stonestrom et al., 2004; Walvoord et al., 2004; Mayers et al., 2005). However, the present study is the first attempt to explore Hg0 transport at the site. The goal of this study was to document the distribution of Hg0 in the unsaturated zone at the ADRS and to evaluate whether the location of possible Hg sources and/or post-burial transport mechanisms can explain the observed distribution pattern.

2. Materials and methods

2.1. Study site

The present climate in the Amargosa Desert is arid-thermic with precipitation averaging 108 mm a−1 from 1980 to 2000 (Johnson et al.,

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Fig. 1. Location of (a) Amargosa Desert Research Site (ADRS) in southwestern Nevada, and (b) deep boreholes (UZB-3 and UZB-2) and shallow soil gas sampling sites (A-series and X-series) within the ADRS adjacent to the waste-burial facility. The control borehole (JFDB) is located about 3 km south of the waste facility (northing 4,065,628 m, easting 528,210 m; 36.73778°N, 116.68404°E, NAD 1927).
The dominant vegetation is creosote bush (Larrea tridentata), a highly water-efficient Mojave Desert shrub. Continuous monitoring of soil matric potentials at the ADRS during 1987–1996 indicates that wetting fronts from infiltrating rain penetrate <1.2 m under native vegetation (Andraski, 1997; Tambusch and Prudic, 2000). Native plants at the ADRS maintain extremely low matric potentials at the base of their ~1-m deep root zone (≤−4 MPa), preventing deeper percolation.

Depth to groundwater at the ADRS ranges from 85 to 115 m (Fischer, 1992). Sediments in the unsaturated zone consist almost entirely of unconsolidated and poorly sorted debris-flow, fluvial, and alluvial-fan deposits (Nichols, 1987). Based on all available observations, the site geology can be characterized by a relatively straightforward layered alluvial stratigraphy. Beneath the surface soil, sediment composition is almost entirely sand and gravel, with minor amounts of silt and clay. However, layers with more abundant fine-grained sediment (and 10–20% clay content) are observed at or near the surface and between depths of 79 and 85 m. Such layers are also identified by geophysical imaging and appear to be continuous over large horizontal distances (Abraham and Lucius, 2004; Tambusch and Prudic, 2000). Borehole cores analyzed for texture are all classified as gravelly to very-gravely sand to sandy loam. Volumetric water contents for texture are all classified as gravelly to very-gravelly sand to sandy loam. Volumetric water contents are relatively low, ranging from 0.05 to 0.14 m³ m⁻³ and estimated effective porosities range from 0.182 to 0.322 m³ m⁻³ (Mayers et al., 2005). Very low unsaturated hydraulic conductivity in the unsaturated zone restricts liquid phase flow and renders gas-phase transport an important mechanism for the movement of water. Gas-phase transport is the primary mechanism for the movement and distribution of volatile constituents including gaseous Hg.

Two deep boreholes with sampling ports between the land surface and the 110-m deep water table and an array of shallow (0.5- and 1.5-m depths) soil gas sampling tubes at the ADRS were used to measure physical, chemical and isotopic conditions (Fig. 1). Sampled locations are contaminated to varying degrees by a nearby commercial waste disposal facility (Striegl et al., 1996; Andraski and Stonestrom, 1999). The facility buried low-level radioactive waste in unlined trenches with maximum depths of 15 m from 1962 to 1992 and hazardous chemical waste from 1970 to the present. Trenches for chemical waste were unlined prior to 1988. In 1994,³H and ¹⁴C were detected in concentrations that greatly exceeded background levels in unsaturated zone gases at distances exceeding 100 m from the location of the buried waste (Striegl et al., 1996; Prudic et al., 1997). Data collected from a 30-m instrumented borehole (JFDB) located ~3 km from the ADRS are considered to be uncontaminated and reflective of background conditions.

