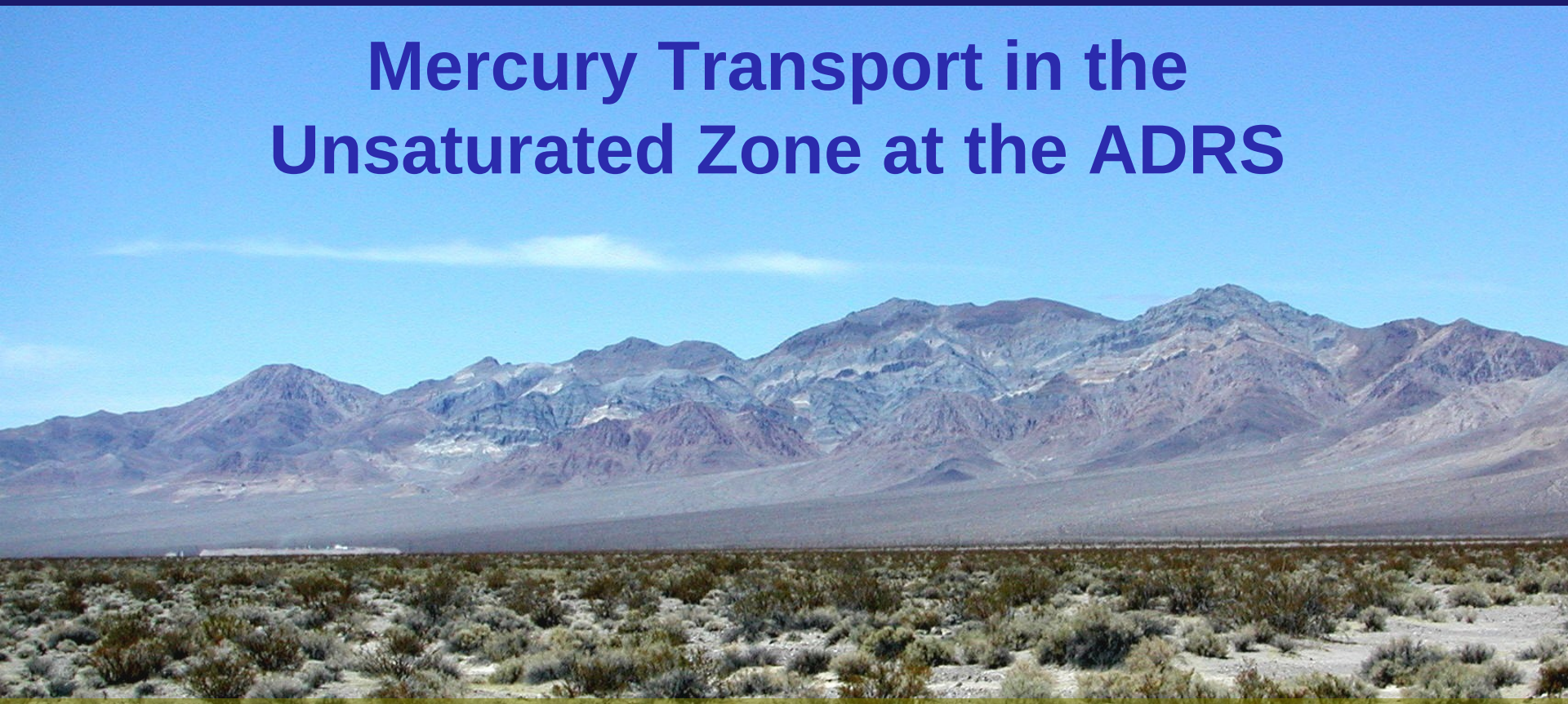
Mercury Transport in the Unsaturated Zone at the ADRS



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Mercury in the Environment

- Hg from medical and municipal waste incinerators (Clean Air Act Amendment 1995 to reduce emissions)
- Hg-containing wastes in landfills (e.g., electrical switches, fluorescent bulbs, batteries, thermostats and thermometers)
- Cinnabar (mercuric sulfide) mine waste

