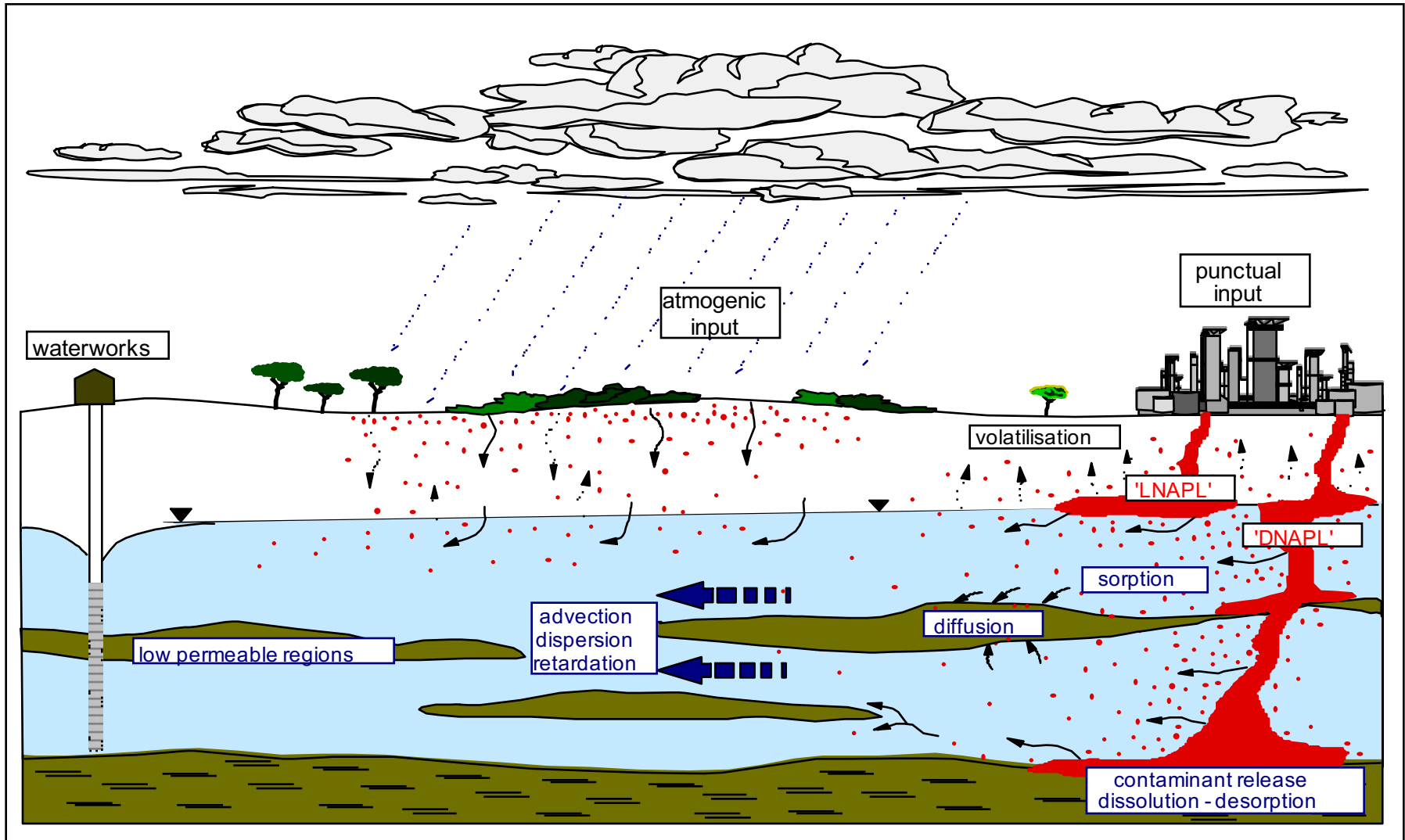




Slow Motion – Time Scales for Soil and Groundwater Remediation

Peter Grathwohl



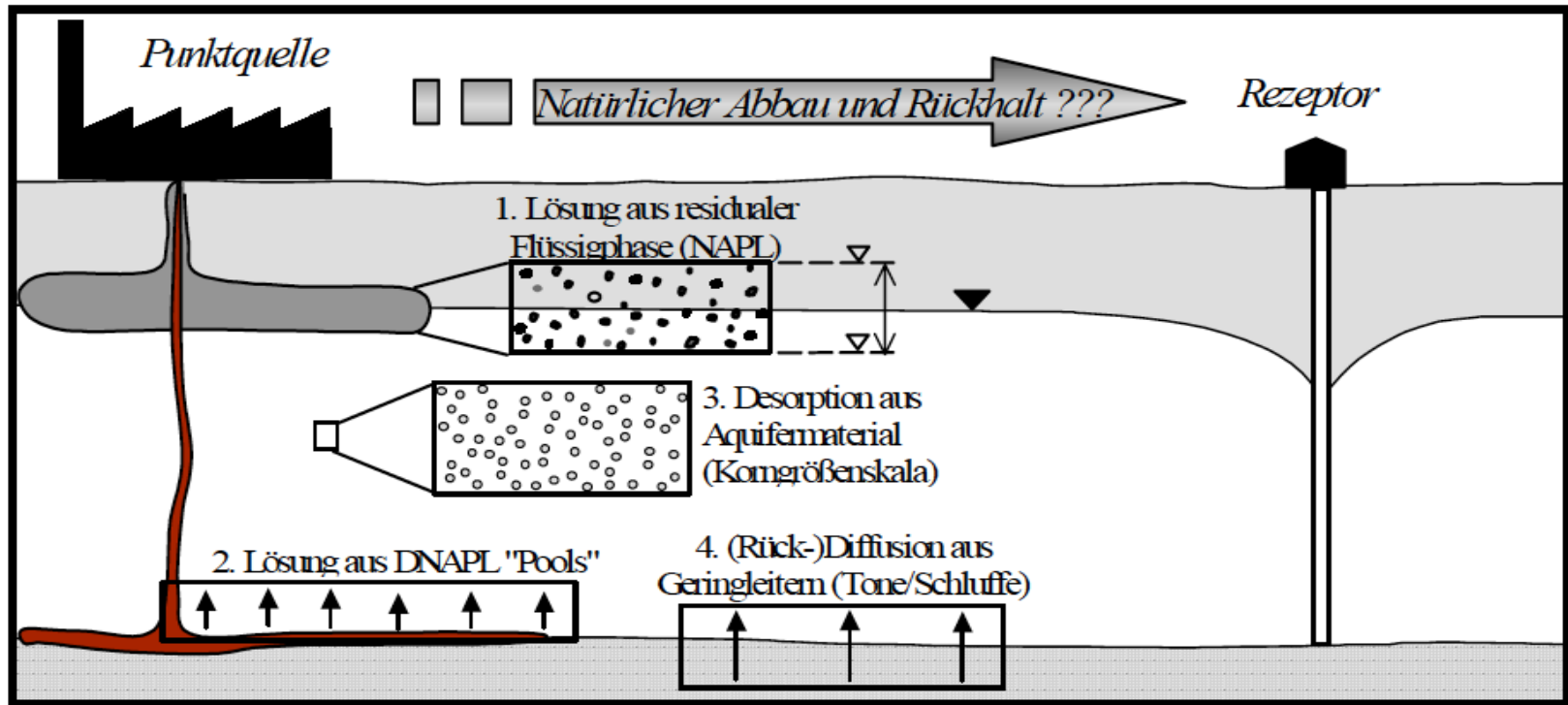


Abb. 1: Typische Szenarien der Schadstoff-Freisetzung aus kontaminierten Bereichen (aus Förstner und Grathwohl, 2003)

Grathwohl, P. (2006): Langzeitverhalten organischer Schadstoffe in Boden und Grundwasser. Grundwasser 11, 3, 157-163

Travis, C.C., Doty, C.B. (1990): Can contaminated aquifers at Superfund sites be remediated? - Environmental Science & Technology, 24 (10): 1464-1466.



Conclusions, GQ 1998, Tübingen

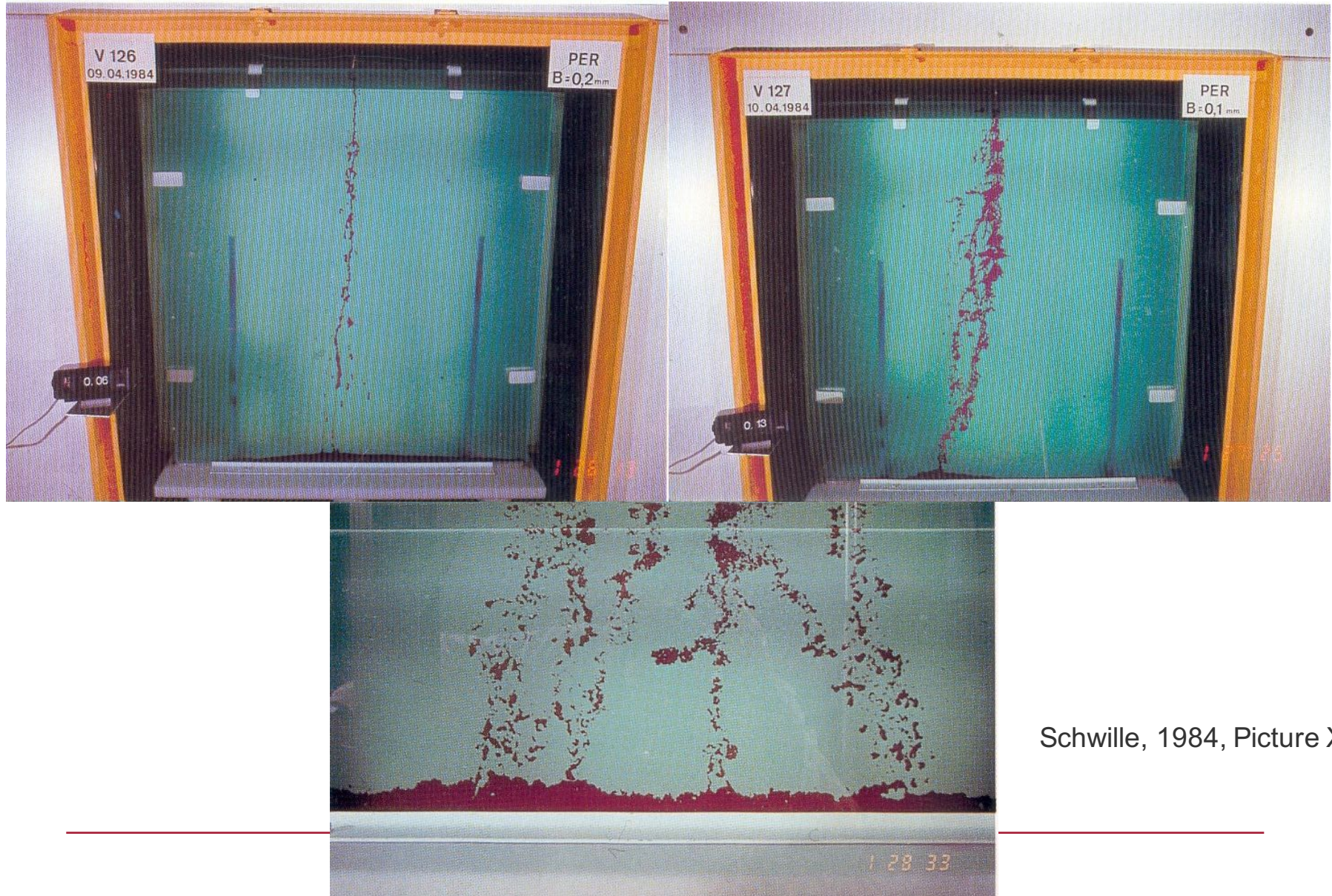


Scenario	Chlorinated solvents; BTEX	PAHs
Dissolved and sorbed contaminants		
Time scale for diffusion limited desorption at the grain scale	< 1 years	1 – > 10 years
Time scale for slow diffusion out of low permeability zones – matrix diffusion	> 10 years	> 100 years
Change of release rates / contaminant concentrations with time	Diffusive fluxes and concentrations decrease first with \sqrt{t} , later exponentially. The resulting concentrations in the groundwater are much lower than saturation; depending on the size of the source, concentrations lower than legal limits may be reached in the groundwater relatively fast.	
Enhanced contaminant removal	1. Increase of temperature (approx. factor 2 per 10°C). 2. Reduction of the effective diffusion distance (size reduction of aggregates or grains).	
Residual NAPL		
Time scale for dissolution of NAPL blobs/ganglia from smear zones	1 - > 10 years	10 - > 100 years
Time scale for the dissolution of NAPL pools	> 10 - 1000 years	> 1000 years
Change of release rates / concentrations with time	Dissolution rates are constant over extended periods of time. Locally the concentrations are far above the legal limit (saturation concentrations in the boundary layer to the NAPL).	
Enhanced in-situ decontamination *	1. Increase of the flow velocity. 2. Cosolvent (alcohol) or surfactant flushing for the mobilization and solubilization of residual NAPL.	