**2.2. Sampling and field methods**

Gas samples for Hg⁰ analysis were collected using trace-metal clean techniques (Olson and DeWild, 1999) from deep unsaturated zone (UZ) boreholes and shallow soil gas sampling tubes (locations indicated in Fig. 1). Boreholes were drilled using the air–hammer drilling method (Hammermeister et al., 1985). Drilling of JFDB, UZB-2 and UZB-3 was done in June 1986, September 1993 and December 1999, respectively. The UZB boreholes were instrumented and completed using methods detailed by Prudic et al. (1997). Each UZB gas sampling port consists of a 0.3-m long stainless-steel screen connected to 6-mm inner diameter (i.d.) nylon tubing that extends to the land surface. The screen is embedded in fine-to-medium gravel. Above and below the gravel layer, layers of finer textured materials composed of sand, silica flour and powdered bentonite were used to isolate the ports and backfill the borehole. The JFDB gas sampling ports consist of a 0.6-m long polyvinylchloride screen embedded in fine gravel and connected to 6-mm i.d. polyethylene tubing (J. Fischer, pers. comm., 1998). Isolation of the JFDB sample ports during backfilling of the borehole was accomplished using procedures similar to those for the UZB boreholes. The shallow soil gas sampling installation consists of individual, 5.5-mm-i.d. steel tubes that were hand-driven to nominal depths of 0.5 and 1.5 m using methods described by Andraski et al. (2003). Battery-operated brushless air-sampling pumps (SKC Inc., Model 224-PCXR8, Eighty Four, PA) were used to purge the tubes (three tube volumes) and then draw soil gas through borosilicate glass columns (0.635 cm-outer diameter) packed with Au-coated glass beads (gold traps), which quantitatively strip Hg⁰ from the gas (Ericksen et al., 2005). All Au traps were pre-cleaned in the lab prior to use by heating to 350 °C under a constant stream of Hg-free Ar at the USGS Wisconsin Water Science Center, Mercury Research Lab, and then hermetically sealing each trap using Teflon stoppers and double bagging in zipped plastic bags. Soil gas was drawn...
through the Au traps at a rate of 2 L min\(^{-1}\) for 20 min. Soda-lime traps fitted with quartz wool were used in-line, upstream of the Au traps, to remove humidity and keep soda-lime particles and dirt from entering the Au trap. In 2003, atmospheric air samples were collected 0.5 m above the land surface at two locations (JFDB and X200Y650) using the same sampling procedures as those for soil gas. Following sample collection, each Au trap was plugged with Teflon stoppers, wrapped with Teflon tape, double-bagged in zipped plastic bags, and sent to the Mercury Research Laboratory for analysis. At least two Au traps were left unused to serve as trip blanks to meet QA/QC protocols established by the lab.

Solid-phase analysis for total Hg was done in April 2004 using archived soil samples from the UZB-3 borehole and shallow soil samples collected at the UZB-3 and JFDB. The UZB-3 borehole samples were collected ahead of the drilling using a solid-tube sampler that was driven into the bottom of the drill hole using a pneumatic hammer. The archived samples were stored in air-tight containers at room-temperature prior to collecting subsamples for Hg analysis. For each shallow-soil location and depth, 2–3 samples were collected using a hand-driven sampling tube and composited for Hg analysis. All soil samples were double-bagged and sent to the Mercury Research Laboratory for analysis.

### 2.3. Laboratory analytical methods

Mercury amalgamated to the Au traps was quantified in the laboratory by thermally desorbing (450 °C) Hg\(^0\) into an ultra-high purity Ar carrier gas, and detected by a cold-vapor atomic fluorescence spectrometry (CVAFS) Hg detector (Tekran model 2500). Several soil vapor samples were also tested for isotope abundance of the five most common Hg isotopes (\(^{198}\)Hg, \(^{199}\)Hg, \(^{200}\)Hg, \(^{201}\)Hg, and \(^{202}\)Hg) using a quadrapole inductively coupled mass spectrometer (Perkin Elmer, model Elan 6100). Total Hg analysis was performed on the soil samples according to U.S. EPA Method 1631 (Olson and DeWild, 1999; U.S. EPA, 2002). Briefly, samples are prepared by room-temperature acid digestion and oxidation with aqua regia. The samples are brought up to volume with a 5% bromine monochloride solution to ensure complete oxidation and heated at 50 °C in an oven overnight. Samples are then analyzed with an automated purge and trap, flow injection system that incorporates Au traps and a cold-vapor atomic fluorescence spectrometer (Tekran model 2600).

