Shell Global Solutions

Type Curve Approach for Assessing Potential Effects on Ground Water From Small Releases of Gasoline at UST Sites

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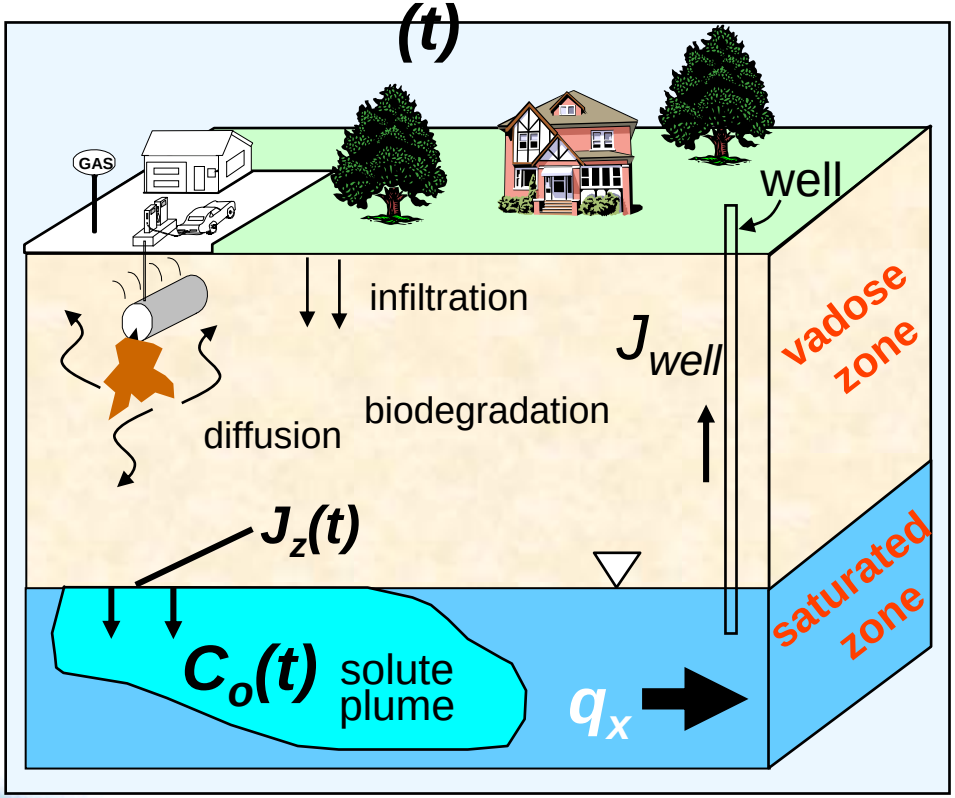
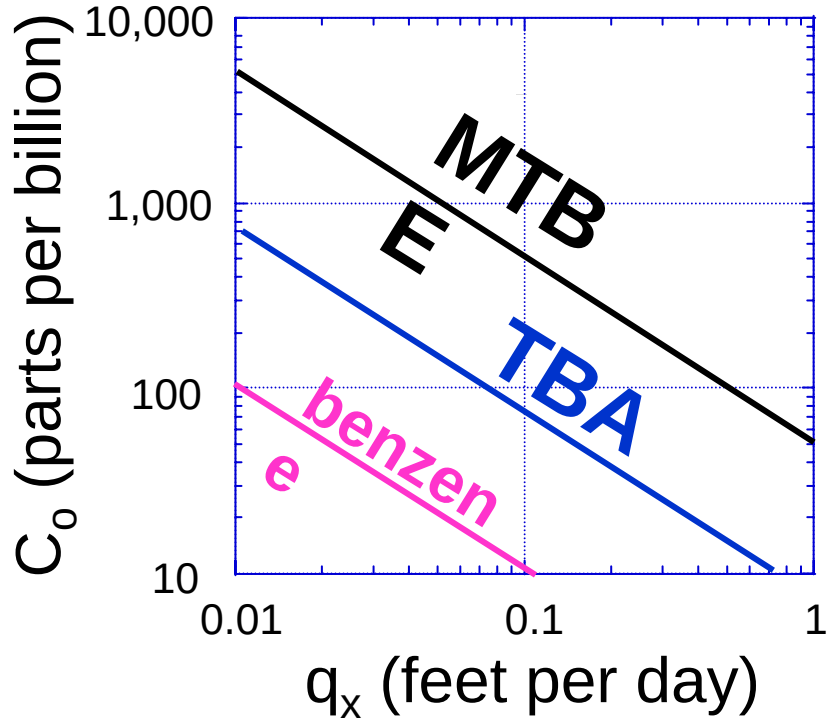
Small Releases - Conceptual Model