* this requires the knowledge of the exact location of the NAPL source



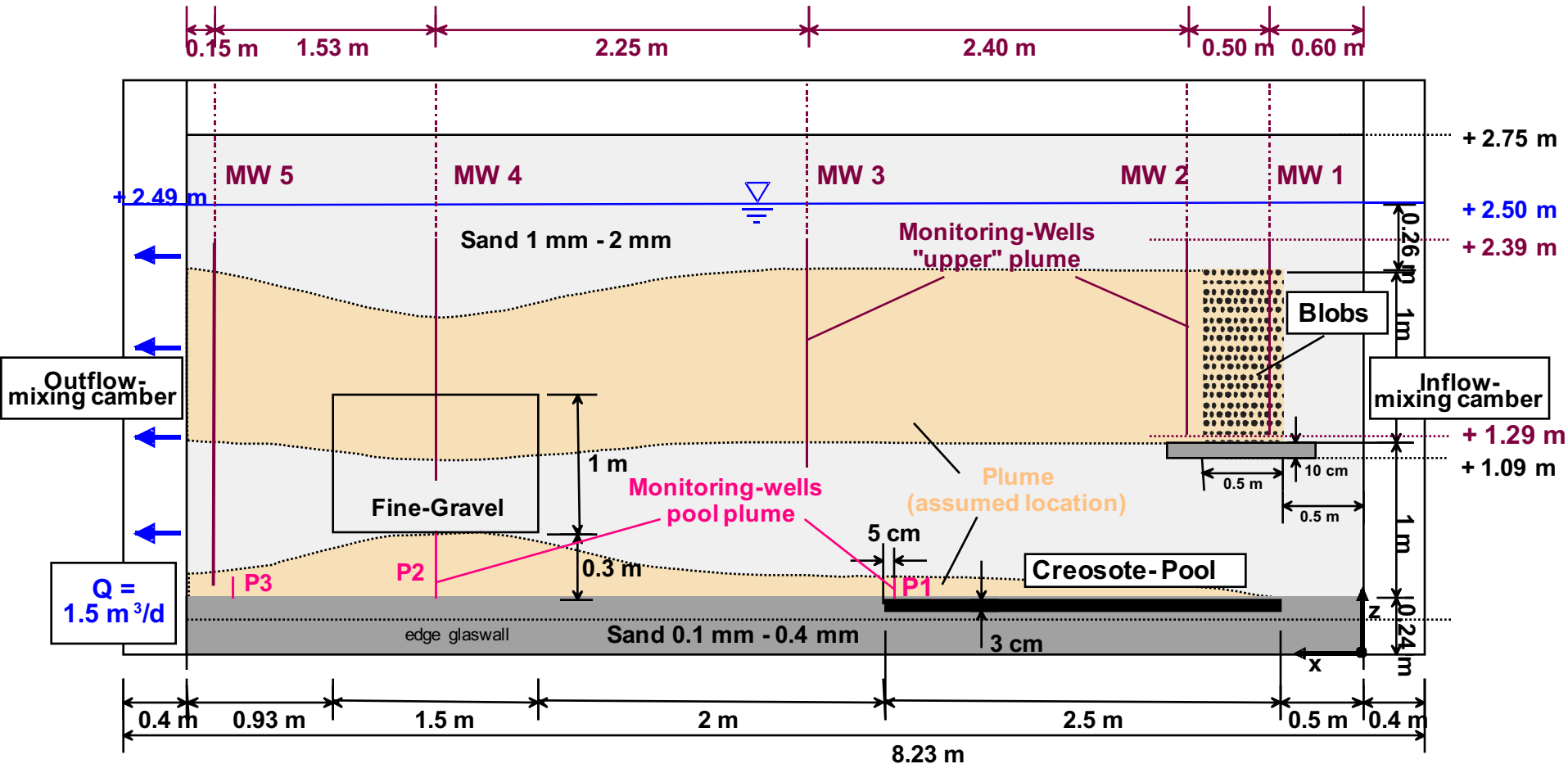
DNAPL-Infiltration: Blobs and Pools



Schwille, 1984, Picture XI



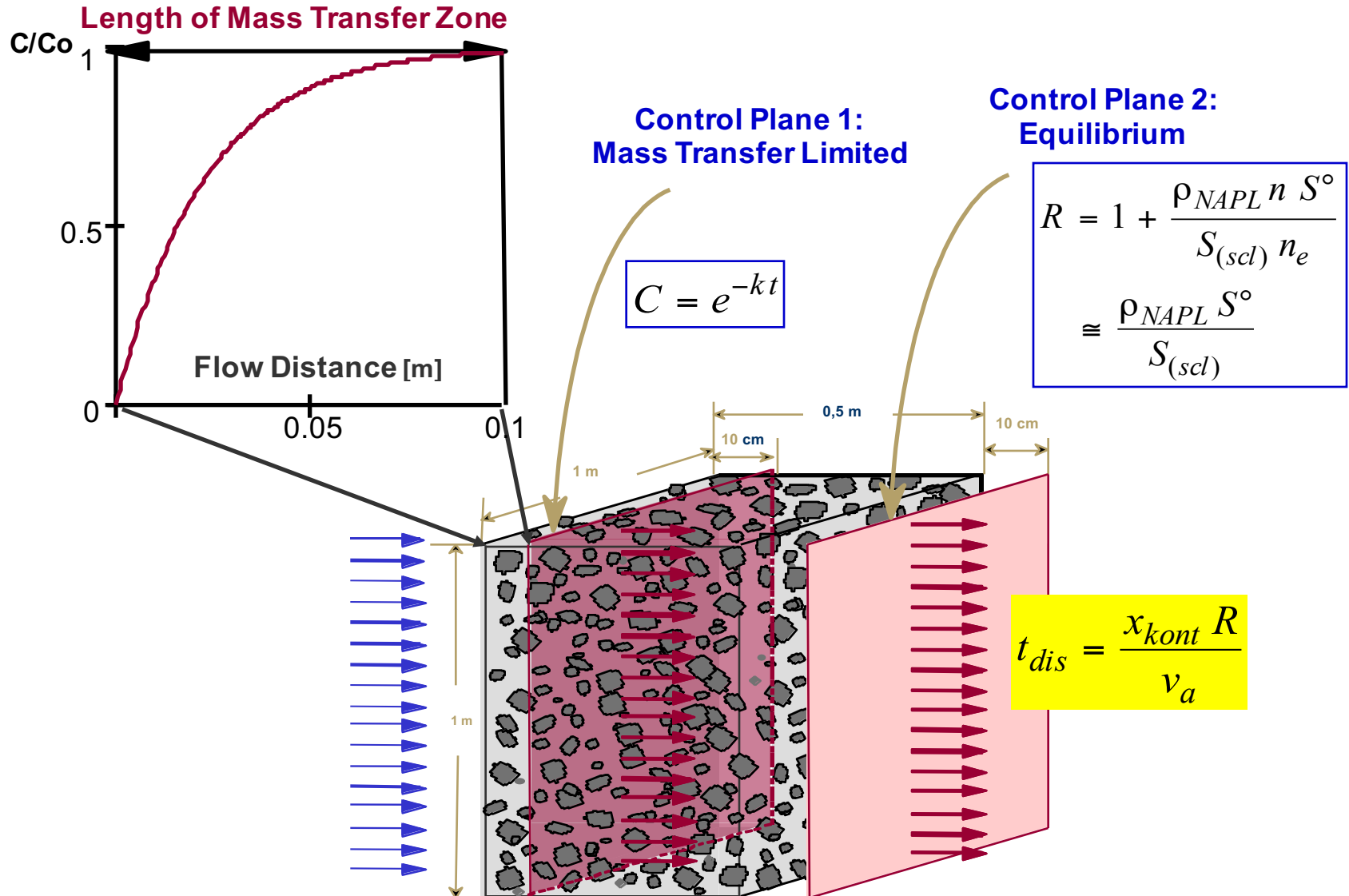
DNAPL: Blobs and Pools



Eberhardt, C., Grathwohl, P. (2002): Time scales of pollutants dissolution from complex organic mixtures: blobs and pools. J. Cont. Hydrol., 59, 1-2, 45-66 (Invited paper Special Issue on Site Remediation)



DNAPL: Dissolution of Blobs





DNAPL-Dissolution Time Scales: Blobs



Contaminants	$\log K_{OW}$	Fraction % ^a	Mass (kg) ^b	C_{sat} (mg l ⁻¹)	R	t_{Lsg} ^c (years)
Trichloroethene (TCE)	2.42	100	22	1 200	65	3.56
Perchloroethene (PCE)	2.88	100	24	150	570	31.2
Naphthalene (Nap)	3.37	4.5	0.74	10.6	247	13.5
Acenaphthene (Ace)	4.33	0.07	0.012	0.02	2 030	111
Phenanthrene (Phen)	4.46	1.7	0.28	0.2	4 920	270
Pyrene (Py)	5.32	0.44	0.073	0.02	12 700	696
Benz(a)pyrene (Bap)	6.04	0.22	0.036	0.0003	425 000	23 300

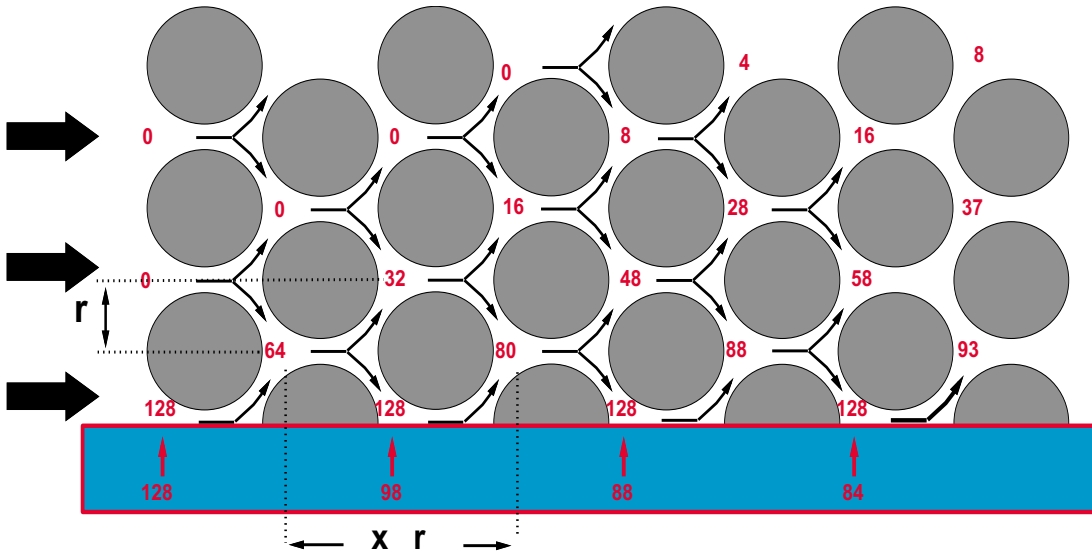
^a weight-% of the compound in the mixture; ^b contaminant mass per 1 m³ porous medium (aquifer)

^c time necessary for dissolution assuming a length of the contaminated zone of 10 m and a flow velocity of 0.5 m d⁻¹ (note that the hydraulic conductivity is reduced in zones containing residual NAPL).