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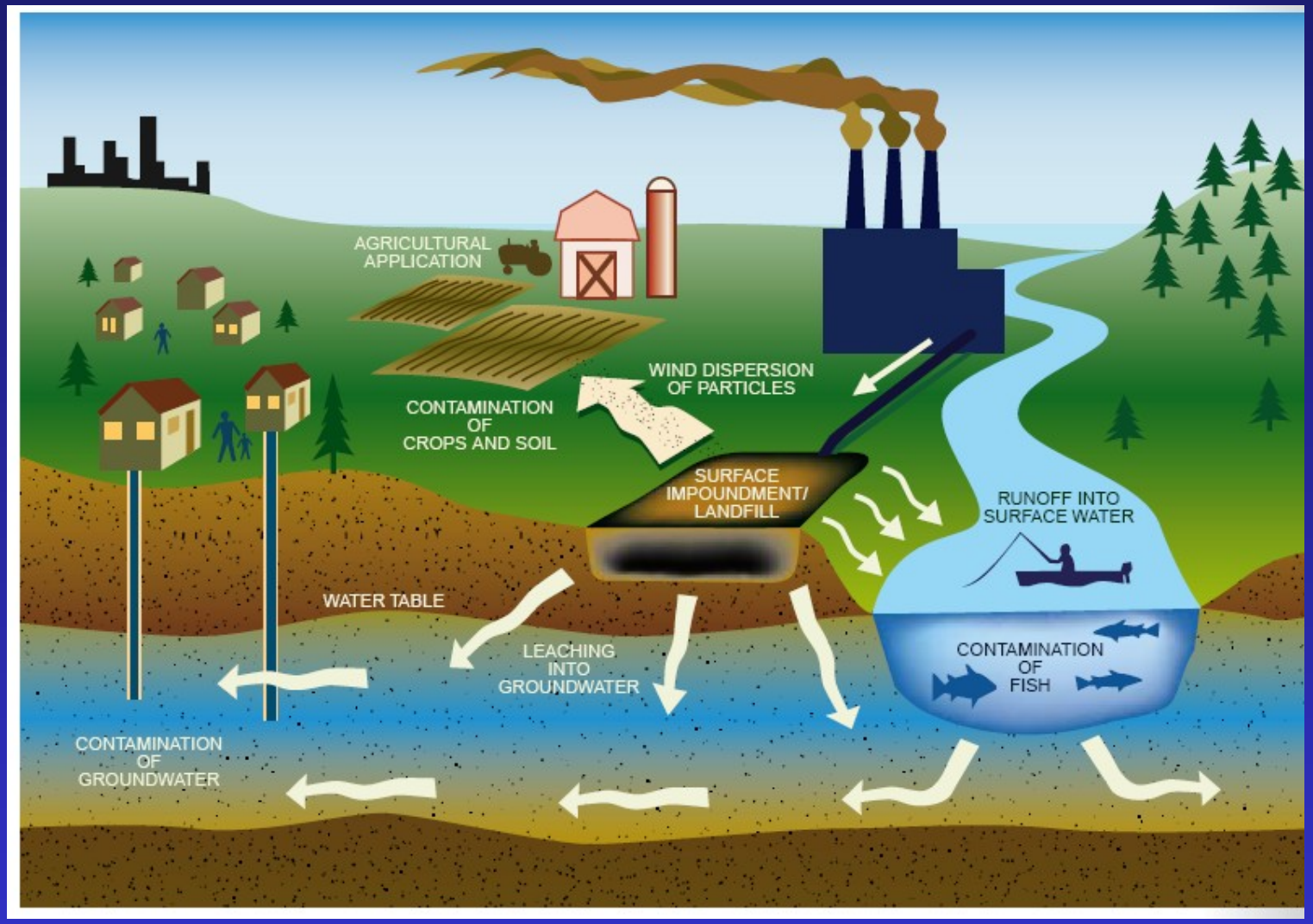
Pathways of Mercury Transport From Landfills



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Sources of Human Exposure to Hg

- Air from atmospheric Hg sources, contaminated drinking water, infant consumption of breast milk high in Hg, consumption of contaminated fish or crops exposed to elevated Hg in soil or water.

Associated Concerns

- Exposure to Hg, a potent neurotoxin may cause brain, liver, kidney and development disorders. Young children and developing fetuses are most vulnerable. U.S. EPA 1997

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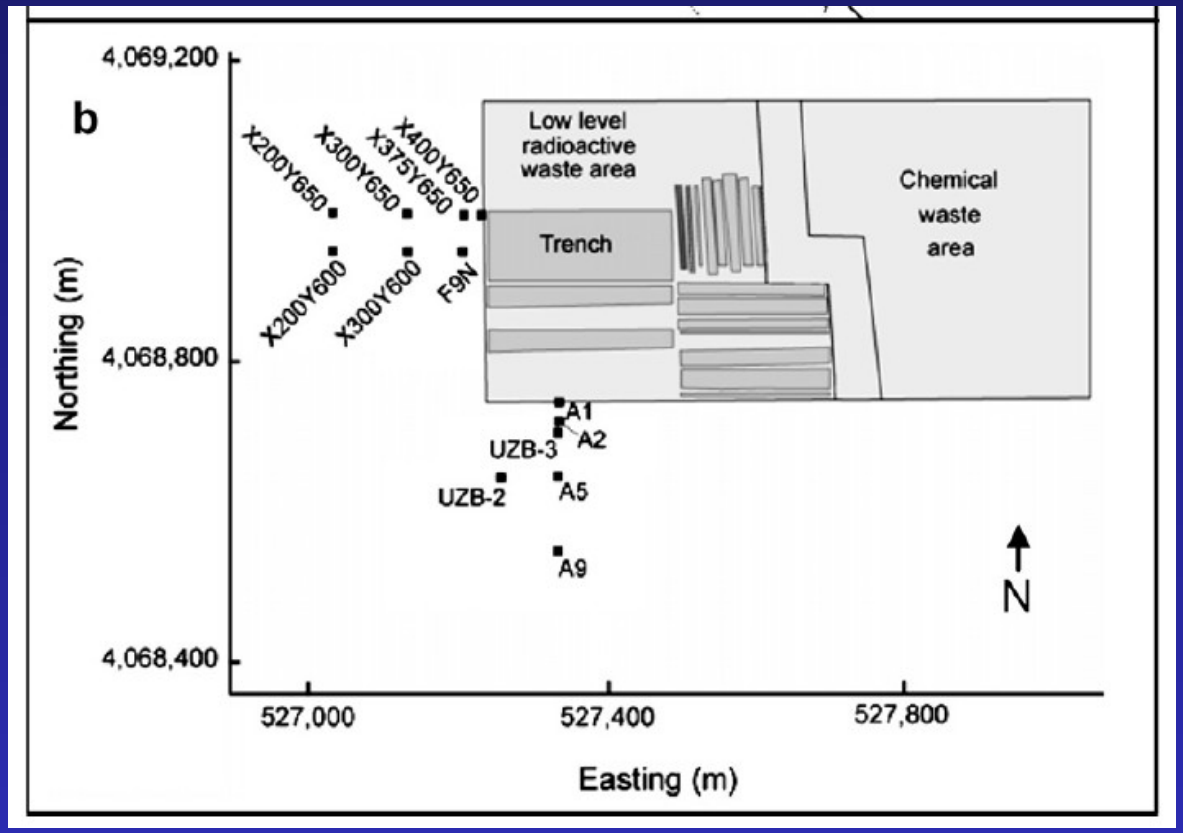
Previous Research on Mercury Transport in the Unsaturated Zone (UZ)