$C_o(t)^* = J_z(t)/q_x(t)$ $C_{well}^* = J_z(t)/J_{well}$





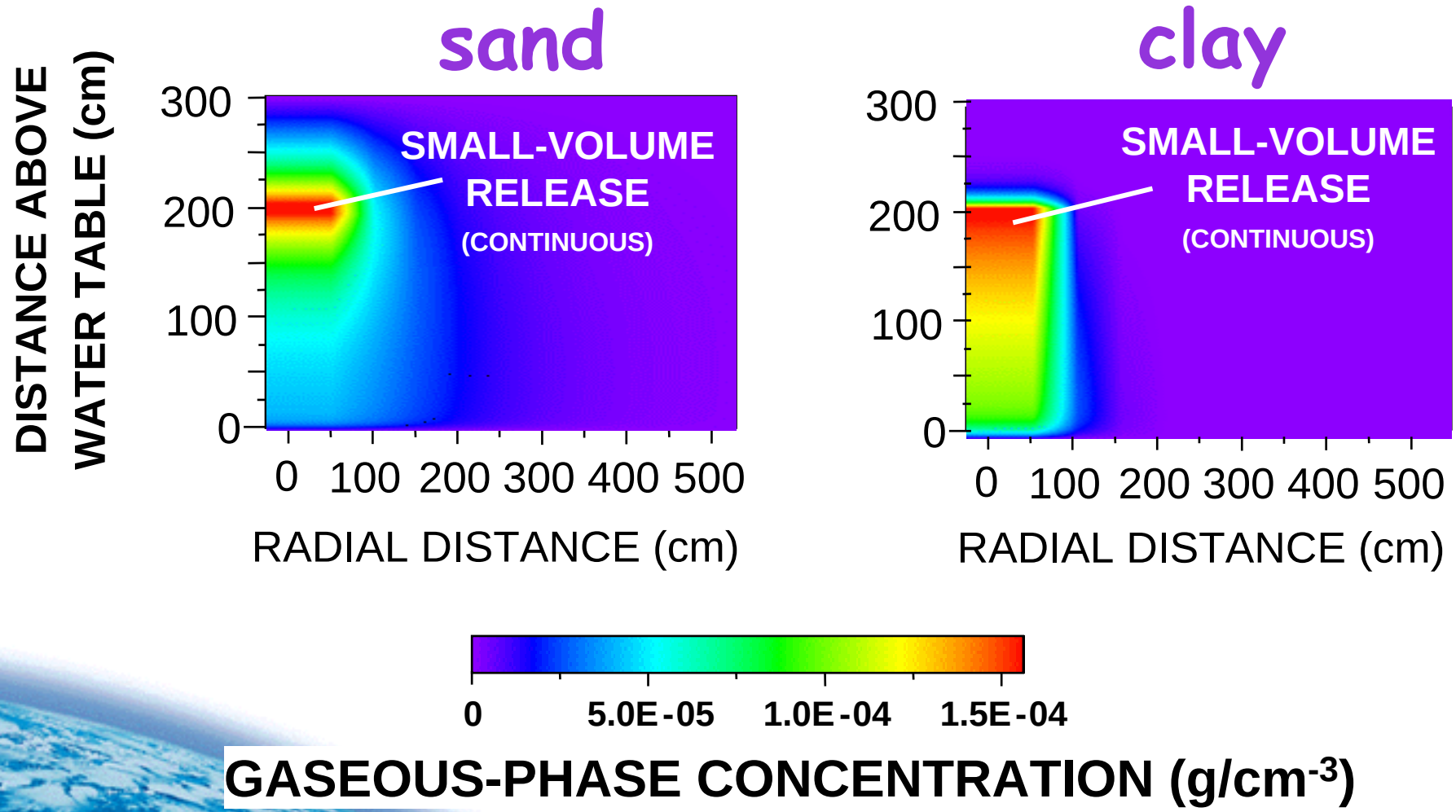
***assumes no mixing/dilution/dispersion in ground water**

Environmental Significance - API Modeling Studies

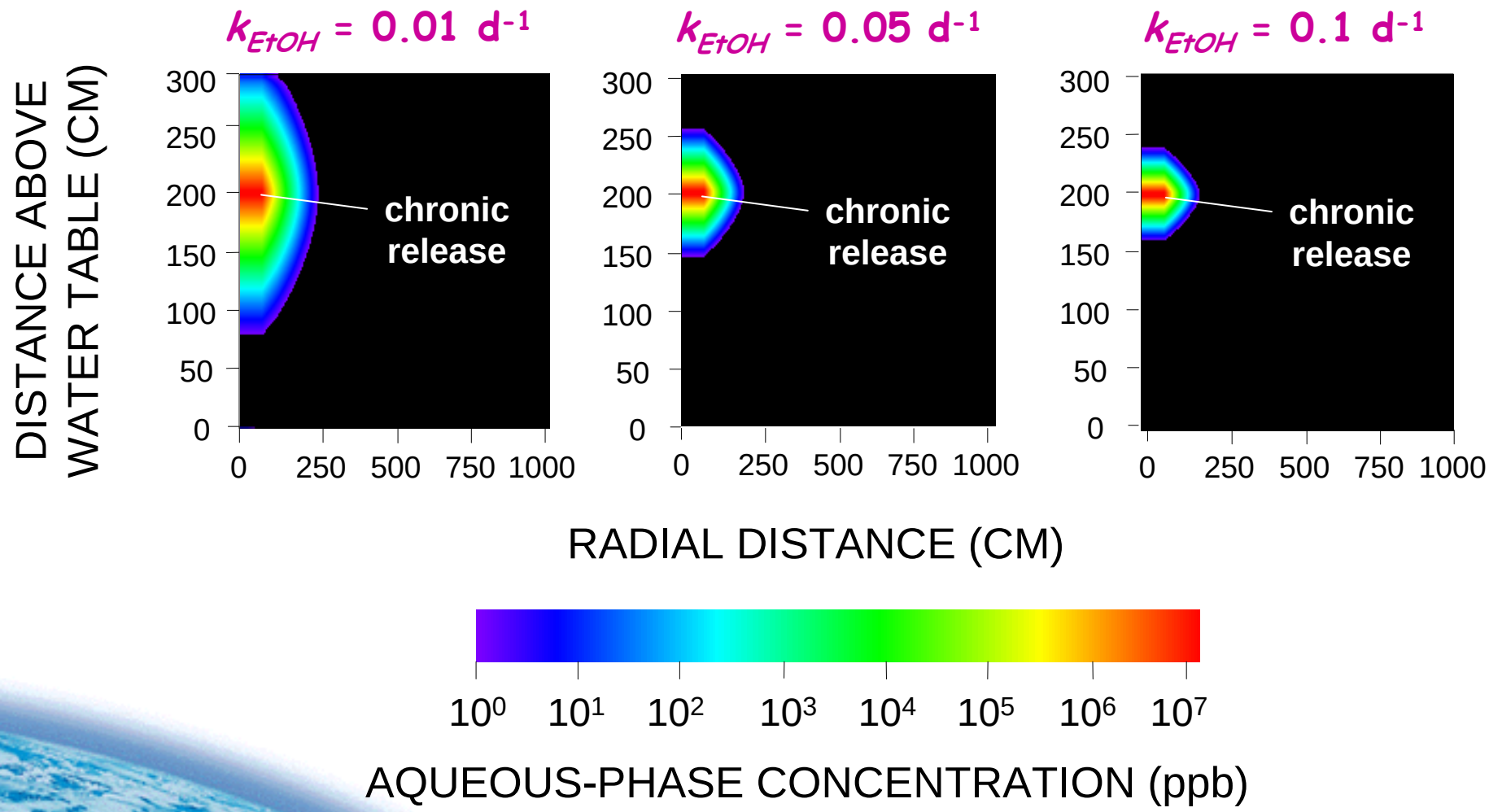
- MTBE: [*Lahvis and Rehmann,* 2000] - API Tech. Res. Bull. No. 10*
- EtOH: [*Lahvis,* 2003] - API Tech. Res. Bull. No. 19*
- TBA (ethanol-blended gasoline): [*Lahvis,* 2005] - API Tech. Res. Bull. No. 22*
- TBA (MTBE-blended gasoline): [*Lahvis*, in press]