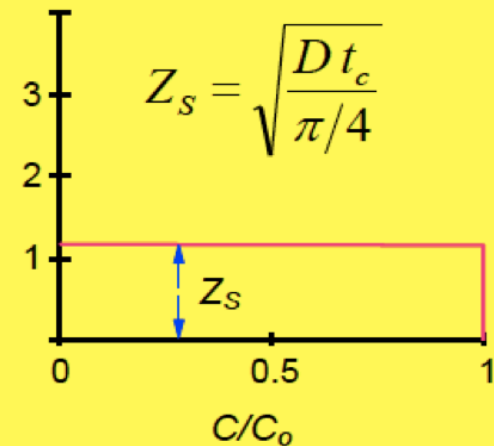
Eberhardt, C., Grathwohl, P. (2002): Time scales of pollutants dissolution from complex organic mixtures: blobs and pools.- J. Cont. Hydrol., 59, 1-2, 45-66



Dissolution of DNAPL-Pools (PCE)



Boundary layer model



$$F = C_o Q = C_o v_a n_e Z_s B_p$$

$$t_{diss} = \frac{M_P}{F_p} = \frac{L_P H_P (W_P) \rho_{DNAPL}}{v_a (W_P) Z_s S_{DNAPL}}$$

$$= \frac{10 \text{ m} \times 0.03 \text{ m} \times 1650 \text{ kg/m}^3}{1 \text{ m/d} \times 0.03 \text{ m} \times 0.150 \text{ kg/m}^3} = 110000 \text{ days}$$

$$Z_s = \sqrt{(D_p + \alpha_t v_a) x / v_a}$$

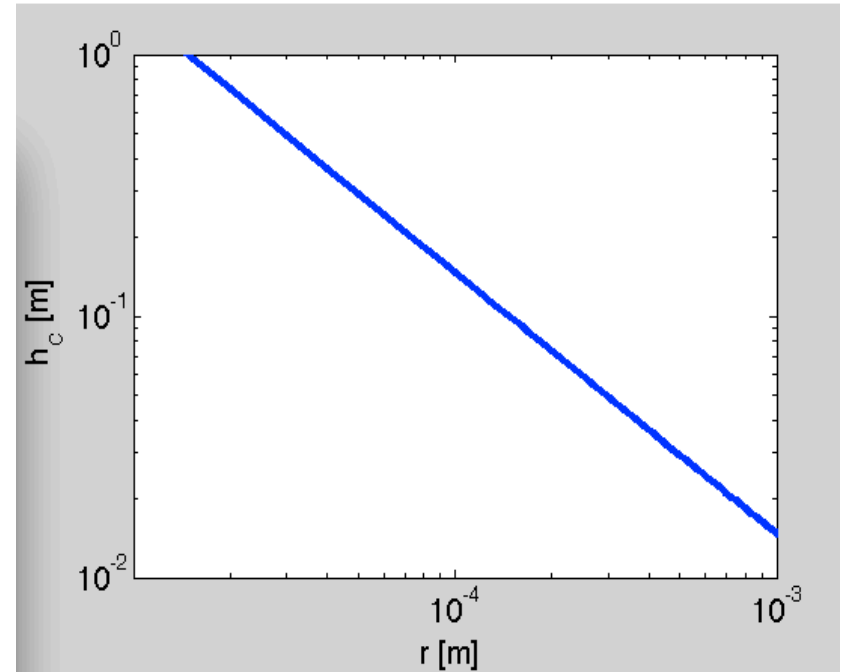
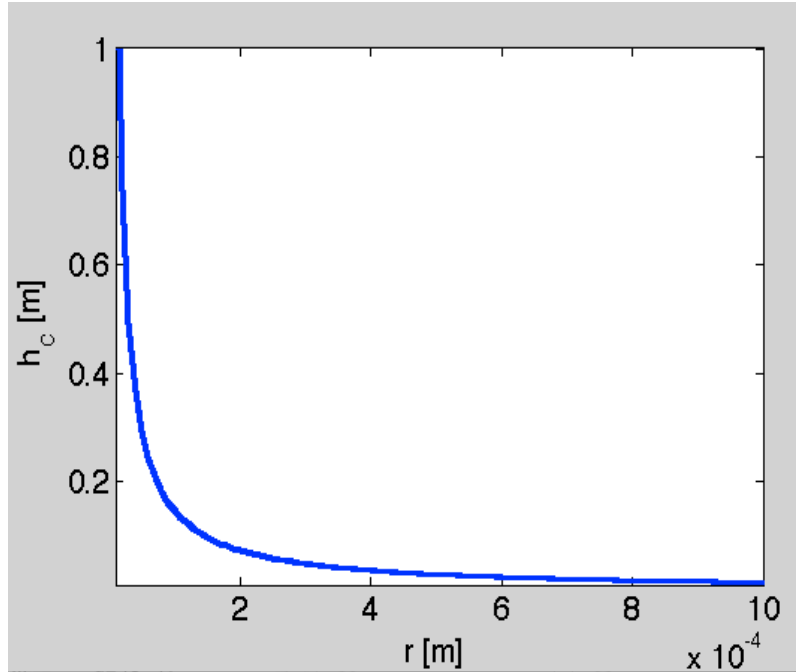
$$Z_s = \sqrt{1 \times 10^{-9} \frac{\text{m}^2}{\text{s}} \times 10 \text{ d}}$$

$$= 0.03 \text{ m}$$

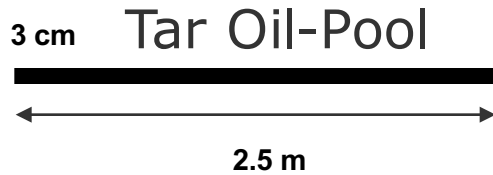
$$100 + 100 \text{ fracture system} = 200 \times 100 \text{ m} \times 0.03 \text{ m} \times 0.001 \text{ m} \times 1650 \text{ kg/m}^3 = 1100 \text{ kg}$$



Height of DNAPL-Pools



$$h_{o,c} = \frac{2\sigma}{(\rho_o - \rho_w)g r_m} = \frac{2 \cdot 0.045 \text{ kg s}^{-2}}{(1623 - 1000) \text{ kg m}^{-3} \cdot 9.81 \text{ m s}^{-2} \cdot 0.0002 \text{ m}} = 0.0736 \text{ m}$$

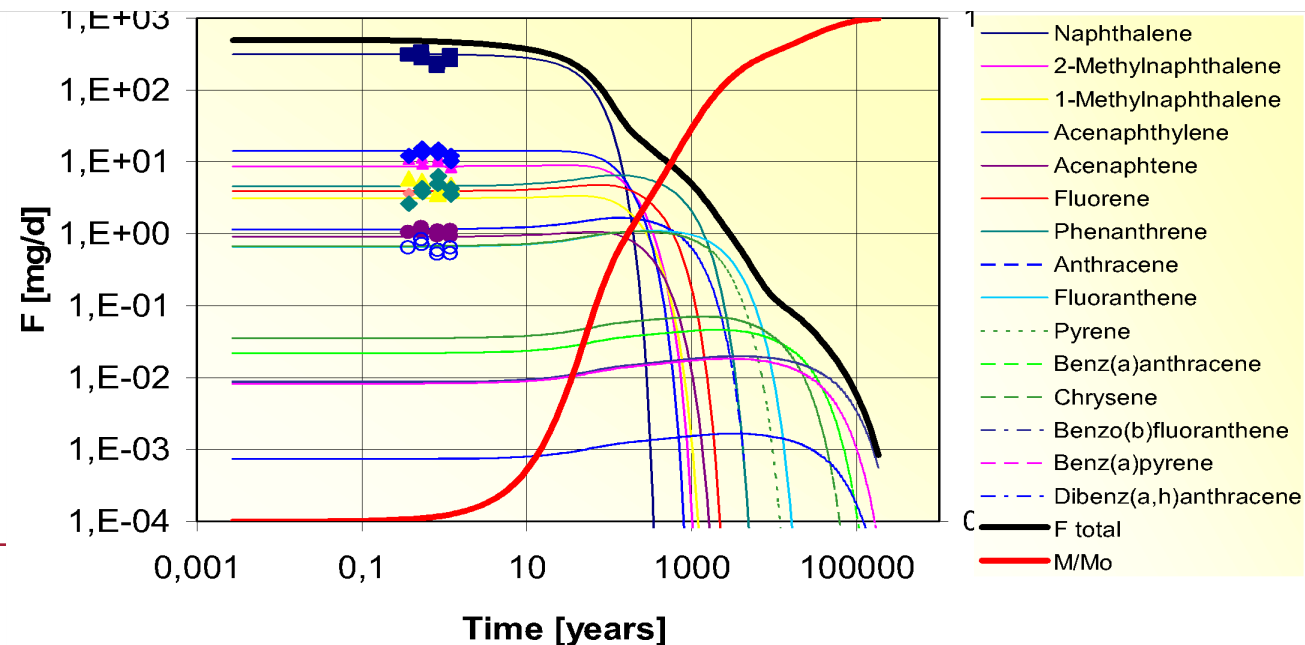
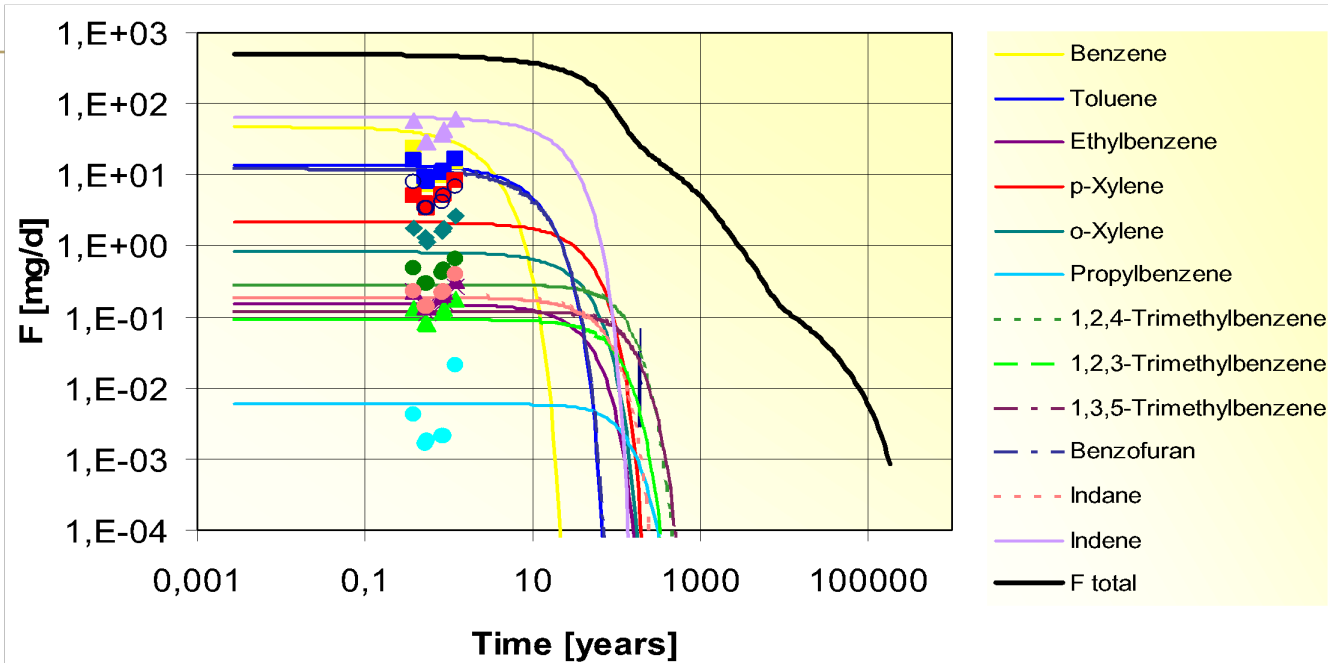