- Mainly focused on shallow vertical migration to the atmosphere above a landfill (Lindberg et al., 2005) or cinnabar mine waste site (Navarro-Flores et al., 2000).

- No previous work considered Hg^0 transport in the deep UZ

ADRS Hg^0 Collection Sites

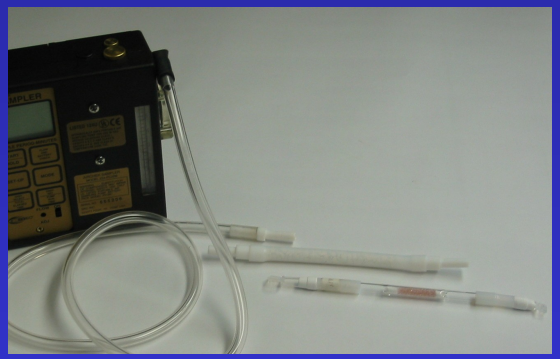


- Deep (30 m) control borehole JFBD located ~3 km to the south

- Deep (110 m) boreholes UZB-2 and UZB-3, 160 m and 100 m south of nearest waste trench
- Shallow (0.5m and 1.5 m) A-series transect extending south of the landfill footprint
- 2 Shallow (0.5 and 1.5 m) X-series transects extending west of the landfill footprint

Sampling Methods

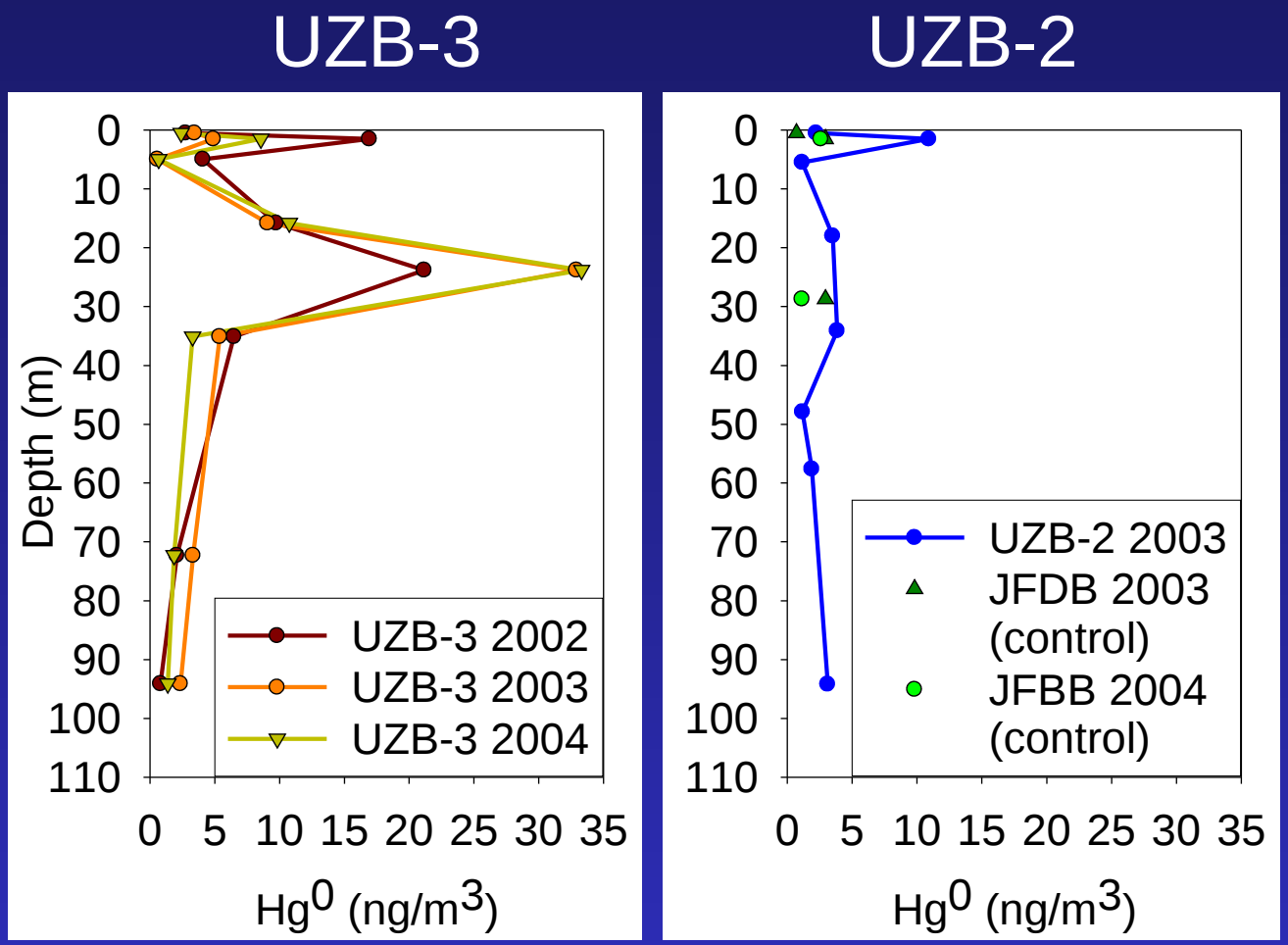
- Gas samples collected using trace-metal clean techniques (Olson and DeWild, 1999) from shallow and deep UZ boreholes at the ADRS; Hg^0 stripped from gas during collection using Au traps.