**** http://www.api.org/bulletins***

Steady-State MTBE Distribution - Soil Gas
(infiltration = 20 cm/yr)



Steady-State EtOH Distribution - Pore Water
(sand, no infiltration)



Mass Loss to Atmosphere Can be Significant…

Ground-Water Infiltration Rate	Fraction of Initial Source Mass (%)*	
	SAND	CLAY
q = 0 (diffusion only)	6.2	12
q = 20 cm/yr	17	93
q = 100 cm/yr	49	99

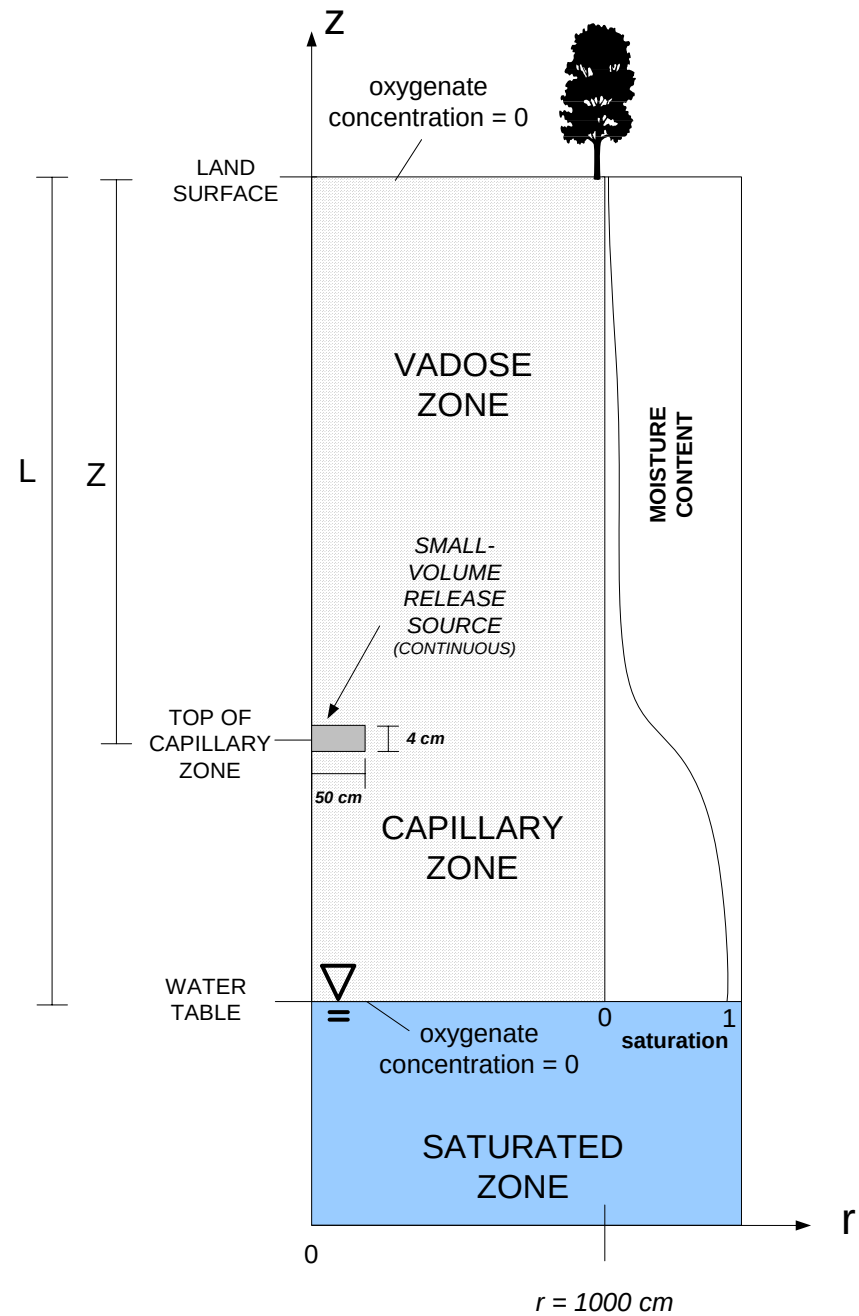
*Source located 2m above water table - 3m thick vadose zone

from Lahvis (2000)

Model Assumptions

- predict potential impact on ground water as a function of:
  - biodegradation

    MTBE -- non reactive
    EtOH -- 1st order, independent of O_2 availability
    TBA -- non reactive, coupled to MTBE
    benzene -- dual Monod, function of O_2 availability
  - soil type
  - infiltration rate (constant)
  - depth to ground water
  - gasoline composition



Some Considerations…

- need exists to develop screening tool for prioritizing sites with small releases
  - quantify risk
  - target sites for remediation
  - potential implications for inspections, testing, monitoring, engineering modification
- tool must be user friendly, yet rational and based on sound science
- tool must be able to screen-in/out sites

Assumptions

- transport is 1-D (conservative)
- soil type can be defined by bulk properties
- infiltration rate is constant
- kinetics are 1st-order