$$F = C_o Q = C_o v_a n_e Z_s B_p$$

$$Z_s = \sqrt{\frac{D t_c}{4/\pi}}$$

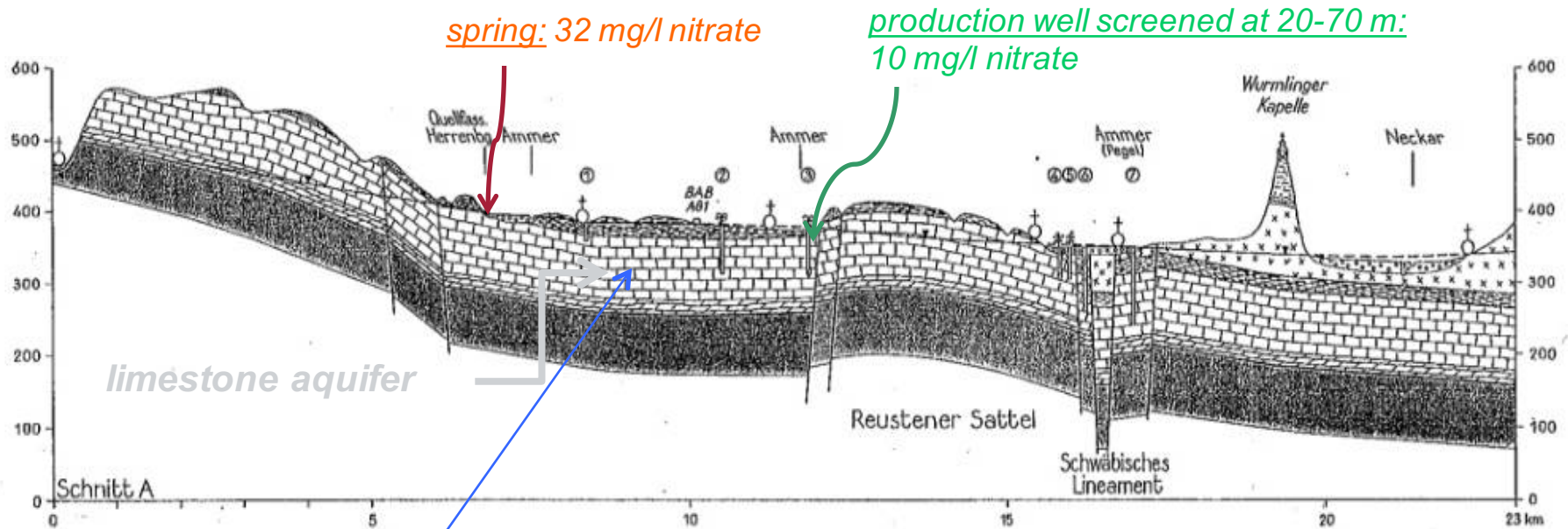
$$t_{Dis} = \frac{M_p}{F_p} = \frac{L_p H_p n \rho_o S^\circ}{C_o v_a n_e Z_s}$$

DNAPL-Dissolution Time Scales: Pools

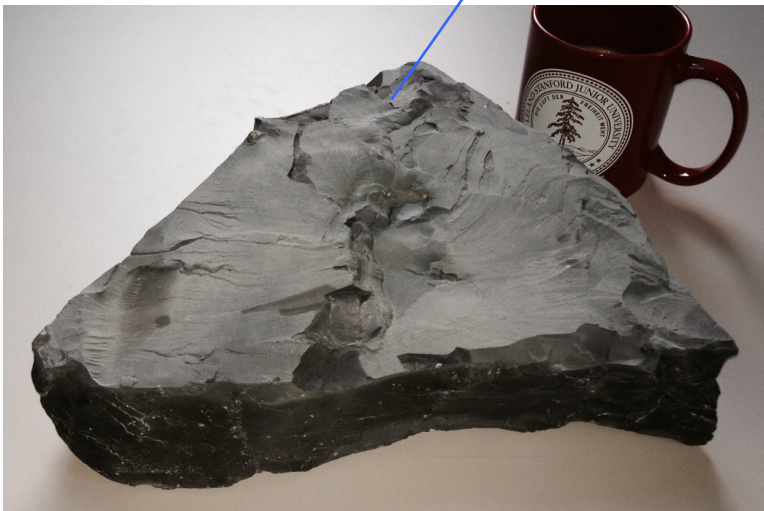




Compounds stored in rock matrix



Time scales of water quality problems, storage and degradation in the subsurface?



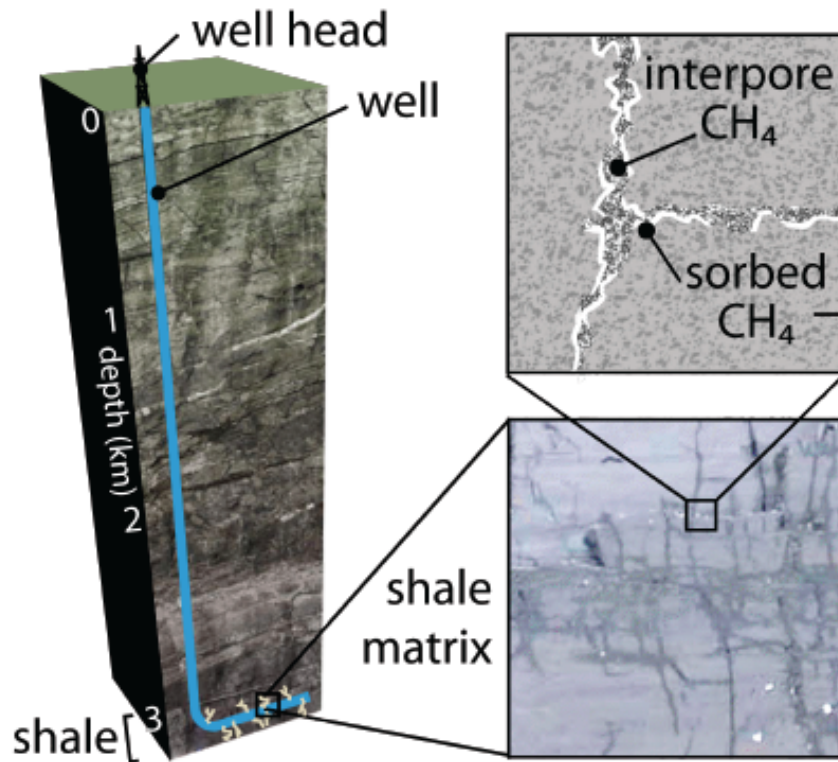
Porosity, diffusion coefficients?

Sorption coefficients?

Reaction in matrix?



“Trapping” of hydrocarbons...



Free phase

$$C_s = \frac{V_{micro}}{V_m} \exp \left[- \left(\frac{RT \left(-\ln \frac{P}{P^o} \right)}{\beta E_o} \right)^n \right]$$

Equipotential surfaces

Kleineidam, S., Schüth, C., Grathwohl, P. (2002): Solubility-normalized combined pore-filling-partitioning sorption isotherms for organic pollutants. *Environ. Sci. Technol.* 36, 4689-4697

Condensed liquid

$$\frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) = \frac{\partial C}{\partial t}$$

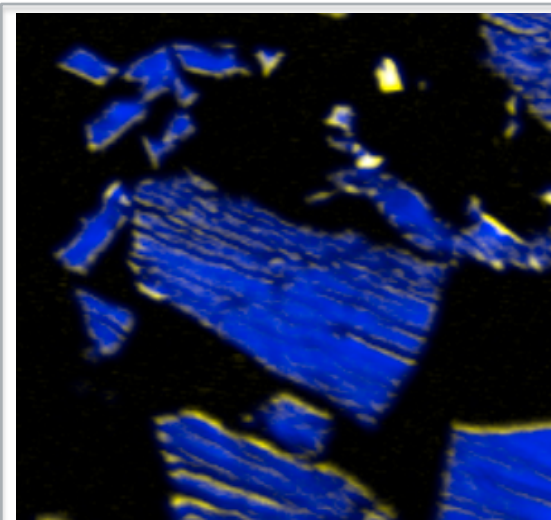
Equation 3

where D is the diffusivity coefficient and t is time. A solution for Equation where gas is sorbing to a solid pore surface is shown in Equation 4 (42):

Tao and Clarens, *Environ. Sci. Technol.*, DOI: 10.1021/es401221j • 29 Aug 2013

$$\frac{V_t}{V_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left(\frac{-n^2 D \pi^2 t}{r_p^2} \right)$$

Equation 4

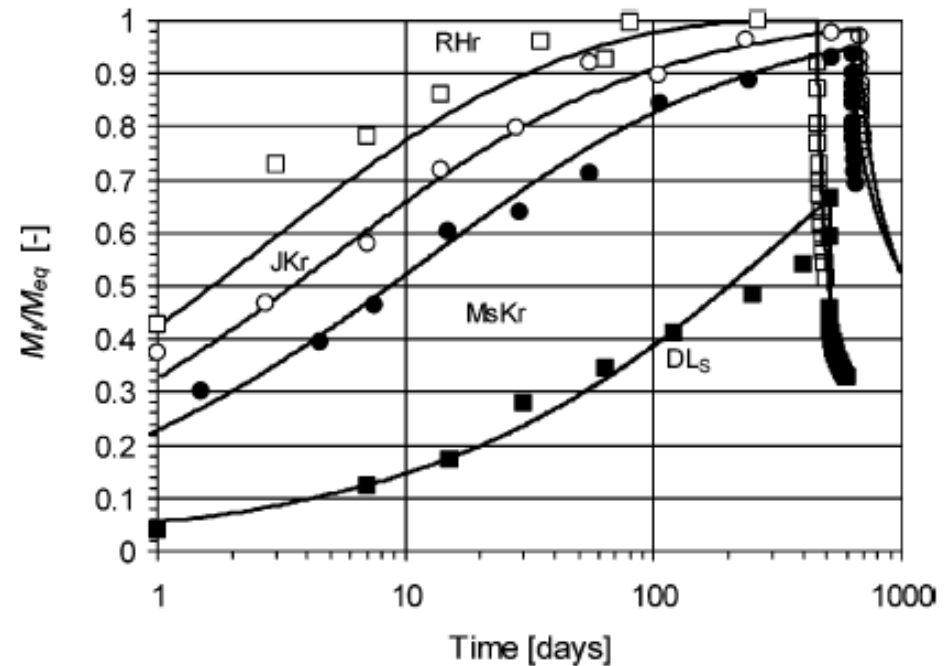


AC sections analyzed by scanning transmission X-ray microscopy (STXM); Canadian Light Source

0 phenanthrene (nm) 170

0 activated carbon (nm) 50

Obst, M., Grathwohl, P., Kappler, A., Eibl, O., Peranio, N., Gocht, T. (2011): Quantitative high-resolution mapping of phenanthrene sorption to black carbon particles. *Environ. Sci. Technol.* 45, 7314–7322

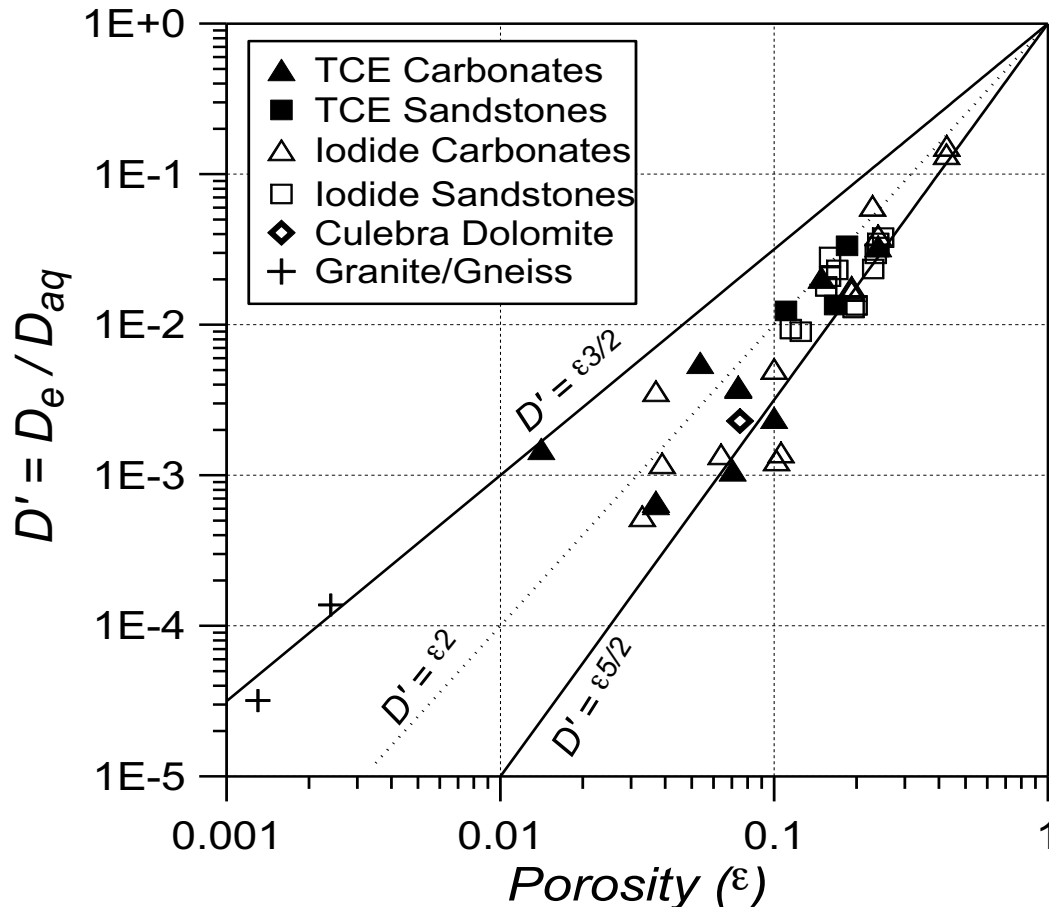


Kleineidam, S., Rügner, H., Grathwohl, P. (2004): Desorption kinetics of phenanthrene in aquifer material lacks hysteresis. *Environ. Sci. Technol.*, 38, 4169 - 4175