### 2.4. Model application

The finite element heat and mass transfer model (FEHM; Zyvoloski et al., 1997) was used to simulate non-isothermal vapor and liquid movement and Hg\(^0\) transport in the UZ. Initial unperturbed conditions for the 2-dimensional 40-years transport simulations represent 16 thousand years of transient UZ drying based on water potential and porewater concentrations of Cl\(^-\), \(^2\)H and \(^18\)O measured at the ADRS, described and presented in Walvoord et al. (2004). The model domain extended 110 m vertically (the entire UZ) and 500 m in the horizontal (radial) direction away from the trench closest to the UZB-3 borehole; variable grid spacing was used. Layered heterogeneity in soil properties observed at the ADRS was implemented in the model following Mayers et al. (2005) (Table 1, Fig. 2). Effective diffusion coefficients (\(D_{\text{eff}}\)) for Hg\(^0\) were calculated by the model for each soil texture based on the Millington–Quirk formulations,

\[
D_{\text{eff}} = D^0 \times a^{(10/3)} / \phi^2; \quad (1)
\]

\[
D_{\text{eff}} = D^0 \times a^{2} / \phi^{(2/3)}; \quad (2)
\]

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<th>Property</th>
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<th>Trench fill</th>
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<td>714.8</td>
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<td>Van Genuchten (n)</td>
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<td>1.18</td>
<td>1.15</td>
<td>1.23</td>
</tr>
</tbody>
</table>

Values are from Mayers et al. (2005) and based on data in Andraski (1996) and Andraski and Jacobson (2000).
where $D^0 = \text{vapor diffusion coefficient for Hg}^0$ in air: $1.194 \times 10^{-5}$ m$^2$ s$^{-1}$ (Massman, 1999); $\alpha = \text{air-filled porosity, and } \phi = \text{total porosity. Model-calculated } D_{\text{eff}} \text{ values ranged from } 2.3 \times 10^{-7} \text{ to } 7.5 \times 10^{-7}$ m$^2$ s$^{-1}$ using MQI and $5.2 \times 10^{-7} \text{ to } 1.2 \times 10^{-6}$ m$^2$ s$^{-1}$ using MQII. Elemental Hg is modeled as a vapor species that does not partition into the liquid phase due to its limited water solubility (Sanemasa, 1975). Gaseous Hg$^0$ is assumed to behave conservatively.

Navarro-Flores et al. (2000) also modeled conservative Hg$^0$ gas transport from buried Hg mining debris using a Fickian-based single phase numerical model and applied an analytical solution to estimate vertical (only) transport rates. An effective Hg$^0$ diffusion coefficient of $1.2 \times 10^{-6}$ m$^2$ s$^{-1}$ was manually specified in the model for cells representing non-fissured porous media, and was held constant with depth. An effective Hg$^0$ diffusion coefficient of $6.9 \times 10^{-7}$ m$^2$ s$^{-1}$ was used for analytically calculating total emission to the atmosphere. These values utilized by Navarro-Flores et al. (2000) compare well to the model-calculated ranges given above.

Simulations were run for 40 years to correspond with the time since waste was first emplaced (1962) and to allow comparison with the 2002–2004 data. Perturbed boundary conditions for the simulations are listed in Table 2. Perturbed conditions include the introduction of a waste trench extending 20 m laterally and 15 m vertically from the center of the radial model domain. Initial concentration of Hg$^0$ was specified at 2.4 ng m$^{-3}$ based on the mean of Hg$^0$ concentrations measured from other landfills (Lindberg et al., 2005).

### 3. Results and discussion

#### 3.1. Distribution of Hg$^0$ in the deep unsaturated zone

The authors are unaware of any published natural background concentrations of Hg$^0$ in deep unsaturated zones. The USGS has collected a limited number of soil gas samples to depths of 2.0 m using 5.5-mm-i.d. steel tubes at a pristine forested site in northern Wisconsin that is comprised of very low Hg-containing glacial outwash. The tubes used in this location, however, were rigorously cleaned with an organic solvent (acetone) and 10% HCl before use. Data from this site are only mentioned here for the purposes of establishing...
low-end bounding values for gaseous Hg in deep soil zones from a pristine setting. In addition, for
the purposes of comparison, typical atmospheric Hg₀ concentration is about 1.5 ng m⁻³ (Krabbenhoff et al., 2005). Deep (below 1.5 m) unsaturated zone profiles measured in 2002–2004 revealed pronounced subsurface peaks in Hg₀ concentrations of 33 and 4 ng m⁻³ at the UZB-3 and UZB-2 boreholes, respectively. It is noteworthy that these boreholes are 100 and 160 m, respectively, away from the nearest disposal trench (Fig. 3a and b). Soil vapor samples tested for isotope abundance revealed no unusual isotopic enrichment, thus preventing the identification of a specific buried source. For comparison purposes, the soil gas profiles (sampled at depths of 0.2, 0.5, 1.0, and 2.0 m) observed at the pristine, northern Wisconsin site showed distinctly declining (surface maximum) profiles, but with much lower overall Hg₀ concentrations than those measured in UZB-3 and UZB-2. At each of the three Wisconsin sampling sites, the 0.2 m depth sample was the greatest observed (mean = 2.6 ng m⁻³, N = 6, SD = 0.8) and all samples collected at the greater depths were notably lower (mean = 1.2 ng m⁻³, N = 18, SD = 0.4). However, the very similar concentrations observed at the ADRS background site (JFDB = 2.4 ng m⁻³) and the pristine Wisconsin site suggests that a lack of pre-cleaning the sampling tubes at the ADRS site, and possible sample contamination, is not likely affecting the observed profiles to a significant degree. In addition, if the sample tubing were contributing an Hg₀ artifact in the ADRS data set, a positive and regular relation between length of the tubing and observed Hg₀ concentration would be expected, but is not seen. These two lines of evidence lead to the conclusion that the observed ADRS profiles are real and not sampling artifacts.

The deep profile at UZB-3 displays a relatively sharp and distinct Hg₀ peak between about 15 and 35 m, with the maximum concentration at a depth of 23.8 m. The measured peak concentration at UZB-3 increased appreciably from 21 to 33 ng m⁻³ from 2002 to 2003, but remained essentially constant from 2003 to 2004. Given the strong agreement between 2003 and 2004 data, the large apparent concentration rise from 2002 to 2003 at the 23.8-m depth is most likely an artifact of the data collection or analysis (a low 2002 measurement) and not due to transport.

UZB-2 Hg₀ concentration data are slightly higher between the depths of 5 and 50 m, but they do not display the distinct peak below 15 and 35 m, with the maximum concentration at a depth of 23.8 m. The measured peak concentration at UZB-2 increased appreciably from 21 to 33 ng m⁻³ from 2002 to 2003, but remained essentially constant from 2003 to 2004. Given the strong agreement between 2003 and 2004 data, the large apparent concentration rise from 2002 to 2003 at the 23.8-m depth is most likely an artifact of the data collection or analysis (a low 2002 measurement) and not due to transport.
3.2. Soil analysis for total Hg

Solid-phase analysis for total Hg from UZB-3 produced values ranging from 17 to 133 μg kg⁻¹, with an average of 76 μg kg⁻¹ (Fig. 3c). One soil sample at 1.5 m depth from control borehole JFDB yielded 49 μg kg⁻¹, which is similar to the value observed in UZB-3 at the equivalent depth (46 μg kg⁻¹). Total Hg concentrations from UZB-3 and JFDB soil samples were well below the maximum background level of 300 μg kg⁻¹ typically reported for soils (Andersson, 1979; Gerlach et al., 2001). The average UZB-3 value of 76 μg kg⁻¹ closely matches the mean upper crust abundance of 80 μg kg⁻¹(Fyfe, 1974). The elevated soil gas concentrations (i.e., >2.4 ng m⁻³ background level) at depths of 1.5 m and from 15–35 m at UZB-3 appear to be the result of transport from an anthropogenic Hg source buried at the landfill and not from in-situ desorption of geologic Hg. This observation is supported by the lack of elevated (above typical background) Hg soil concentration in UZB-3 and the general lack of positive correlation (r = −0.23) between the solid-phase data and the soil-vapor data from UZB-3.

3.3. Distribution of Hg⁰ in the shallow unsaturated zone

Elemental Hg concentrations at shallow depths (≤1.5 m) at UZB-3 reach a maximum within the thin gravel unit at ~1–2 m below land surface. Here, measured concentration was greatest in 2002 (17 ng m⁻³; UZB-3) and fluctuated with time perhaps due to mixing and dilution from the atmosphere (Fig. 3a). UZB-2 also showed a shallow peak at 1.5 m with a concentration of 11 ng m⁻³ in 2002 (Fig. 3b).

The Hg⁰ concentration data from shallow soil gas sampling locations projecting southward and westward from the waste facility generally revealed larger Hg⁰ concentrations at the 1.5 m-depth than at the 0.5 m-depth (Fig. 4a–d). This vertical pattern can be partially attributed to atmospheric dilution. In addition, the shallow gravel layer, with favorable gas transport soil conditions, may serve as a pathway for enhanced lateral transport thus providing a higher concentration source for vertical diffusion both upward and downward. Data from UZB-2 and UZB-3 also display Hg⁰ concentration peaks within the shallow gravel unit (1.5 m) further supporting this conceptual model.

The north-to-south soil gas sampling transect generally shows decreasing Hg⁰ concentrations in the shallow gravel unit at 1.5 m depth with increasing distance from the landfill (Fig. 4a and c). This pattern is less pronounced along the east-to-west transect in 2002 (Fig. 4b) and is actually reversed in 3 of 4 east-to-west transect locations sampled in 2003. These locations are just 50 m from the 2002 transect (Fig. 4d), suggesting that spatially-variable properties, including soil pH, organic matter, vegetation cover, wind, light, etc., that influence Hg⁰ soil volatilization as noted by Johnson et al. (2003) and Gustin et al. (1997, 2002) may affect the shallow spatial pattern. The greatest Hg⁰ concentrations measured in the shallow gravel unit were observed south of the facility at 0–32 m from the southern fence line. At the fence line (A1), measured Hg⁰ was 46 ng m⁻³ in 2003. Just 25 m south of the fence line, concentrations decreased to 16 ng m⁻³, which compared closely with the UZB-3 concentration of 17 ng m⁻³ at the same depth in 2002. The spatial distribution of Hg⁰ at a depth of 0.5 m appears fairly random within both transects and probably most strongly reflects subtle differences in diffusive soil properties at the local scale that control the rate of atmospheric mixing and dilution.

3.4. Comparison to transport of other gas-phase contaminants

The deep Hg⁰ unsaturated zone profiles (Fig. 3a and b) display a similar pattern to profiles of tritiated water vapor derived from the landfill (Fig. 5a and b; Mayers et al., 2005), although the deep ³H peak in UZB-3 (~25-m depth) is more subdued than the Hg⁰ peak. Tritium partitions between the gas and liquid phases, and therefore ³H vapor diffusion should be effectively retarded in order to maintain isotopic equilibrium with the less mobile liquid phase. Due in part to this expected retardation, current transport theory and modeling efforts have been unsuccessful in adequately explaining ³H concentration profiles (Striegl et al., 1996; Mayers et al., 2005).