Scaling Model for Evaluating Transport

Governing Transport Equation
1-D Vertical (steady-state)

$$D\frac{\partial^2 G}{\partial z^2} - q\frac{\partial C}{\partial z} - \lambda C = 0$$

diffusion

advection
(gw infiltration)

biodegradation

D = effective diffusion coefficient
q = ground-water infiltration rate
λ = first-order rate constant
C = aqueous-phase concentration
G = gaseous-phase concentration
z = distance

Transformed Equation
(dimensionless analysis)

$$\frac{\partial^2 C}{\partial x^2} - P_e\frac{\partial C}{\partial x} - D_m C = 0$$

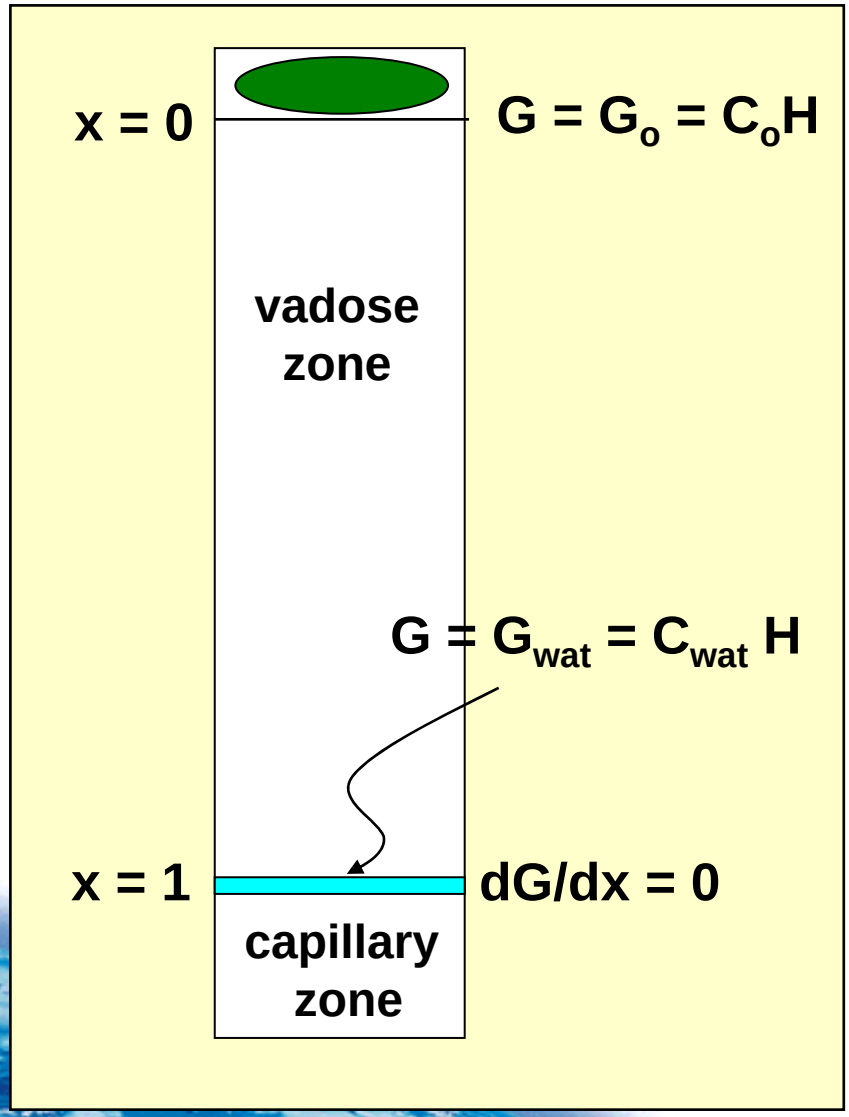
where,

$$P_e = \frac{qL}{DH}, \quad D_m = \frac{\lambda L^2}{DH}, \quad x = \frac{z}{L}$$

P_e = scales advection and diffusion
D_m = scales biodegradation and diffusion

H = Henry's Law constant

Development of Type Curves



- solution to transformed equation varies depending on applied boundary conditions resulting in different sets of type curves