Grain scale sorption/desorption time scales are short



Diffusion coefficients



D_e from Archie's Law

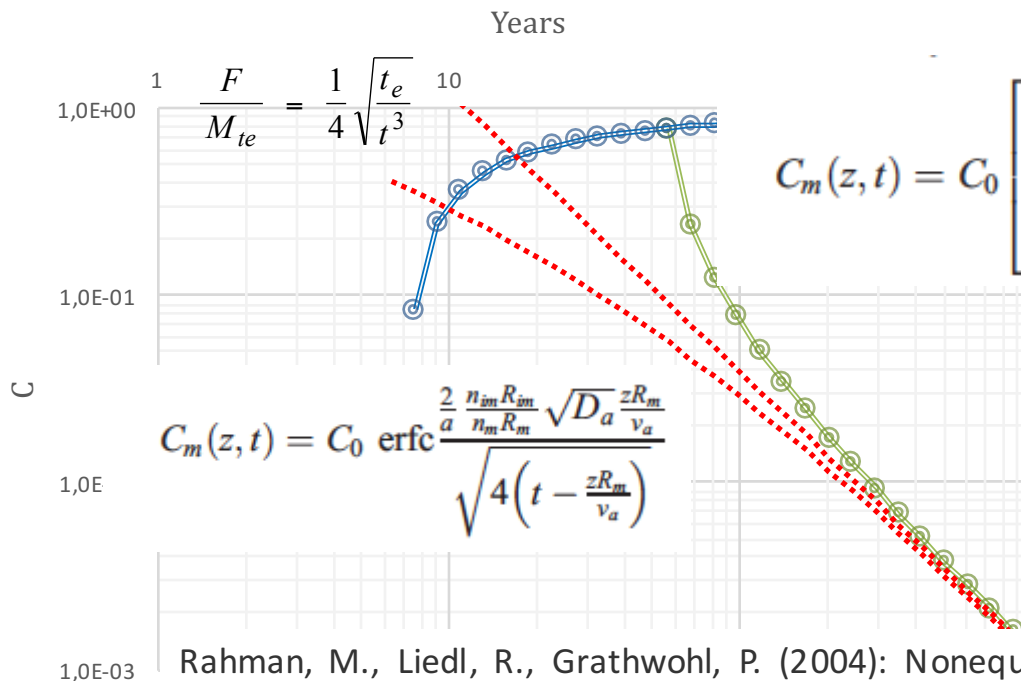
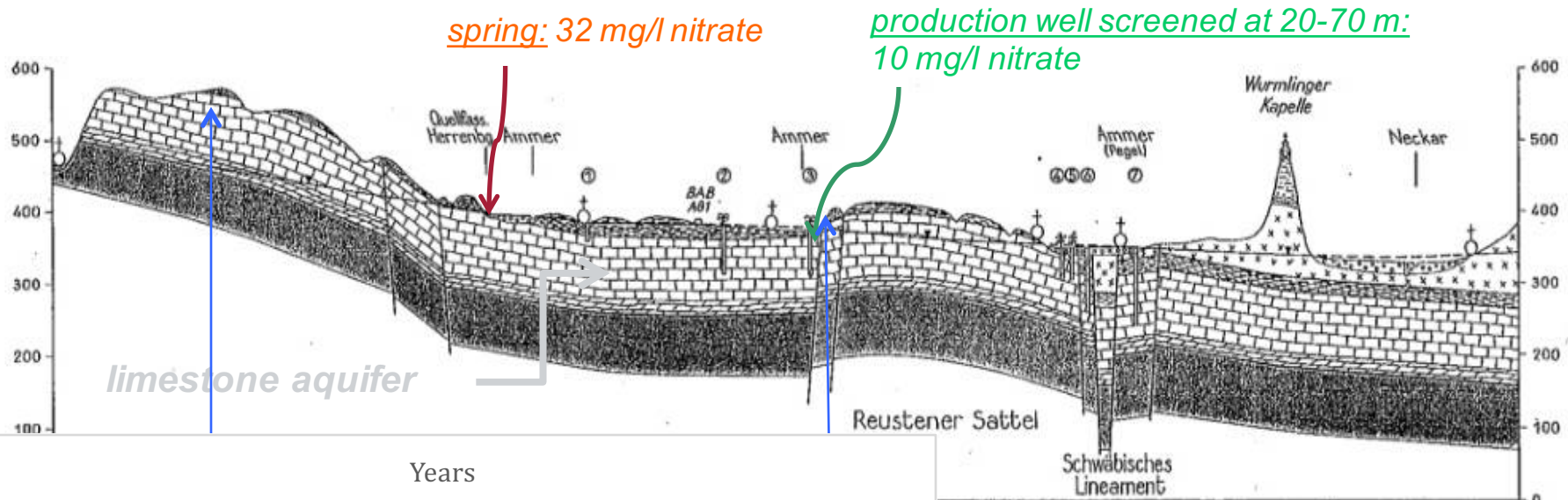
$$D_e = D_{aq} \epsilon^m \Rightarrow \frac{D_e}{D_{aq}} = \frac{\epsilon}{\tau_f} \Rightarrow D' \approx \epsilon^m$$

$$D_e \approx 2 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$$

$$\begin{aligned} D_a &\approx \frac{D_e}{\alpha} = \frac{D_e}{\epsilon + K_d \rho_b} \\ &= \frac{2 \times 10^{-9}}{0.05 + 2 \times 2.6} \\ &= 4 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1} \end{aligned}$$



Compounds stored in rock matrix



$$C_m(z, t) = C_0 \left[\operatorname{erfc} \frac{\frac{2}{a} \frac{n_{im} R_{im}}{n_m R_m} \sqrt{D_a} \frac{z R_m}{v_a}}{\sqrt{4 \left(t - \frac{z R_m}{v_a} \right)}} - \operatorname{erfc} \frac{\frac{2}{a} \frac{n_{im} R_{im}}{n_m R_m} \sqrt{D_a} \frac{z R_m}{v_a}}{\sqrt{4 \left(t - \frac{z R_m}{v_a} - t_0 \right)}} \right]$$

Porosity: 0.03

Sorption: $K_d = 0$

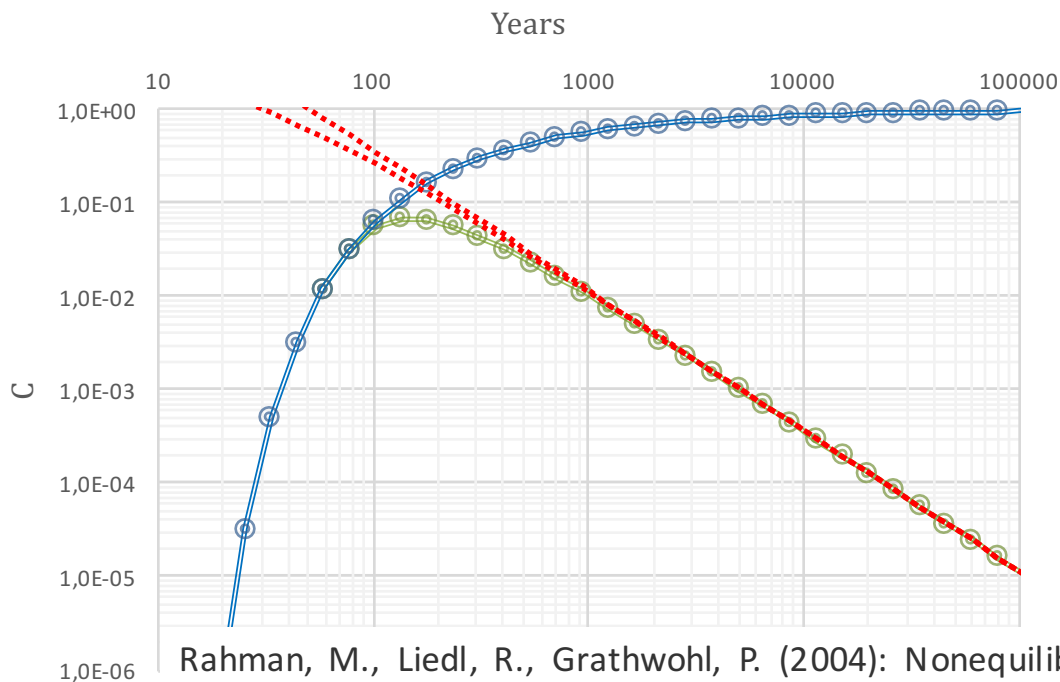
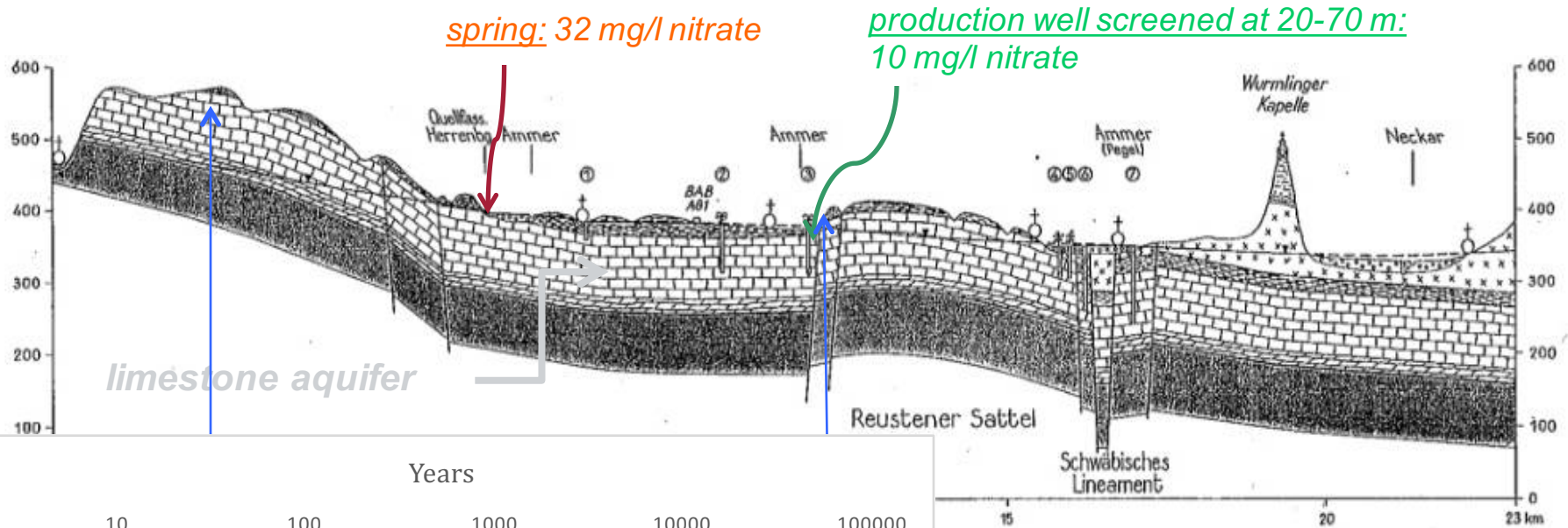
Velocity: 4 m/d (1.6 m/a)

Distance: 10 km (10 m)

Application time: 50 a



Compounds stored in rock matrix



“TCE”

Aperture: 3 mm

Porosity: 0.03

Sorption: $K_d = 1$

Velocity: 4 m/d (1.6 m/a)