Lab Methods

- Sealed gold traps sent to the Mercury Research Laboratory at the USGS Wisconsin Water Science Center for analysis via CVAFS (cold-vapor atomic fluorescence spectrometry) of Hg^0 amalgamated to Au traps.
- Archived soil samples tested for ^{198}Hg, ^{199}Hg, ^{200}Hg, ^{201}Hg and ^{202}Hg and also for total Hg.

ADRS Deep UZ - Hg^0 in Vapor Phase

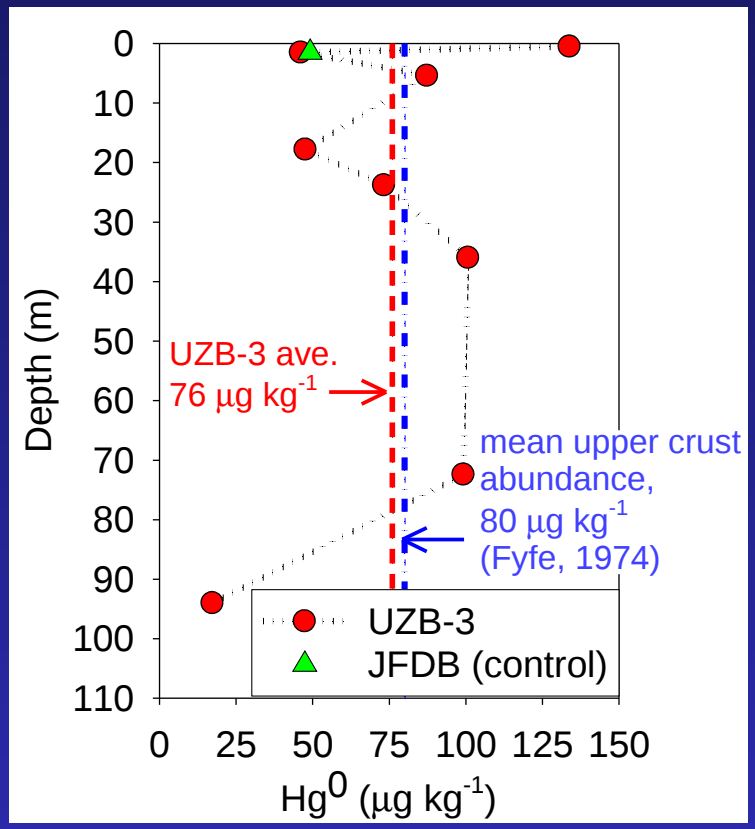


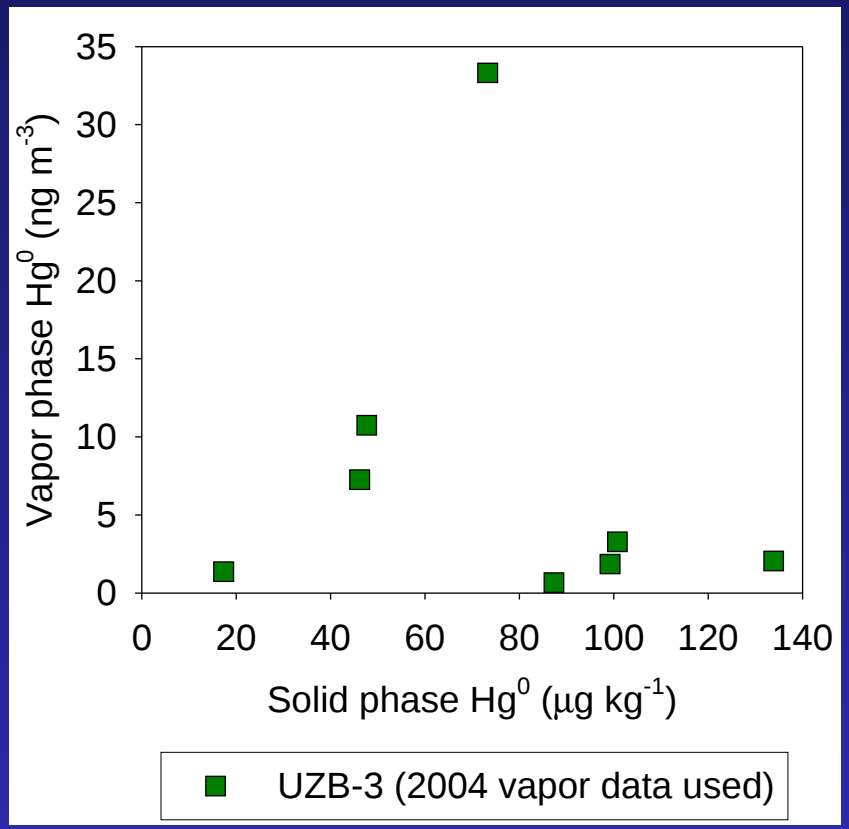
- Deep (below 1.5 m) peak Hg^0 concs. of 33 ng m^{-3} in UZB-3 & 4 ng m^{-3} in UZB-2
- Elevated 2.7 – 22 times above typical atmospheric conc ~1.5 ng m^{-3} (*Krabbenhoft et al.*, 2005)
- Also elevated relative to control borehole (JFDB) concentrations

- Profile patterns similar to other volatile constituents measured at the ADRS

[Results from Walvoord et al., 2008]

ADRS Deep UZ - Total Hg in Soil





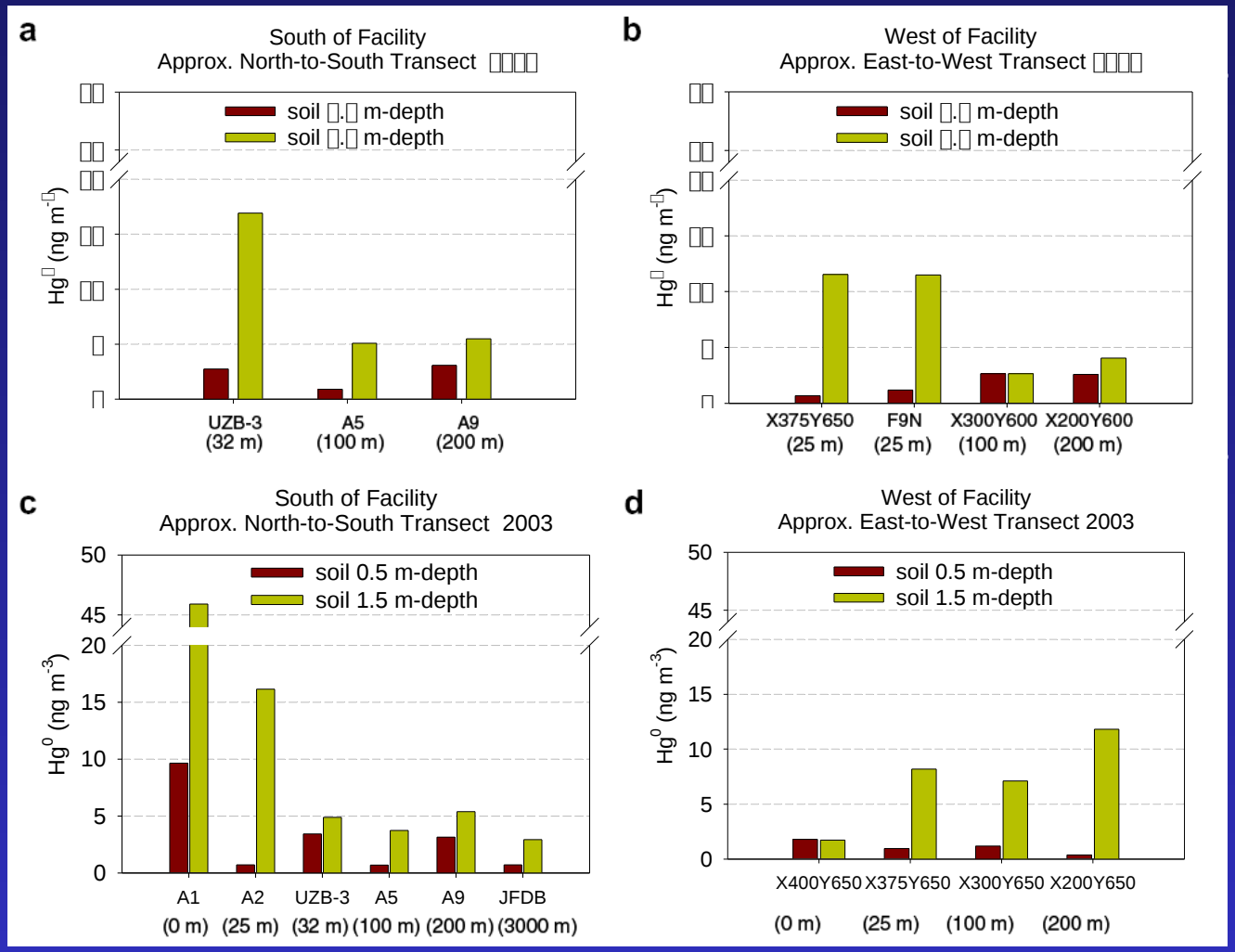
[Results from Walvoord et al., 2008]

- Total Hg in UZB-3 ranged from 17 to 133 µg kg^{-1}
- Average total Hg in soil at UZB-3 is very comparable to mean upper crust abundance.
- Lack of positive correlation between solid and vapor phase Hg rules out influence of desorption of geologic Hg on vapor data.

Observed Deep Unsaturated Zone Hg^0 Transport

- Distinct Hg^0 peak in UZB-3 between 15 and 35 m depth. Somewhat elevated concentrations in this interval at UZB-2.
- Data support long-distance (>100 m) lateral transport and 15-35 m vertical transport of Hg^0 from an anthropogenic source in 40 years or less.
- Long-distance migration through the unsaturated zone is not a mercury pathway previously considered.

ADRS Shallow UZ - Hg^0 in Vapor Phase



Generally greater conc. in gravel layer at 1.5 m vs. 0.5 m from the surface

N-S transect shows generally decreasing Hg conc. at the 1.5 depth. Trend is less pronounced at 0.5 m depth and in E-W transects

Values in parentheses above represent distances from the nearest waste disposal trench. Figure from Walvoord et al., 2008.

Observed Shallow UZ Hg^0 Transport

- Greater concentrations generally observed at 1.5 m vs. 0.5 likely reflects 1) mixing and dilution from the atmosphere in the shallowest samples and 2) enhanced lateral transport and thus higher concentration source in the 1-2 m shallow gravel unit.

- Temporal variation and lack of consistent spatial trends in shallow Hg^0 suggest the influence of parameters other than distance from source. These include small scale differences in: 1) diffusive soil properties that control the rate of atmospheric mixing and dilution and 2) properties that control Hg^0 soil volatilization such as soil pH, organic matter, vegetative cover, wind, light exposure, etc.

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Deep UZ Hg^0 Transport Comparison

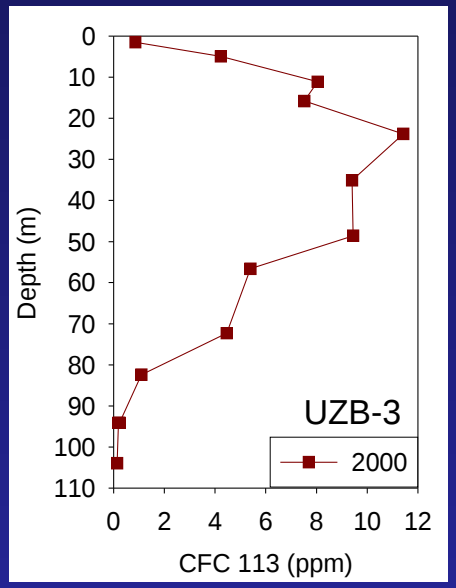
CFC-113

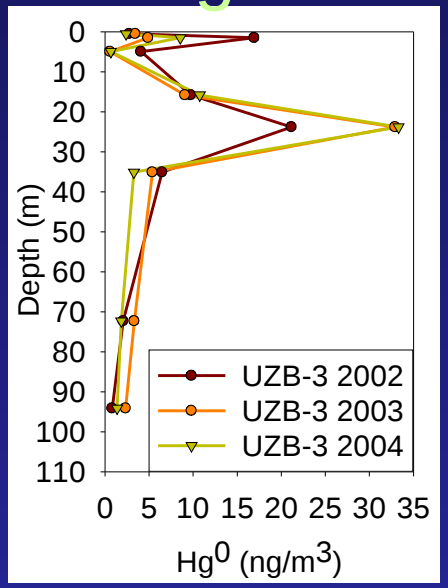
Hg^0

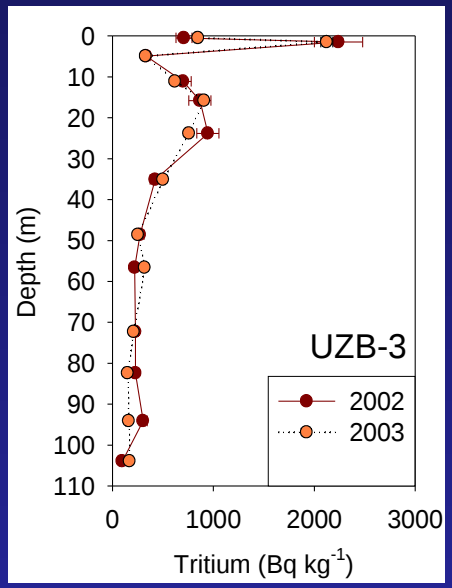
Tritium

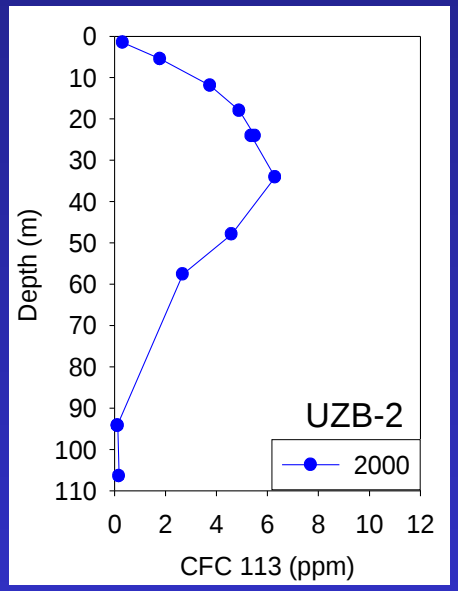
UZB-3

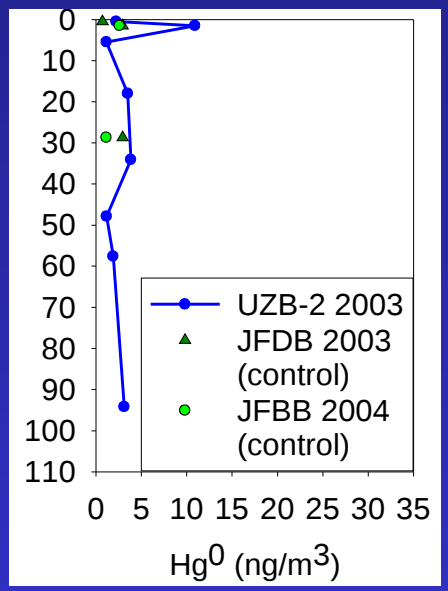
UZB-2

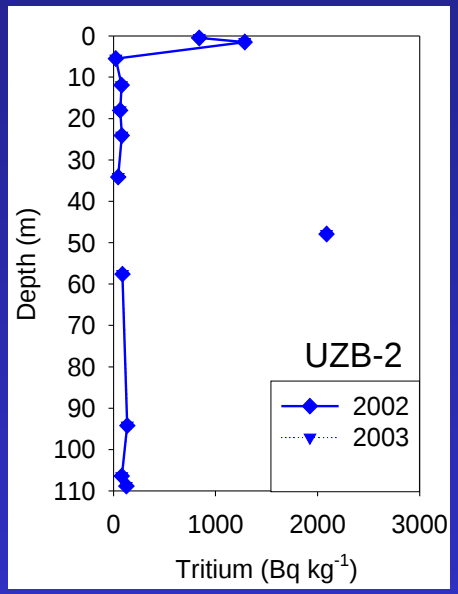








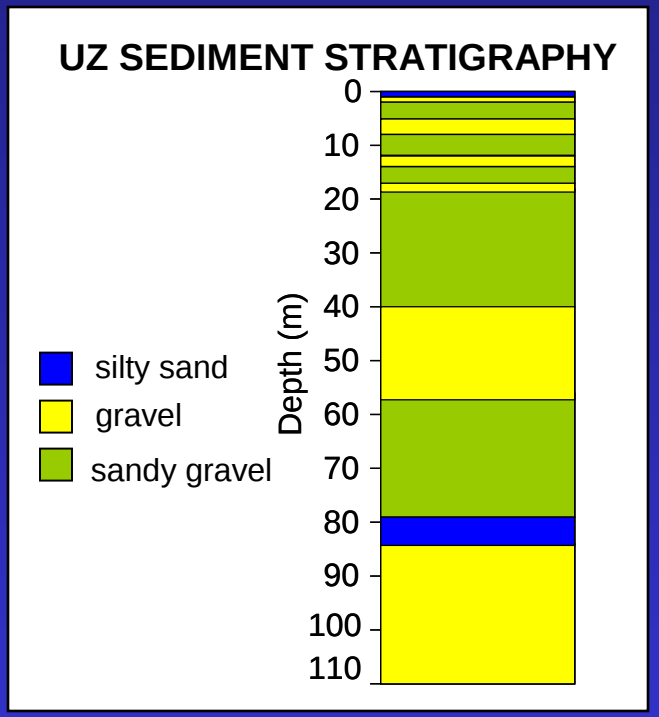




[Stonestrom et al., 2004] [Walvoord et al., 2008] [Mayers et al., 2005]

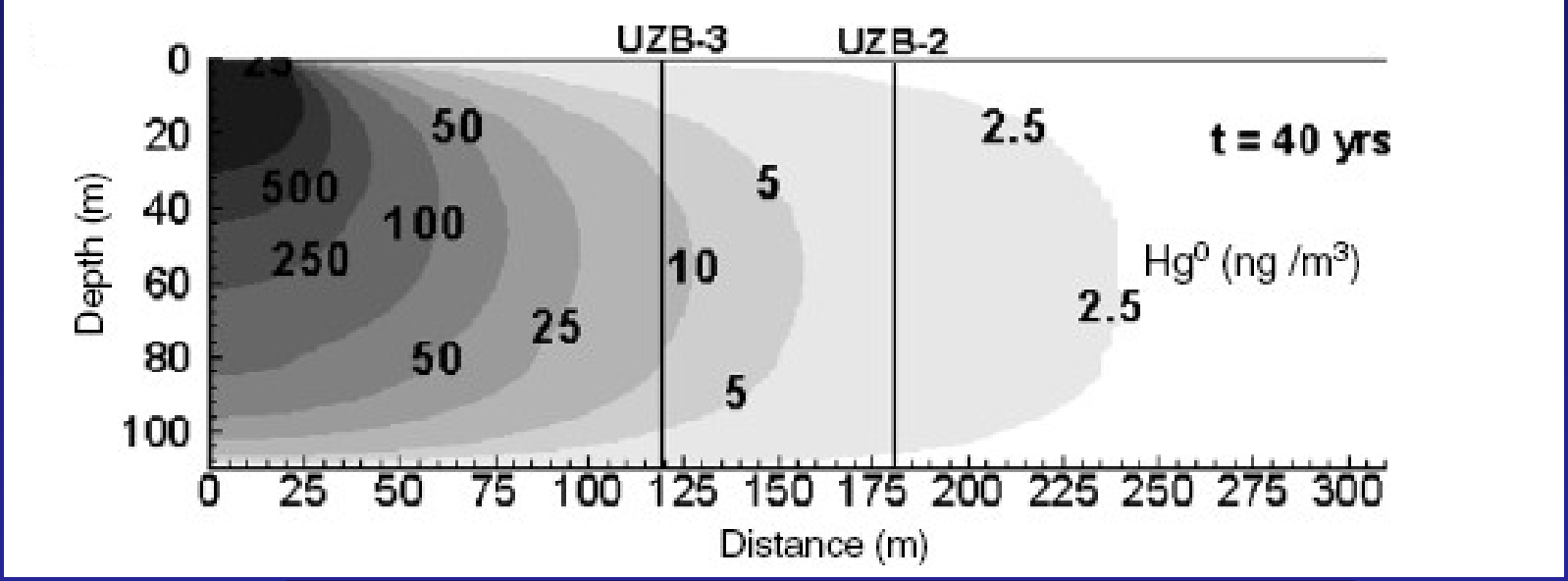
Hg^0 Transport Modeling

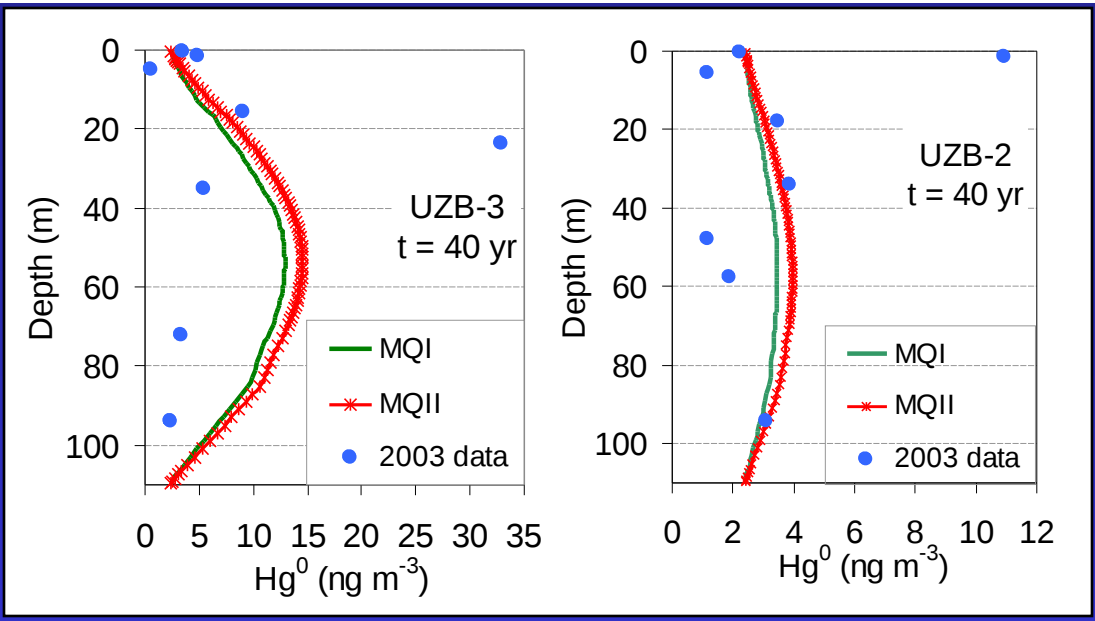
- The Finite Element Heat and Mass transfer model (FEHM) used to simulate non-isothermal vapor and liquid movement and Hg^0 transport in the UZ.
- Initial conditions for the 2-d **40-yr** transport simulations represent 16,000 yrs of transient drying as estimated by *Walvoord et al.,* 2004.
- Model domain: 110 m vertically (the entire UZ) and 500 m radially. Heterogeneous, layered geology.
- The Hg^0 source (to 15 m deep) used as fitting parameter to match the accumulated mass measured in UZB-3.



Hg diffusivity in air (D^0) = 1.194e-5 m^2 s^{-1} (Massman, 1999)
MQI D_{eff} = D^0 * air-filled porosity$^{(10/3)}$ / porosity^2
MQII D_{eff} = D^0 * air-filled porosity^2 / porosity$^{(2/3)}$

Hg^0 Transport Modeling Results





[Walvoord et al., 2008]

Summary

- Transport of elemental Hg through arid UZs may serve as a viable long distance (10^2 m) pathway for mercury migration from landfills.

- The inability to numerically reproduce the general shape of the observed Hg^0 profiles reflects (1) the inadequacy of current empirical models used to estimate differences in effective diffusion coefficients between stratigraphic units, (2) an undescribed mechanism generating complex convective gas flow, (3) a major gap in our understanding of gas-phase transport in the UZ, or some combination of the three.