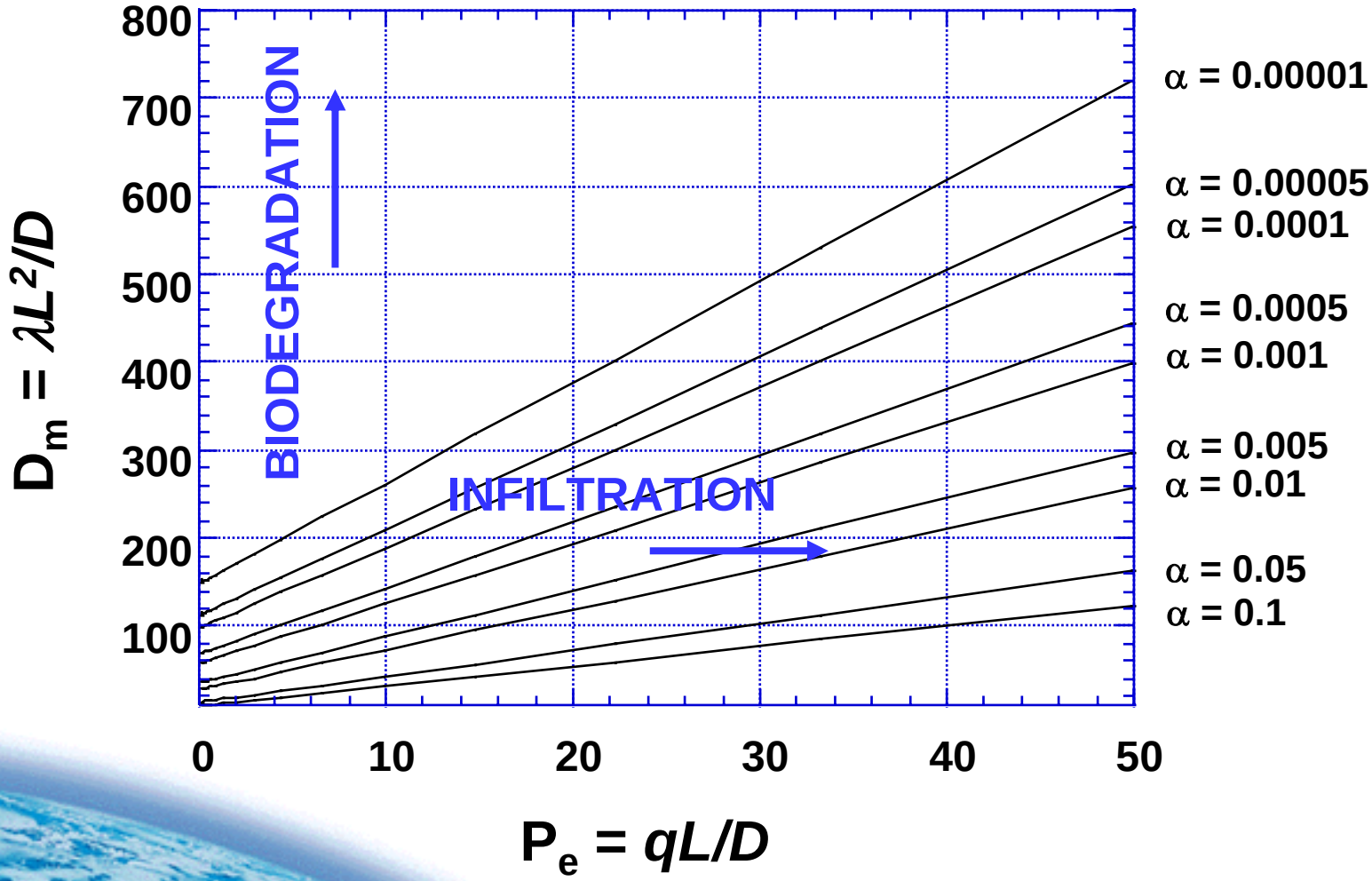
- solution is given by concentration (C_{wat}) or mass flux (J_{wat}) at the water table for various values of P_e and D_m

  - solution expressed in terms of dimensionless attenuation factor (α):

$$\alpha = C_{wat}/C_o$$

$$\alpha = J_{wat}/J_o$$

Example Type Curves (for concentration)



attenuation coefficient

$\alpha = C_{wat}/C_o$

Predicting Impact on Groundwater (General Approach)

Site-Specific Assessment

a) knowns - depth to groundwater (L); source concentration C_o (measured or assumed)

assume default values for D, q, λ

Default values: *D(benzene)* = 0.001 cm^2/s (*EPA, 1996*)
q = 18 cm/yr (*EPA,1996*)
λ^* = 0.01 d^{-1} - aerobic (Howard, 1991)
λ = 0.001 d^{-1} - anaerobic (Howard, 1991)