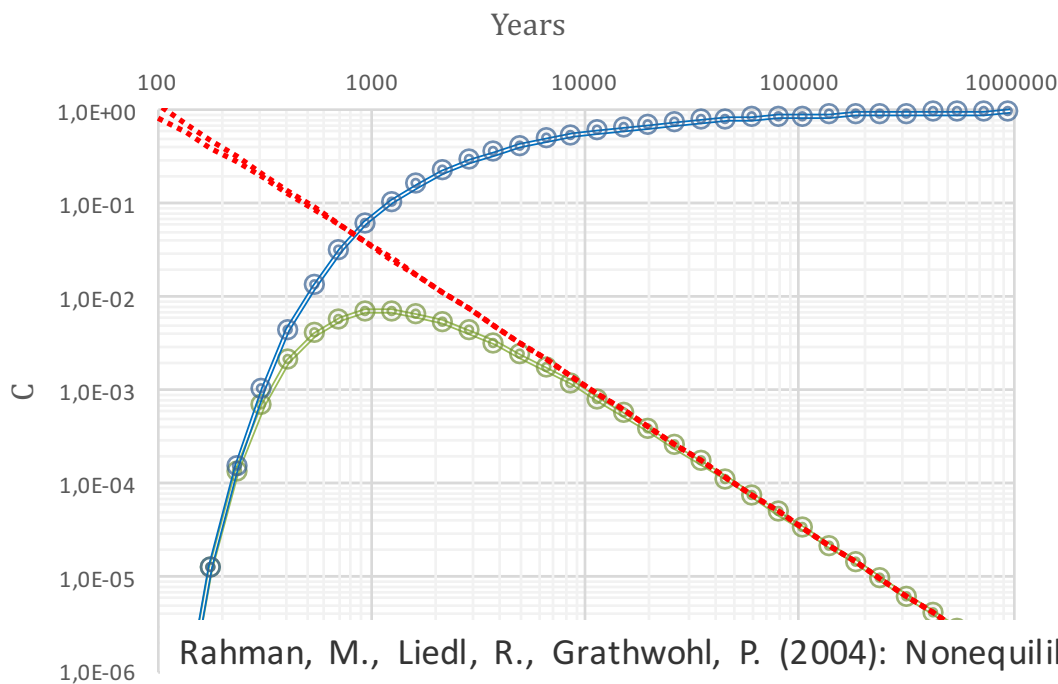
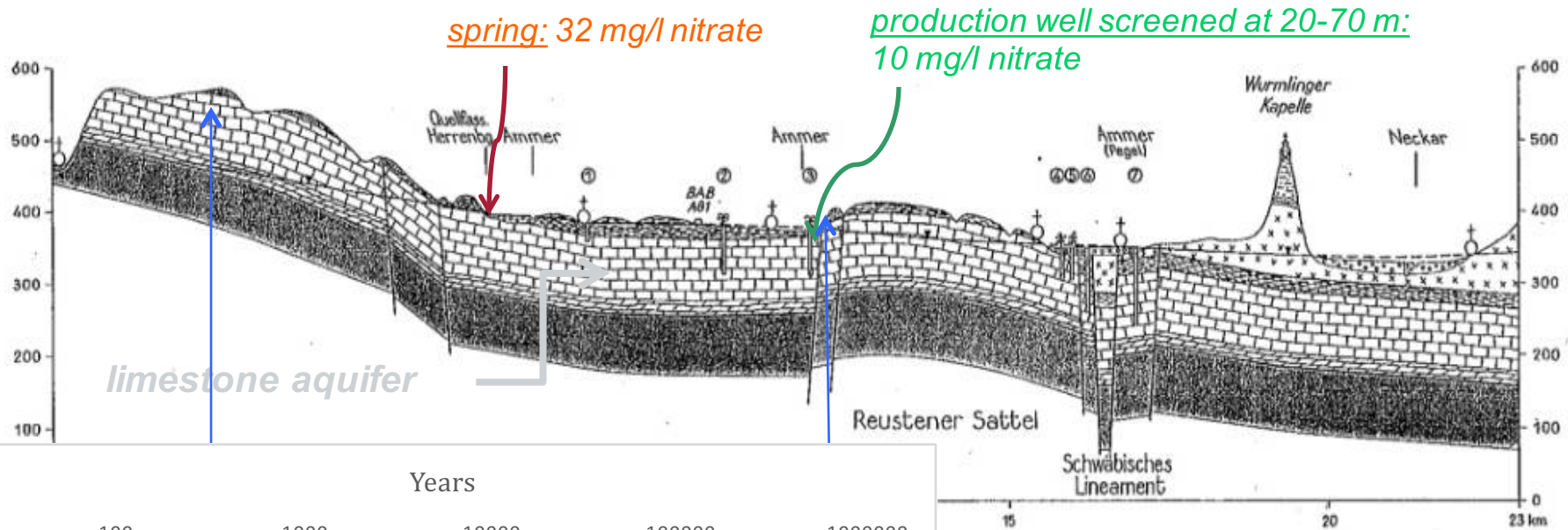
Distance: 10 km (10 m)

Application time: 50 a

Rahman, M., Liedl, R., Grathwohl, P. (2004): Nonequilibrium sorption during macropore transport of organic contaminants in soils – laboratory experiments and analytical modeling. Water Resour. Res. 40



Compounds stored in rock matrix



"Atrazine"

Aperture: 3 mm

Porosity: 0.03

Sorption: $K_d = 10$

Velocity: 4 m/d (1.6 m/a)

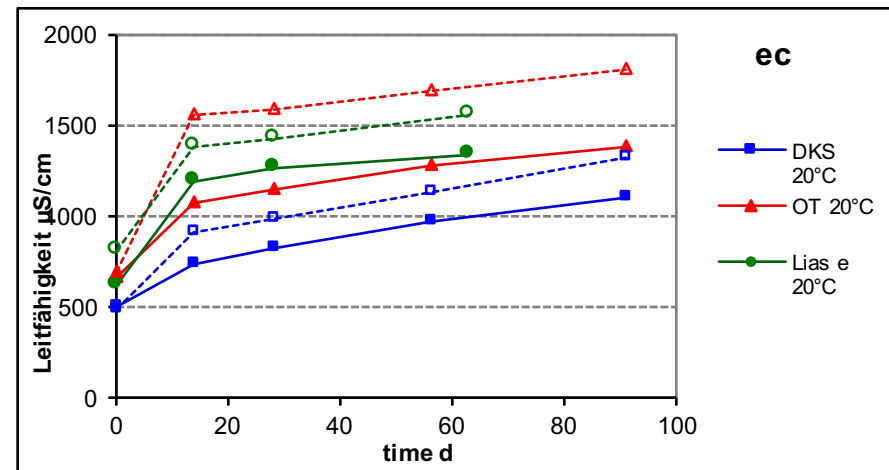
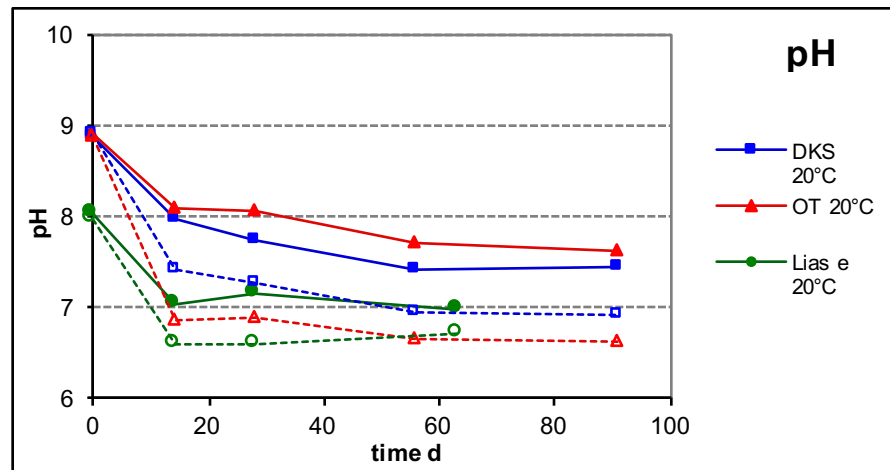
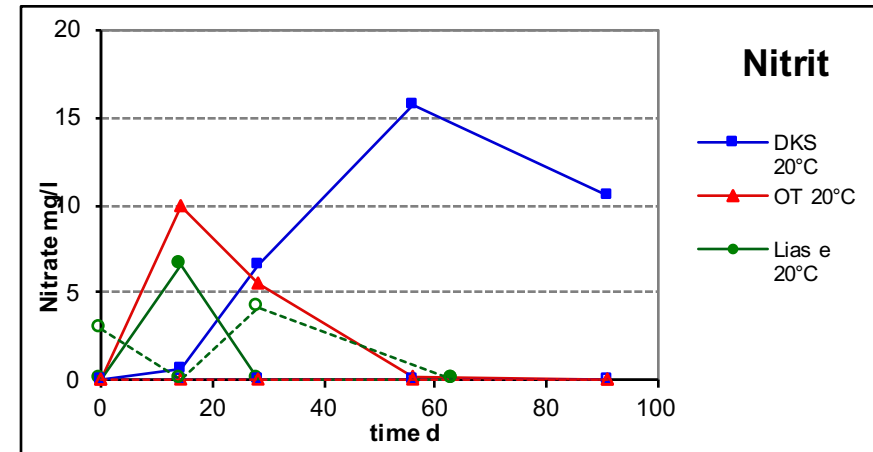
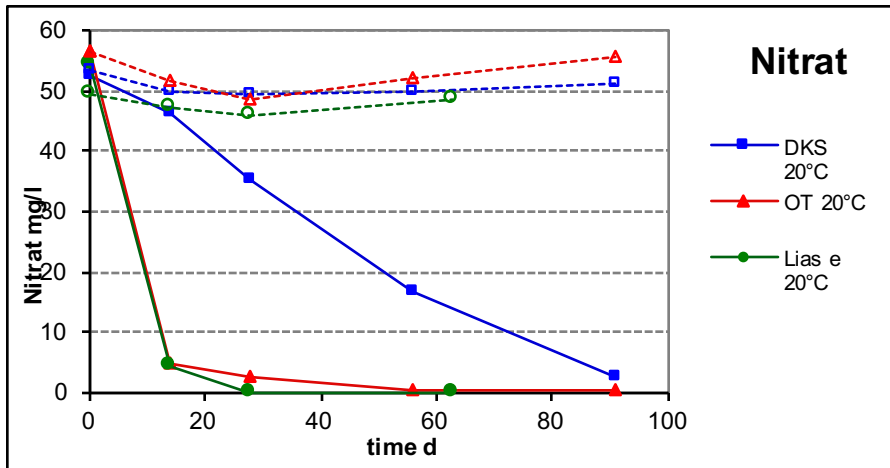
Distance: 10 km (10 m)

Application time: 50 a

Rahman, M., Liedl, R., Grathwohl, P. (2004): Nonequilibrium sorption during macropore transport of organic contaminants in soils – laboratory experiments and analytical modeling. Water Resour. Res. 40



Matrix reactions: Nitrate



Coupled Diffusion and Abiotic Reaction of Trichlorethene in Minimally Disturbed Rock Matrices

Charles E. Schaefer,^{*,†} Rachael M. Towne,[†] David R. Lippincott,[†] Volha Lazouskaya,[‡] Timothy B. Fischer,[§] Michael E. Bishop,[§] and Hailiang Dong[§]

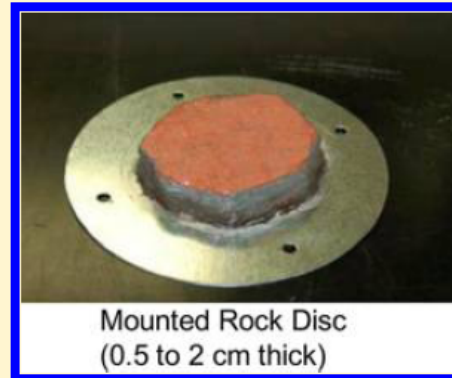
[†]CB&I, 17 Princess Road, Lawrenceville, New Jersey 08648, United States