Elemental Hg concentration profiles can also be compared to anthropogenically-derived trichlorotrifluoroethane (CFC-113) profiles resulting from transport from the landfill (Fig. 5c and d) (Stonestrom et al., 2004). CFC-113, like Hg⁰, is highly volatile and does not notably partition into the liquid phase in the unsaturated zone. CFC-113 concentrations in UZB-3 and UZB-2 peaking at 11,400 and
6300 ppb, respectively, greatly exceed maximum background concentrations of 0.2 ppb measured in control borehole JFDB (Baker and Luo, unpublished data), clearly pointing towards the landfill source as the origin. Unlike the sharper Hg\textsuperscript{0} peak shape, CFC-113 profiles from UZB-3 show a more uniform diffusive shape that is typical of Fickian-type gas transport. From UZB-3 and UZB-2, the peak concentration in CFC-113 decreases by less than a factor of two, whereas the deep (below 1.5 m) peak concentrations in Hg\textsuperscript{0} and \textsuperscript{3}H decrease by about a factor of 10.

The stronger resemblance between Hg\textsuperscript{0} and \textsuperscript{3}H profiles than between Hg\textsuperscript{0} and CFC-113 profiles is somewhat surprising. Tritium is much less volatile than Hg\textsuperscript{0} and the liquid water component in the unsaturated zone acts as a major sink for \textsuperscript{3}H, effectively retarding its transport in the gas-phase. Vertical liquid fluxes in the deep unsaturated zone at the ADRS are estimated to be <0.01 mm a\textsuperscript{-1} (Walvoord et al., 2004), thereby providing essentially no vertical enhancement of \textsuperscript{3}H in the liquid phase. Striegl et al. (1996) suggest that the most likely transport mechanism to explain the \textsuperscript{3}H profiles involves lateral liquid flow along preferential flow paths, although there is no evidence for such phenomena at the ADRS. If this is the case, then the similarity between Hg\textsuperscript{0} and \textsuperscript{3}H profiles remains all the more perplexing, since Hg\textsuperscript{0} is thought to support negligible partitioning into the liquid water phase. As such, it would be expected that the Hg\textsuperscript{0} distribution would show a greater similarity to CFC-113, which behaves as a conservative gas.

3.5. Model results

Multi-phase flow and transport modeling results indicate that long-distance Hg\textsuperscript{0} transport through the unsaturated zone from a shallow buried source...
is feasible over decadal timescales. However, despite implementing a layered heterogeneous soil property field (Fig. 2), model results display a nearly uniform diffusive transport pattern (Fig. 6a). Calculated MQI and MQII effective diffusion coefficients vary by about a factor of 2–3 among the different sediment layers with the in situ air-filled porosities. This differential effect is overwhelmed by the influence of vertical vapor diffusion, thus producing the nearly uniform spreading pattern. Gaseous Hg$^0$ vapor diffusion coefficients are about five orders of magnitude greater than typical liquid diffusion coefficients. Results using the MQI implementation were similar to the MQII formulation, so only MQII results are shown in Fig. 6a. The simulated Hg$^0$ plume is approximately centered within the

unsaturated zone due to the imposed boundary of zero concentration at the atmospheric (surface) boundary and 100% liquid saturation (0% air-filled porosity) condition at the water table boundary. Model-simulated profiles at distances equivalent to UZB-3 and UZB-2 distances from the nearest trench show a poor match to the data (Fig. 6b and c). Fixed source Hg$^0$ concentrations for the model simulations were varied from 200 to 4000 ng m$^{-3}$. A source concentration of 2000 ng m$^{-3}$ best reproduced the accumulated mass in the UZB-2 and UZB-3 profiles, but did not reproduce the general shape of the profiles. The shape of the modeled profiles more closely resembles measured CFC-113 profiles (Fig. 5c and d). Thus, the model adequately simulates diffusive non-reactive
gas transport at the ADRS. The poor fit to the Hg\textsuperscript{0} data suggests that the conceptual and numerical models do not completely represent the complexity of the system. Given the resemblance in concentration profiles between \textsuperscript{3}H and Hg\textsuperscript{0}, it is probable that the complexities influencing their transport, which are lacking in current models (and theory), may be similar.

3.6. Model limitations and uncertainty

The lack of information regarding Hg disposal at the landfill, such as the timing, quantity, and composition of Hg buried at the landfill, precludes estimation of a rigorous Hg\textsuperscript{0} source term. Yet even making minor assumptions, such that transport began no earlier than 1962, and placing few constraints on Hg\textsuperscript{0} concentrations in the trench, simulated results cannot sufficiently reproduce measured UZ profile data. The effects of temperature fluctuations near the surface and barometric pressure changes were not addressed in the model. Diurnal and seasonal temperature fluctuations that would support thermally-driven gas diffusion are unlikely to have a significant impact on transport, particularly lateral transport. Barometric pressure fluctuations may assist in purging the near surface sediment of elevated Hg\textsuperscript{0} concentrations by atmospheric dilution (Auer et al., 1996) and perhaps even drive lateral advective flow (Massman, 2006). Whether or not atmospheric pressure fluctuations could act in enhancing lateral transport at the depths observed at the ADRS is unknown and remains a limitation in most unsaturated zone flow and transport models.

For model simulations, Hg\textsuperscript{0} transport was assumed to be non-reactive and take place in the gas-phase only. Assumptions are based on previous studies that indicate Hg\textsuperscript{0} is not physically or chemically reactive in unsaturated porous media and has limited water solubility (Sanemasa, 1975). Results from the study presented here coupled with the comparison to \textsuperscript{3}H and CFC-113 profiles suggest that these assumptions may require further investigation.

Model results indicate that a high degree of anisotropy with respect to gas-phase movement would be required to explain the measured profiles.

Fig. 6. Unsaturated zone Hg\textsuperscript{0} transport modeling results displayed (a) in cross-sectional view, and (b) as vertical profiles at UZB-3 and UZB-2 for comparison with 2003 data. Model results were generated using a 2000 ng m\textsuperscript{-3} Hg\textsuperscript{0} trench source and the MQII formulation for calculating effective diffusion coefficients.
Yet even when soil texture differences, and thus effective diffusion coefficients, among the layers were largely exaggerated, minimal changes in the predicted plume profile resulted (not shown). The inability of the numerical model to reproduce the measured Hg0 profiles reflects (1) the inadequacy of current empirical models used to estimate differences between stratigraphic units based on soil characteristics, (2) a currently unidentified mechanism generating complex advective gas flow, (3) a major gap in understanding of gas-phase transport in the unsaturated zone, or some combination of all 3. Results from a recent gas tracer study conducted at the ADRS (Walvoord, unpublished data) supports the first suggestion and will improve the characterization of transport properties. Future field and modeling work to address the effects of barometric pumping on gas-phase transport in the deep unsaturated zone may help resolve the discrepancy between modeled and observed Hg0 profiles.

4. Conclusions

Transport of elemental Hg through arid unsaturated zones is a viable long-distance (10^2 m) pathway for Hg migration from landfills. Horizontal transport of Hg0 probably does not present an immediate threat at the low levels detected at the relatively remote ADRS. However, vertical upward Hg0 transport can provide a much shorter pathway for exposure to Hg0 to waste site workers and biota, even considerable distances away from the landfill. This may be cause for concern at less isolated arid (shallower burial depth) waste sites or sites having larger masses of disposed Hg. Comprehensive conceptual models of Hg fate and transport from landfills should include the potential for off-site unsaturated zone migration. Future work is needed to better understand controlling transport processes and quantify gas-transport parameters. Greater insight will enable us to create models that more accurately predict Hg0 transport through the unsaturated zone.

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