*** requires confirmation of O_2 availability**

b) calculate P_e and D_m

c) predict attenuation

Model Parameters (Example Values)

	MTBE	benzene	ethanol
D (m^2/d)	----------	0.001 - 0.01	----------
λ (1/d)*	0.005	0.1	0.5
L (m)	----------	1 - 10	----------
q (m/yr)	----------	0.01 - 0.5	----------
H	0.026	0.18	0.00025
P_e	0.11 - 520	0.015 - 76	11 - 55,000
D_m	19 - 1.9E04	56 - 5.6E04	2E05 - 2E08

(* for scaling purposes only)

$$P_e = \frac{qL}{DH}$$

$$D_m = \frac{\lambda L^2}{DH}$$

- as P_e increases, transport becomes dominated by infiltration

  increasing P_e ⟶

  (benzene < MTBE < ethanol)

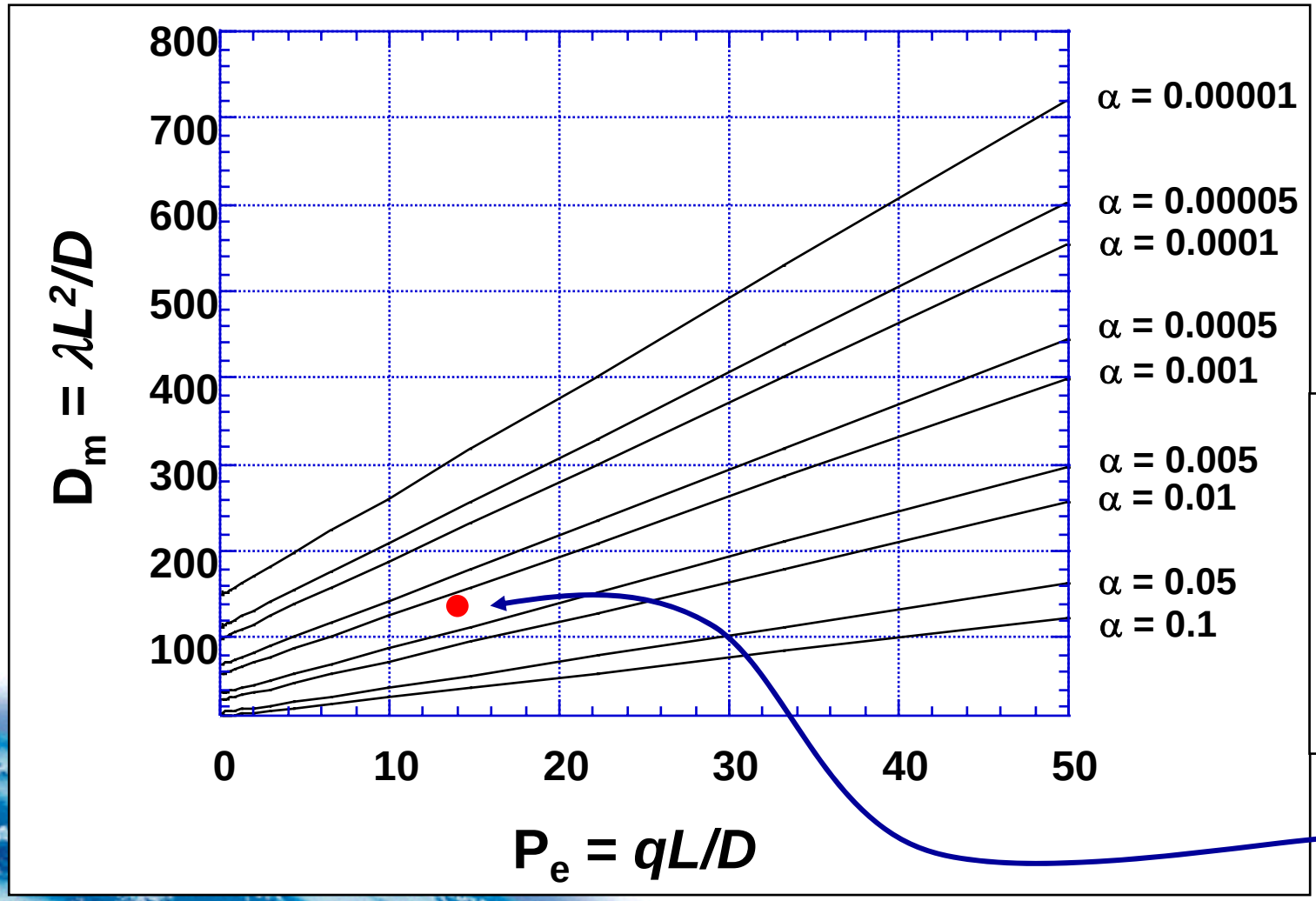
- as D_m increases, transport becomes dominated by biodegradation