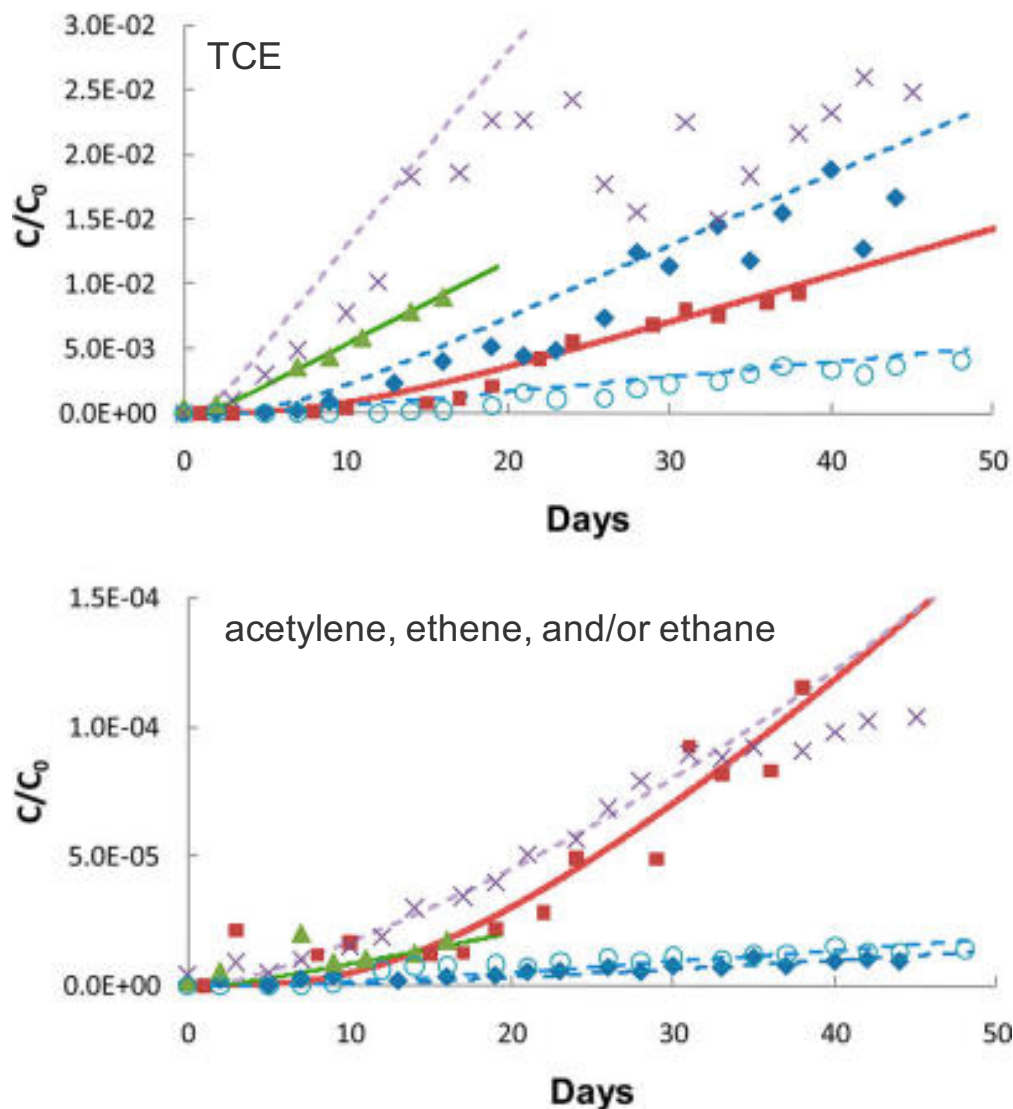
[‡]Department of Plant and Soil Sciences, University of Delaware, Newark, Delaware 19716, United States

[§]Department of Geology, Miami University, Oxford, Ohio 45056, United States

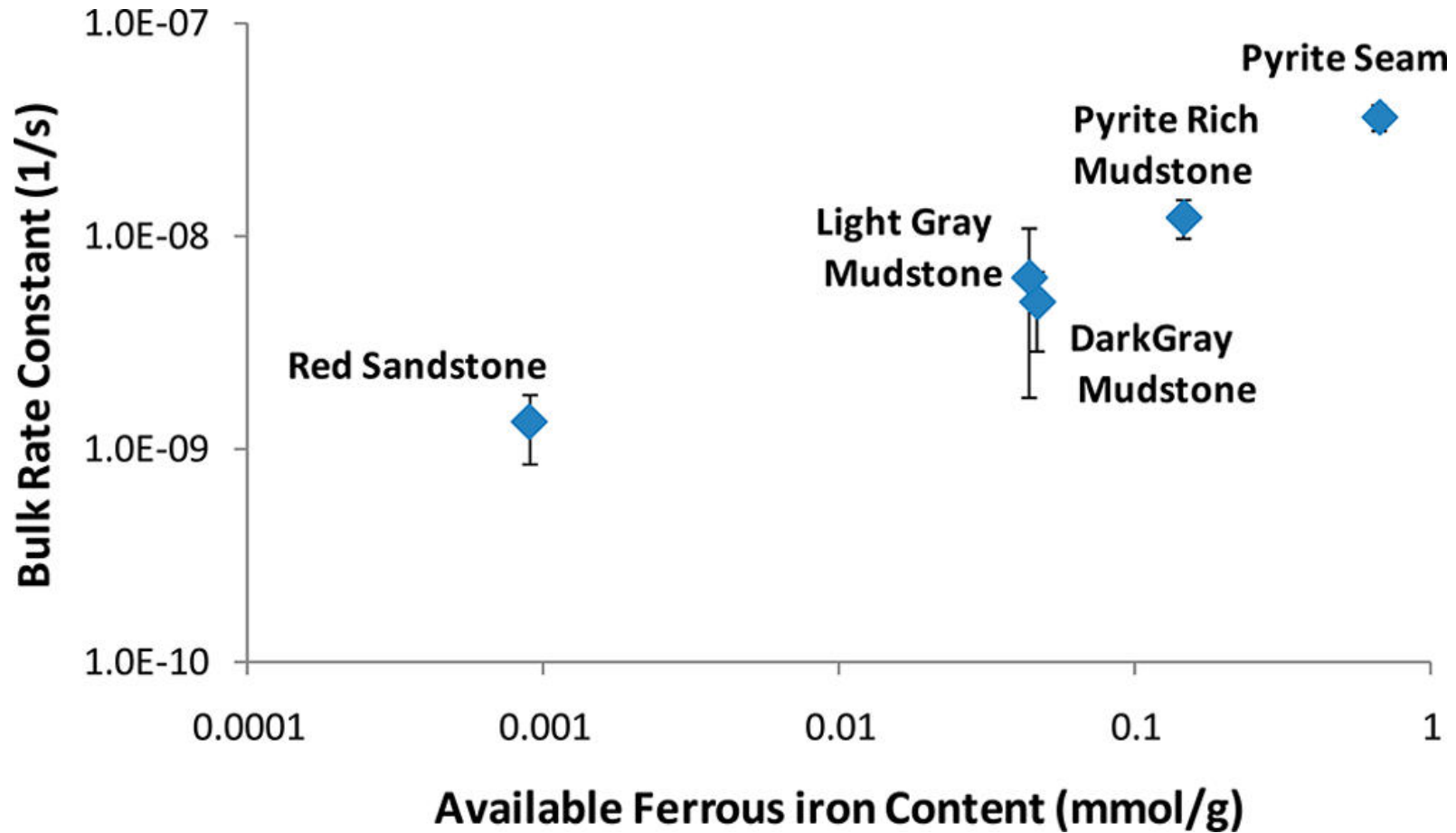
Supporting Information

ABSTRACT: Laboratory experiments were performed using minimally disturbed sedimentary rocks to measure the coupled diffusion and abiotic reaction of trichloroethene (TCE) through rock core samples. Results showed that, for all rock types studied, TCE dechlorination occurred, as evidenced by generation of acetylene, ethene, and/or ethane daughter products. First-order bulk reaction rate constants for TCE degradation ranged from 8.3×10^{-10} to $4.2 \times 10^{-8} \text{ s}^{-1}$. Observed reaction rate constants showed a general correlation to the available ferrous iron content of the rock, which was determined by evaluating the spatial distribution of ferrous iron relative to that of the rock porosity. For some rock types, exposure to TCE resulted in a decrease in the effective diffusivity. Scanning electron microscopy (SEM) indicated that the decrease in the effective diffusivity was due to a decrease in the porosity that occurred after exposure to TCE. Overall, these coupled diffusion and reaction results suggest that diffusion of TCE into rock matrices as well as the rate and extent of back-diffusion may be substantially mitigated in rocks that contain ferrous iron or other naturally occurring reactive metals, thereby lessening the impacts of matrix diffusion on sustaining dissolved contaminant plumes in bedrock aquifers.



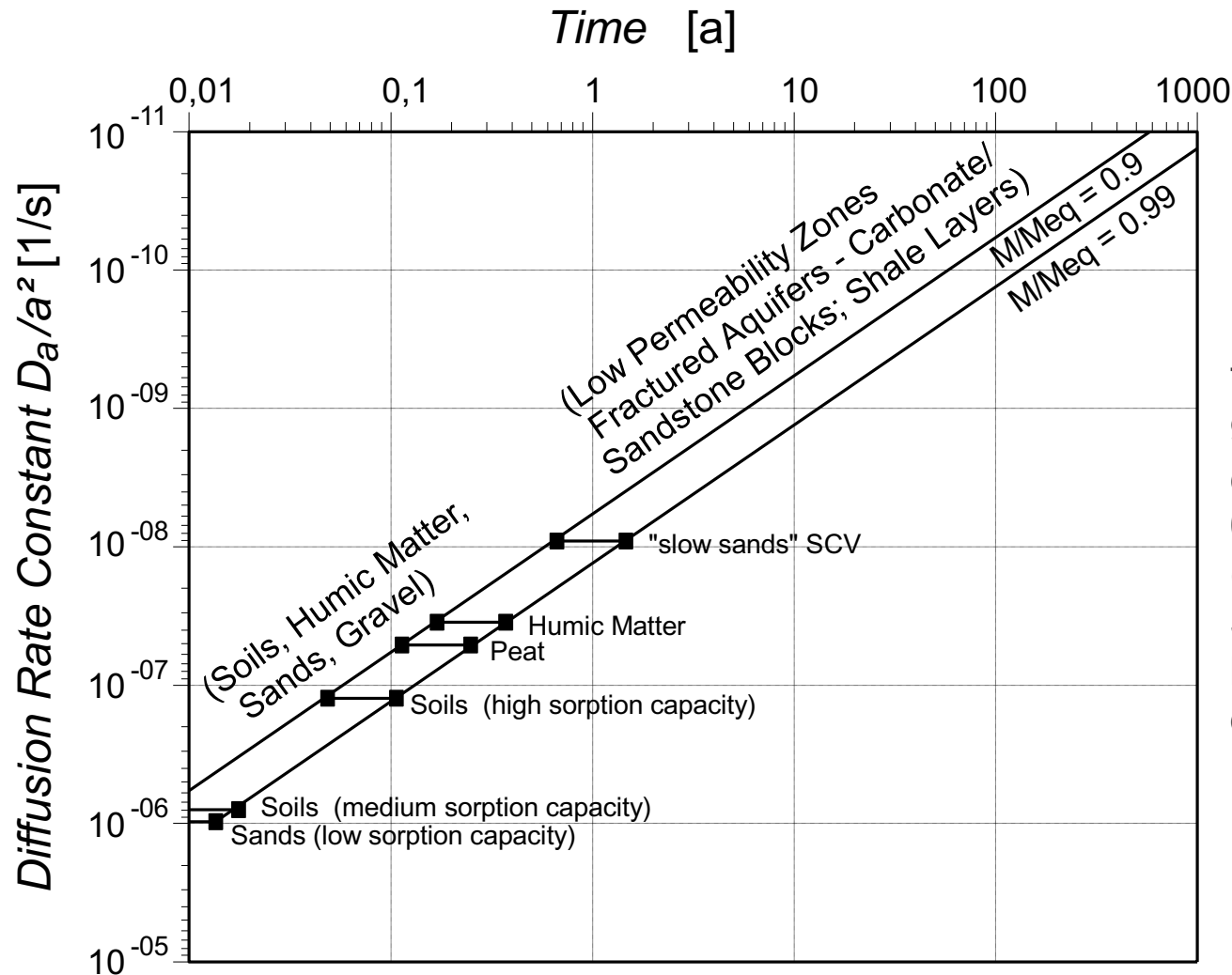


Comparison of experimental data (symbols) and model simulations (solid and dashed lines for eq 2) for TCE (top) and daughter products (bottom) for each rock type. Molar units are used. Both TCE and daughters are plotted as a function of the initial molar TCE concentration in the source side of the diffusion cell. As discussed for Figure S4, a decrease in the porosity for the pyrite seam created a decrease in the diffusional flux over time, which is why the model overpredicts the late-time date for the pyrite seam. ♦ (blue) – red sandstone, ■ (red) - light gray mudstone, ▲ (green)– dark gray mudstone, ° — – pyrite seam, ○ – pyrite rich mudstone.