  increasing D_m ⟶

  (MTBE < benzene < ethanol)

Type Curve Application Example

Knowns: C_o = 1,700 ppb, L, soil type
-- predict groundwater concentration



attenuation coefficient

$$\alpha = C_{wat}/C_o$$

Example (benzene)

q (m/yr)	0.18 (default)
L (m)	5
D (m²/d)	0.001
H	0.18
λ (1/d)	0.001 (default)
P_e	14
D_m	140

C_{wat} = 3.4 ppb

Conclusions

- recent evidence suggests that vapor releases are more common than liquid releases, their environmental risk needs to be quantified on a site-by-site basis
- the environmental significance of small releases can be determined based on transport in the vadose zone
- approach requires confirmation of conceptual model (site characterization) and type-curve analysis
- key parameter is λ
- best prediction from calibrated model (site data)
  (examples, *Lahvis et al.*, 2004; *Baehr et al.*, 2001)
- model prediction should be validated with monitoring

1st-Order Rate Constants (MTBE)

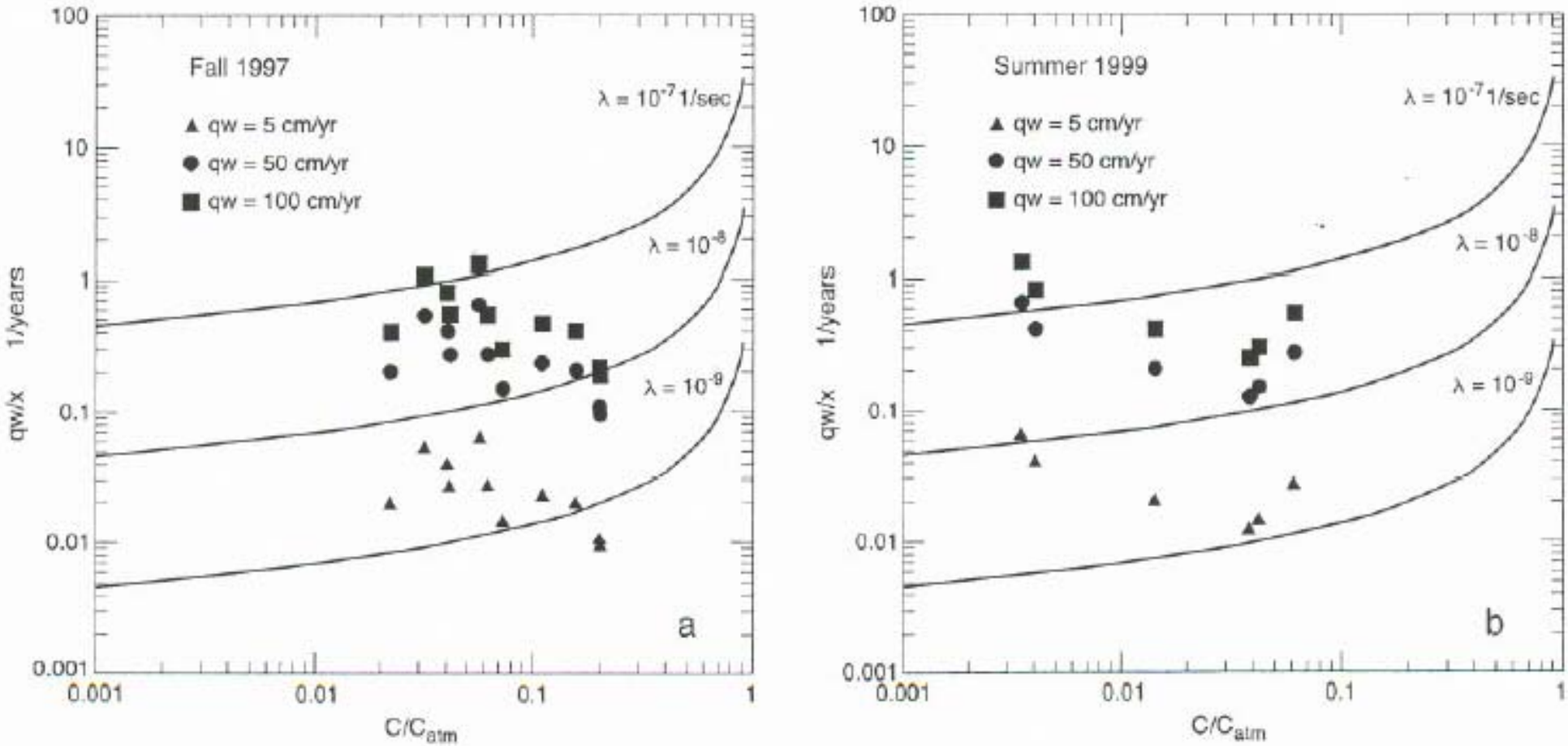


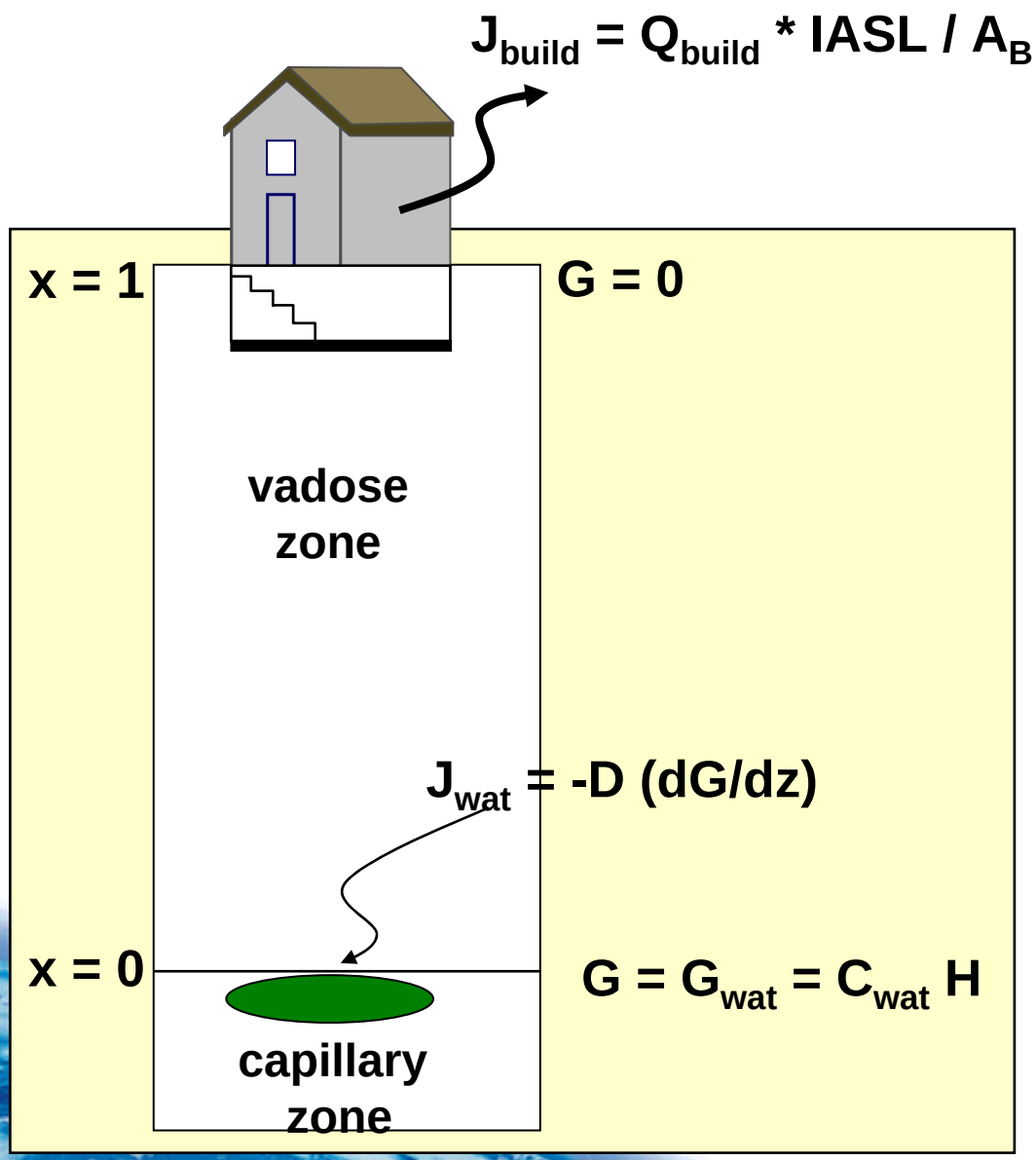
Figure 9. MTBE unsaturated zone attenuation observed in relation to a decay model: (a) 1997 and (b) 1999.

$$1E\text{-}09\ s^{-1} < \lambda_{MTBE} < 1E\text{-}07\ s^{-1}$$

from Baehr et al. (2001)

But Wait …
There's
More !

Type-Curve for Screening-Level VI Application

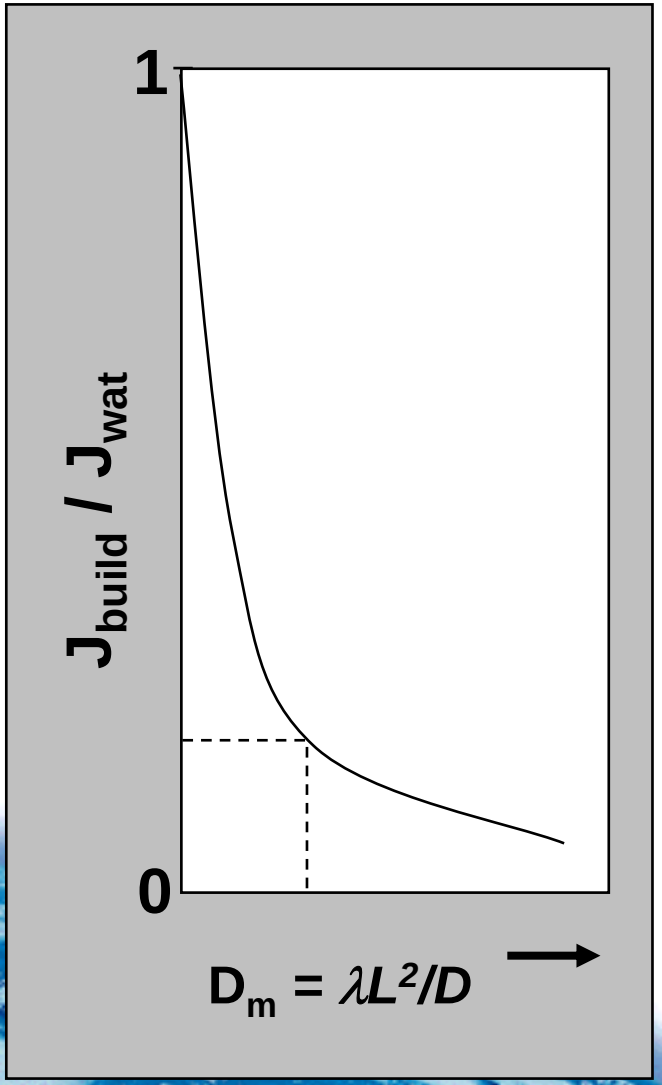


Transformed Eqn.

$$\frac{\partial^2 C}{\partial x^2} - P_e \frac{\partial C}{\partial x} - D_m C = 0$$

- assume $P_e = 0$ (no infiltration) results in single type curve (D_m)
- $G = 0$ ($x = 1$) conservative
- type curve used to calculate C_{wat} for various values of D_m

Type-Curve for Screening-Level VI Application (example)

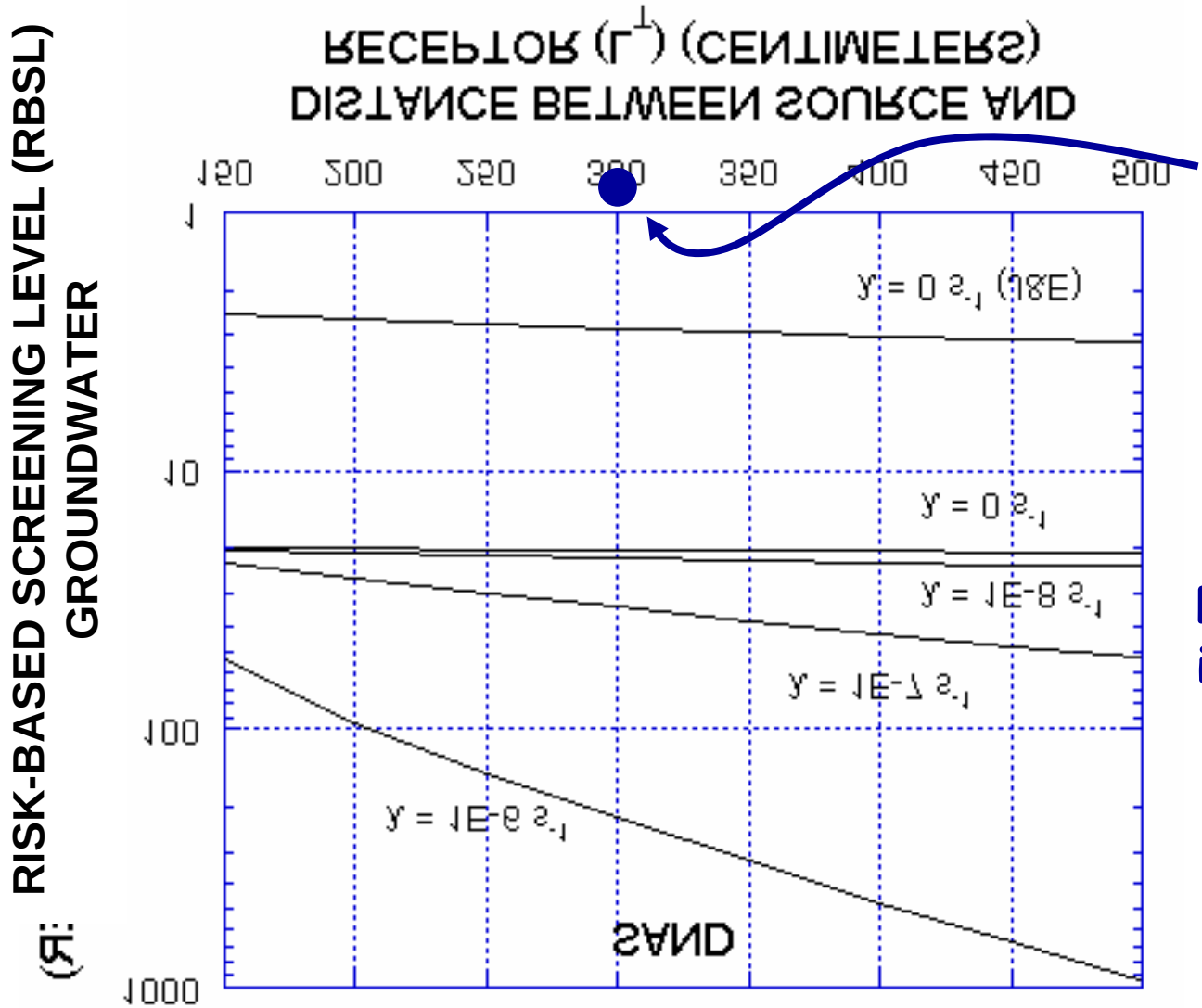


- calculate J_{build}

  $J_{build} = Q_{build} * IASL / A_B$

- determine D_m
- plot
- determine J_{build}/J_{wat}
- calculate J_{wat}
- calculate C_{wat} (need to know depth to gw)

  $C_{wat} = J_{wat}L/D$



For:
L = 3 m
Soil = sand
λ = 1E-6 s^{-1}
(0.1 d^{-1})

RBSL = 200 ppb instead of 5 ppb

Lahvis, M.A., DeVaull, G.E., and R.A. Ettinger, 2001, Effects of diffusion-coefficient heterogeneity and biodegradation on transport to indoor air at gasoline spill sites, NGWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water--Prevention, Detection, and Remediation, Houston, Texas, November 14-16, 2001.