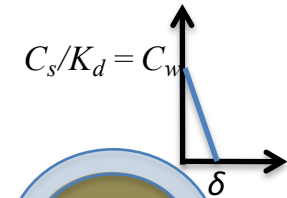
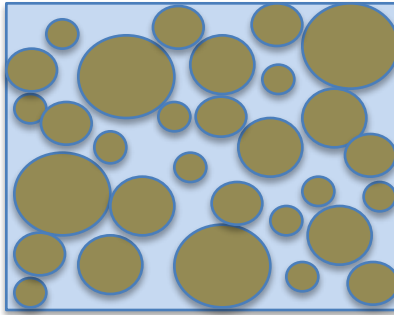


Summary: Diffusion time scales



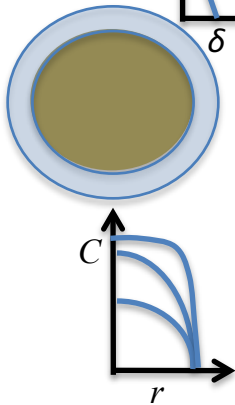


Desorption at the grain scale



$$\frac{\partial C_s}{\partial t} = -\frac{D_{aq}}{\delta} \frac{6}{\rho_s d} \frac{C_s}{K_d}$$

$$\frac{C_s}{C_{s,0}} = \exp\left(-\frac{D_{aq}}{\delta} \frac{6}{K_d \rho_s d} t\right) = \exp\left(-\frac{Sh D_{aq}}{K_d \rho_s d^2} t\right)$$

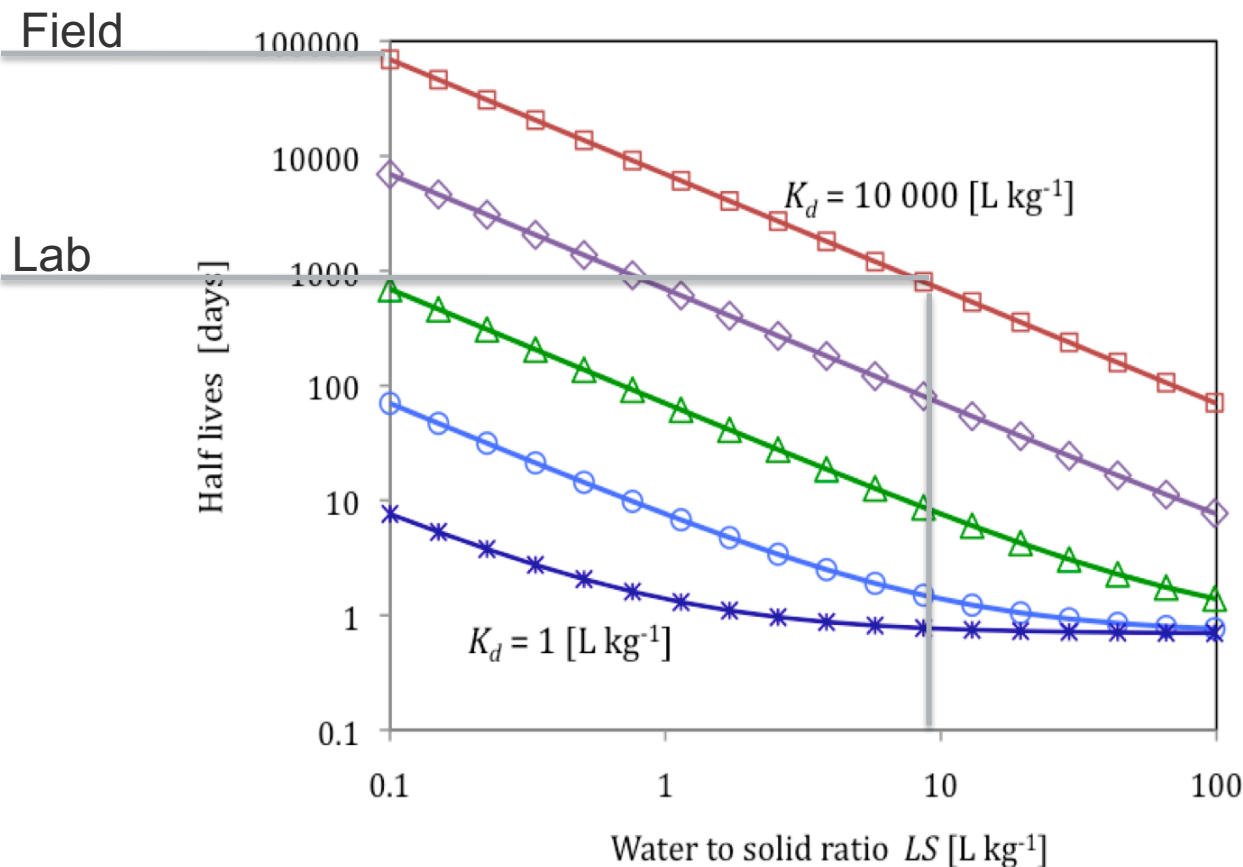


$$\frac{\partial C_s}{\partial t} = -\frac{D_e}{\varepsilon + K_d \rho_s} \left[\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right]$$

$$\frac{C_s}{C_{s,0}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \exp\left(-n^2 \pi^2 \frac{D_e}{\varepsilon + K_d \rho_s} \frac{4 t}{d^2}\right)$$



Why are compounds stable in soils?



$$\theta \frac{\partial C_w}{\partial t} + \rho \frac{\partial C_s}{\partial t} = -\lambda \theta C_w$$

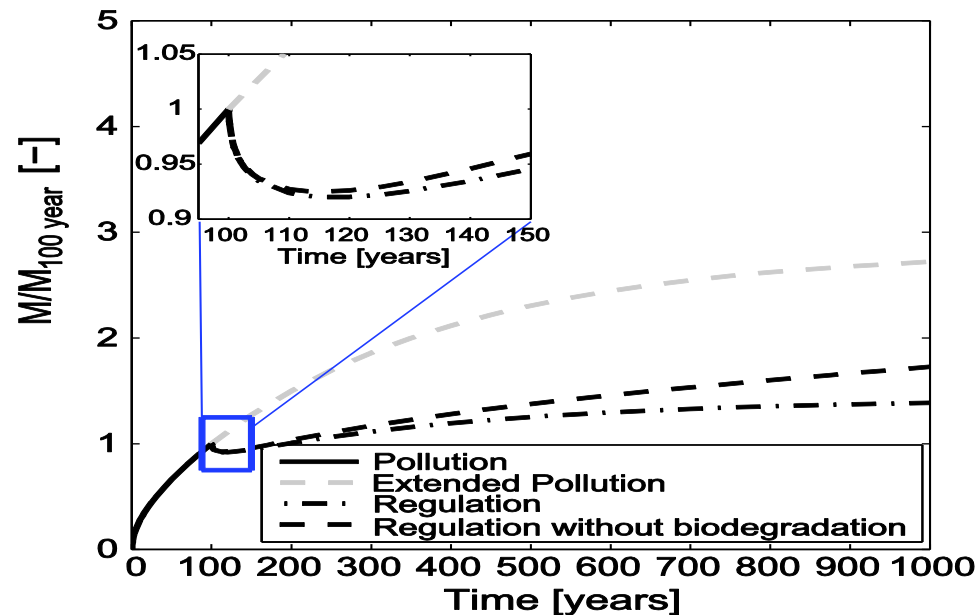
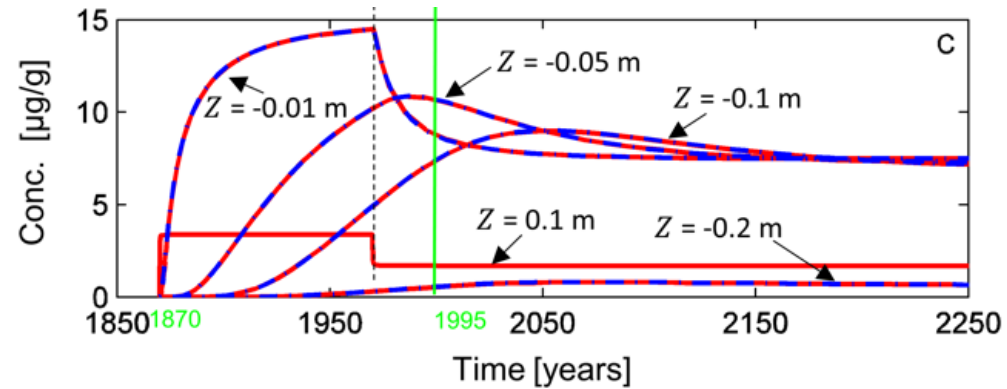
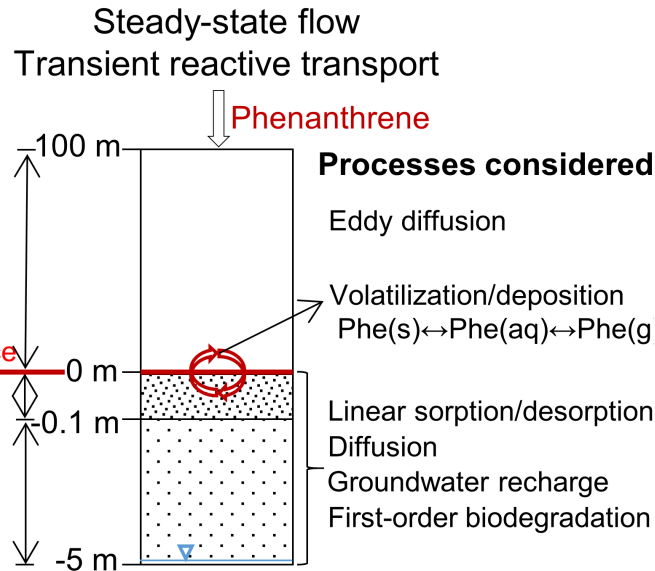
$$C_s = K_d C_w$$

$$\frac{\partial C_w}{\partial t} = -\frac{\lambda}{1 + K_d \frac{\rho}{\theta}} C_w$$

Half-lives of first order biodegradation as a function of water to solid ratios (LS of approx. 0.1 is representative for field condition; LS of 10 – 100 commonly used in batch experiments) for hypothetical compounds with different K_d -values ranging from 1, 10, 100, 1000 to 10 000 L kg⁻¹ (inverse to the water solubility).



Why are compounds stable in soils?





Conclusions, GQ 1998, Tübingen



Scenario	Chlorinated solvents; BTEX	PAHs
Dissolved and sorbed contaminants		
Time scale for diffusion limited desorption at the grain scale	< 1 years	1 – > 10 years
Time scale for slow diffusion out of low permeability zones – matrix diffusion	> 10 years	> 100 years
Change of release rates / contaminant concentrations with time	Diffusive fluxes and concentrations decrease first with \sqrt{t} , later exponentially. The resulting concentrations in the groundwater are much lower than saturation; depending on the size of the source, concentrations lower than legal limits may be reached in the groundwater relatively fast.	
Enhanced contaminant removal	1. Increase of temperature (approx. factor 2 per 10°C). 2. Reduction of the effective diffusion distance (size reduction of aggregates or grains).	
Residual NAPL		
Time scale for dissolution of NAPL blobs/ganglia from smear zones	1 - > 10 years	10 - > 100 years
Time scale for the dissolution of NAPL pools	> 10 - 1000 years	> 1000 years
Change of release rates / concentrations with time	Dissolution rates are constant over extended periods of time. Locally the concentrations are far above the legal limit (saturation concentrations in the boundary layer to the NAPL).	
Enhanced in-situ decontamination *	1. Increase of the flow velocity. 2. Cosolvent (alcohol) or surfactant flushing for the mobilization and solubilization of residual NAPL.	

* this requires the knowledge of the exact location of the NAPL source

Thank you

Funding:

