


The Combination of Matrix Diffusion and Abiotic Decay Makes Two Slow Natural Attenuation Processes a Dynamic Duo

TRC Presentation to
Battelle Chlorinated Conference

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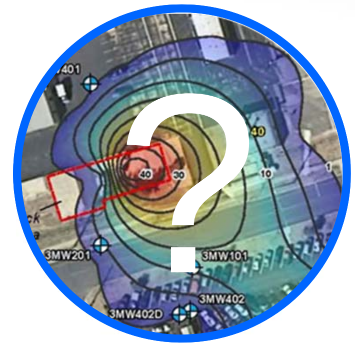
Purpose and Agenda



Purpose:

- Demonstrate when the beneficial effects of abiotic decay and matrix diffusion need to be considered in CVOC plume behaviors.

Agenda:

- Beneficial and Negative Effects of Diffusion into low permeability zones
- Causes of abiotic decay of CVOCs?
- When can naturally occurring CVOC abiotic decay affect back diffusion?
- When can matrix diffusion and abiotic decay team up for CVOC plume stability?

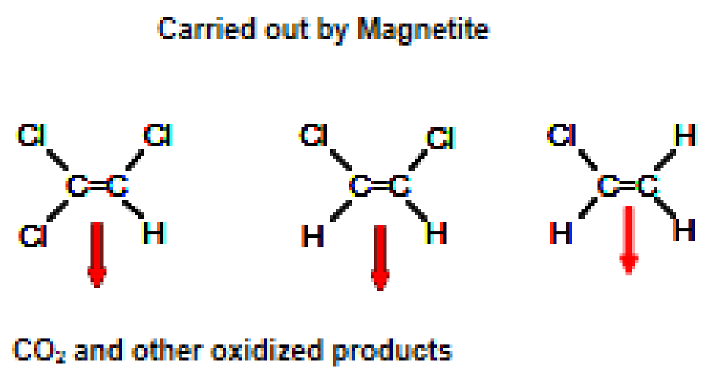
Clay & Silt Zones Can Be Cause of Back Diffusion

- Say this is a 1960 VOCs release (i.e., an old source).
  - Migrating in the high K zones (the green dyed water moving through the sand).
  - Diffusion occurring into & out of low K zones (dark colored clay zones).

Video image from: Doner and Sale, http://projects-web.engr.colostate.edu/CCH/research.shtml

Natural Decay of CVOCs via Iron Minerals

- Abiotic Decay via Iron Minerals
  - Background from He, et. al. 2009, and J.T. Wilson
  - Decay of TCE, etc., to CO_2 and other oxidized products

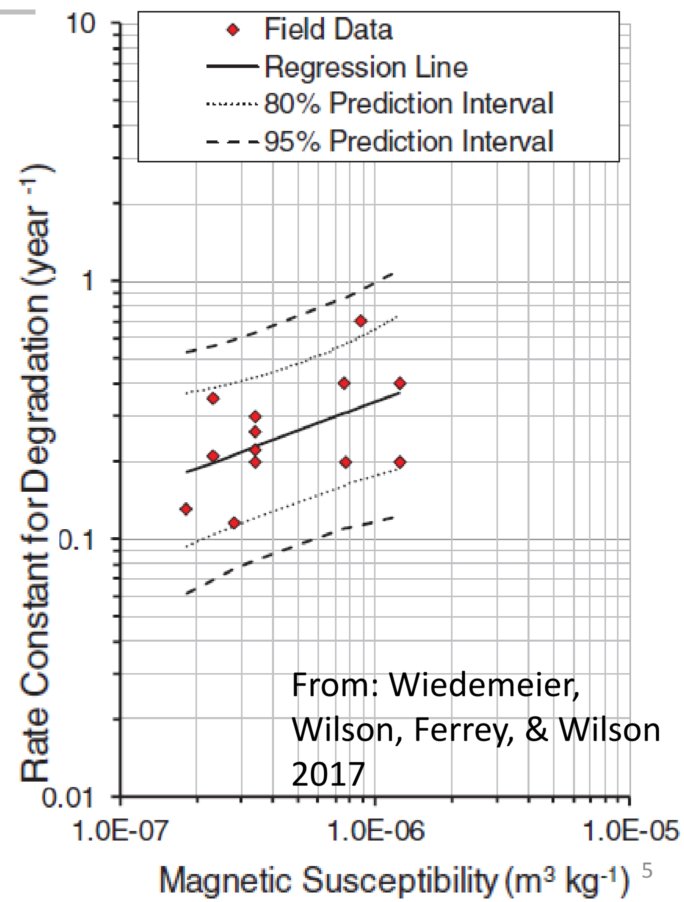


From: Wilson, 2015

- Degradation mechanism
  - Free radical decay
- Daughter Products
  - CO_2, etc.
  - No Typical Daughter Products
- Degradation can go un-noticed

Natural Decay of CVOCs via Iron Minerals

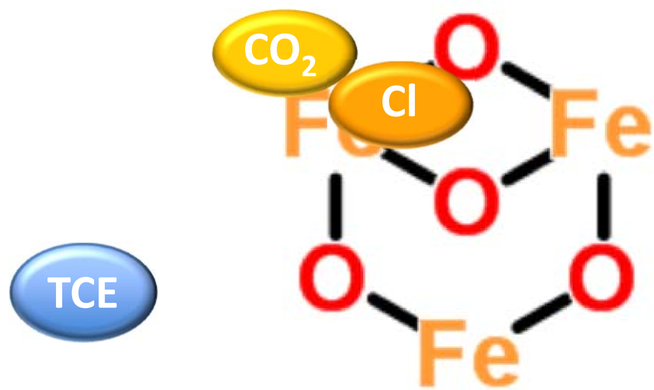
- He, et.al. (2009) details the mechanisms of CVOC decay by magnetite .
- Wilson et al. demonstrate
  - The practicality of abiotic decay via iron minerals.
  - A general correlation to decay rate (i.e., half life)



From: Wiedemeier, Wilson, Ferrey, & Wilson 2017

Natural Decay of CVOCs via Iron Minerals

- So, magnetite causes CVOC degradation.
- What is magnetite?
- It can't be that common. Right?



Field Data on Presence of Magnetite

- Microbial Insights data base
  - 500 samples – all with some magnetic susceptibility
  - Typical average 1×10^{-7} m^3/kg
- TRC data – 6 of 7 sites tested were positive for magnetic susceptibility
- Observations:
  - Fine grained zones have highest magnetic susceptibility.
  - ND was for a dolomite, free of sand/silt/clay (i.e., no detrital sediment & no authigenesis).

Site	Soil-Rock Type	Magnetic Susceptibility (10^{-7} M^3/kg)		Avg. Half-Life per Wilson's Correlation (yrs)
		Min-Max	Avg.	
1	Sandstone	0.1-5.9	1.41	4.6
2	Sandstone	5.8-25.8	11.4	0.5
2	Shale	--	76.2	0.09
3	Cyclothem	0.68-1.7	1.3	6.93
4	Dolomite	ND	ND	No Decay
5	Sand	--	3.2	2.3
5	Clay	--	71.0	0.09
6	Sand	1.1-22.2	5.7	1.2
7	Sand	0.4-15	5	2.4

Field Data on Presence of Magnetite (cont)

Does Magnetic Susceptibility REALLY Indicate Abiotic Decay?

- Abiotic Decay Assay by: Microbial Insights (Dr. Freedman – Clemson University)
  - Approach: spike soil/rock sample with ^{14}C labeled TCE
  - Detection of ^{14}C in CO_2 is positive demonstration of abiotic decay & an estimate of decay rate.
- 1 TRC sample (so far):
  - Magnetic Susceptibility: $15x10^{-7}$ m^3/Kg
  - Abiotic Assay: decay rate=2.4 yr^{-1}, $t_{1/2}$= 0.3 yrs
  - Fits in Wilson's correlation between magnetic susceptibility and decay rate.

For more detail on the ^{14}C Abiotic Assay :

See Dr. John Wilson's Presentation later in this conference

What's the Effect of Low Permeability Zones' Diffusion combined with Abiotic Decay

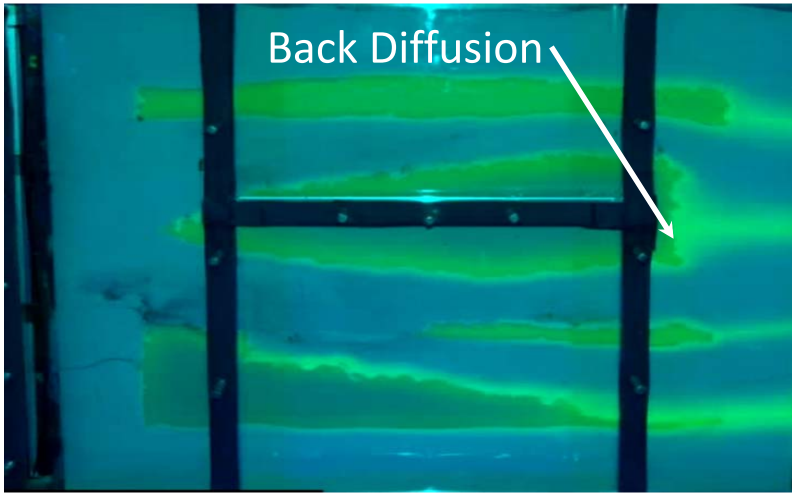
- Diffusion into Low K Zone can be:

Negative:

Back diffusion that extends CVOC source areas for decades.

Positive:

Diffusion into zones with higher decay rates



- When is combination of matrix diffusion and abiotic decay of benefit?

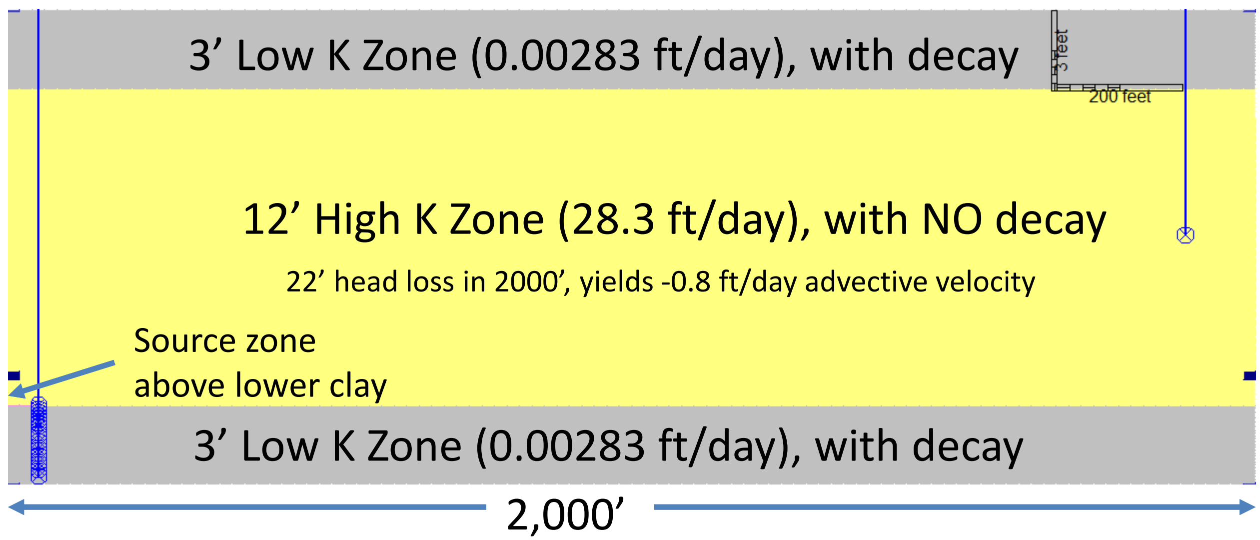
Video image from: Doner and Sale, http://projects-web.engr.colostate.edu/CCH/research.shtml

Simulate Combination of Matrix Diffusion and Abiotic Decay

- Model setup: Very similar to Sale, et. al. 2013
  - Vary decay rate in low K zone to illustrate if/when its of value
- MODFLOW/MT3DMS
  - Cross sectional view
  - Very tight layer spacing to simulate diffusion in vertical
    - 1 cm in interface between high and low permeability)
  - Decay in water (Chemical Reactions Package)
  - Decay in soil (Diffusion Package)

Model Setup

- Model Setup – Cross Section

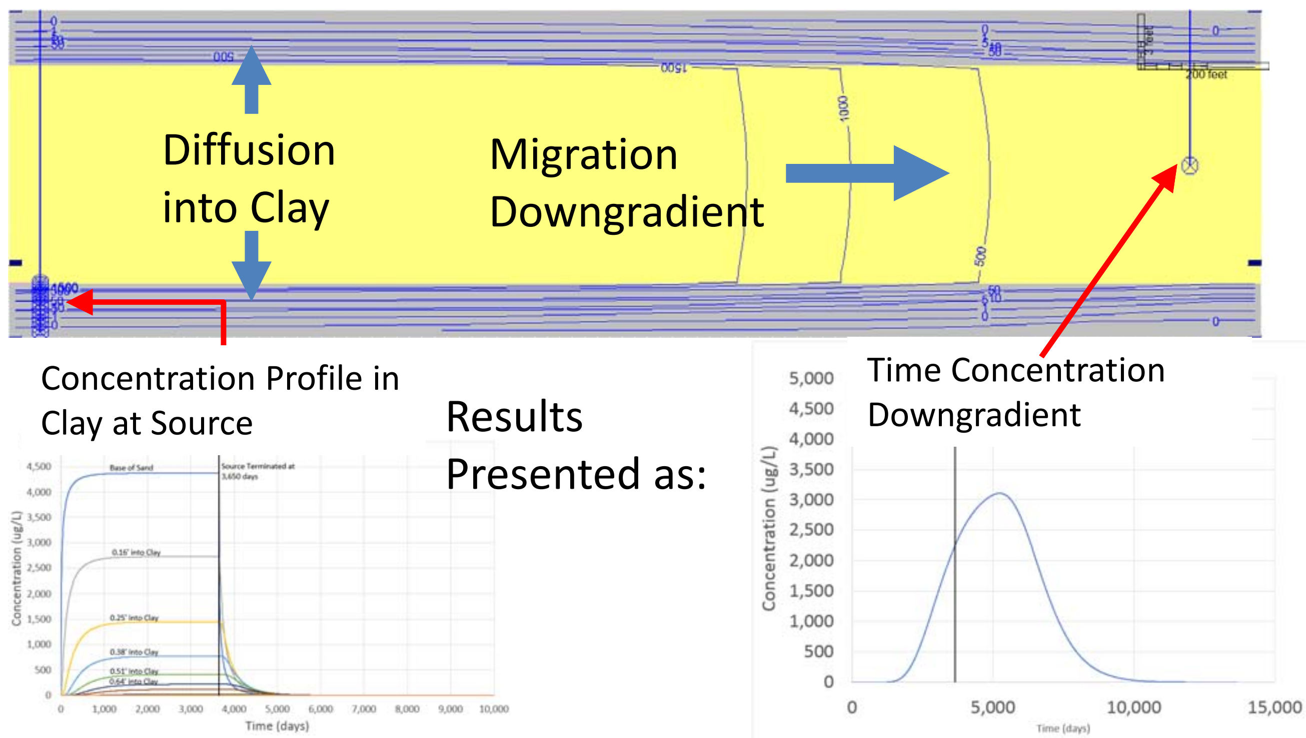


- Source Zone:
  - 5,000 ug/L for period of 10 years
  - No Source for period of 30 years
  - For a "typical" release date of 1975, 40 yrs = 2015

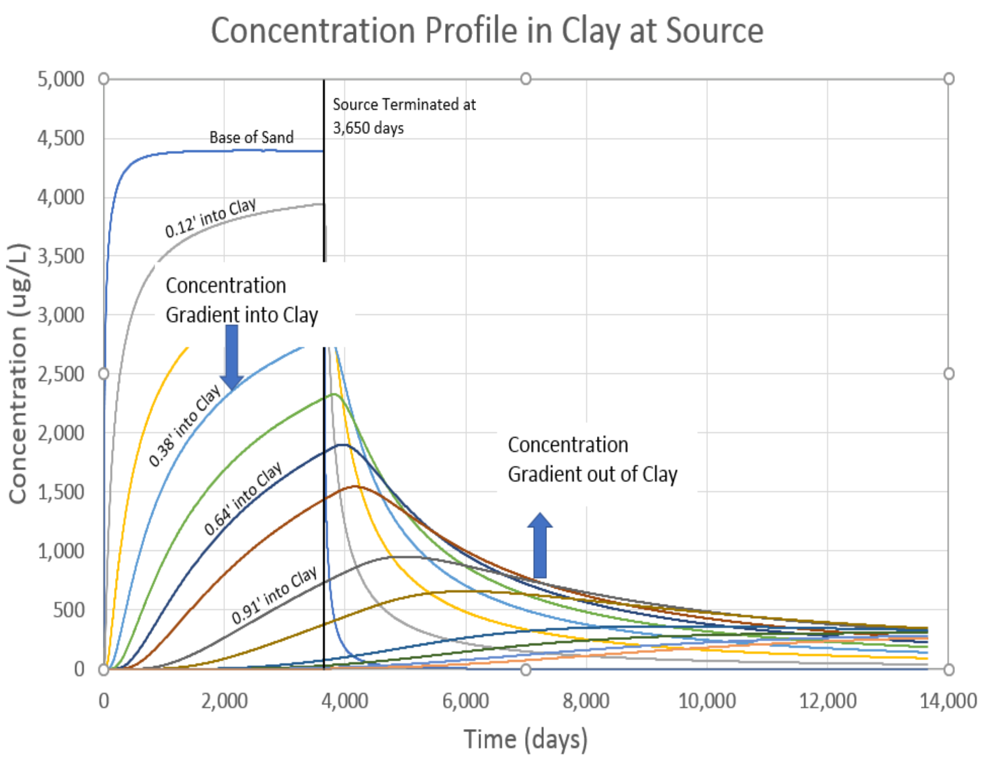
Typical Model Results

Base2H2D4

- Model simulations

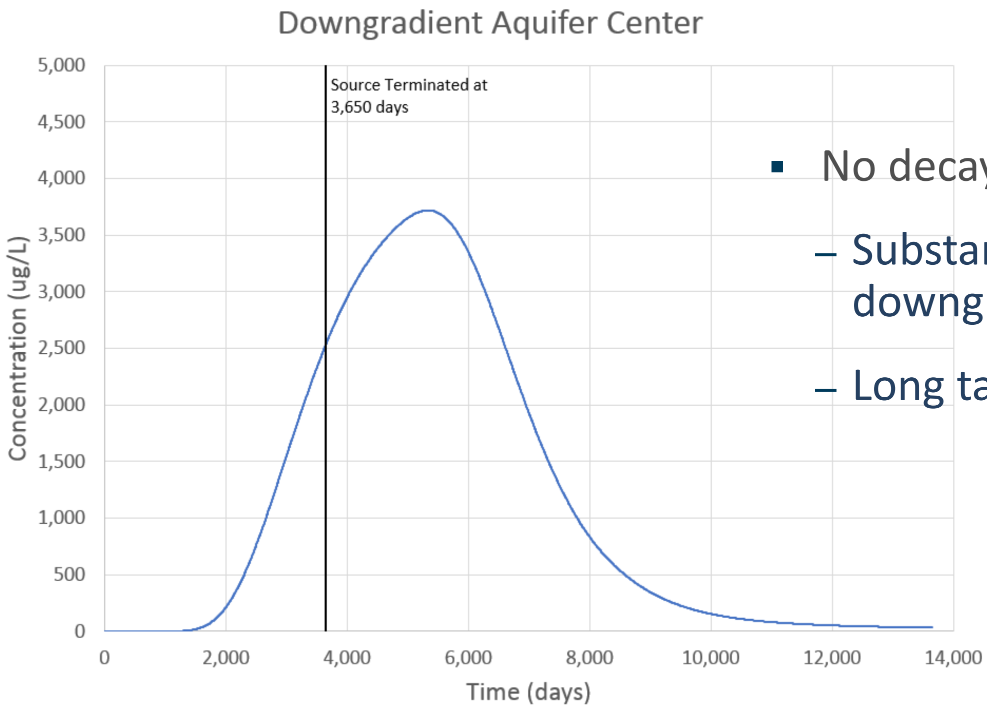


Model Results – No Decay



- No Decay allows unrestricted diffusion into clay.
- Then total mass back diffusion.
- Migration downgradient
- Long tail

Model Results – No Decay

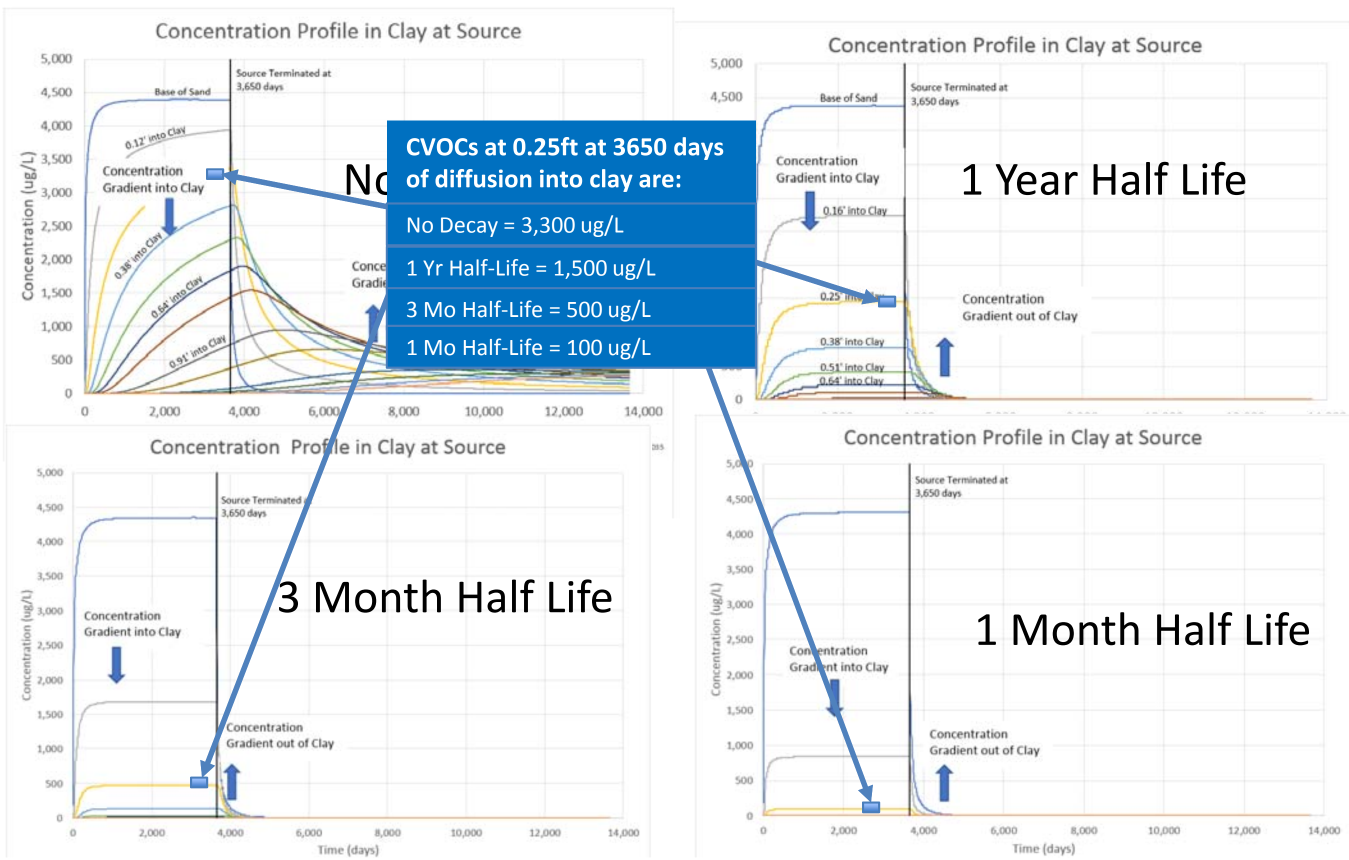


- No decay in clay allows for:
  - Substantial migration downgradient
  - Long tail

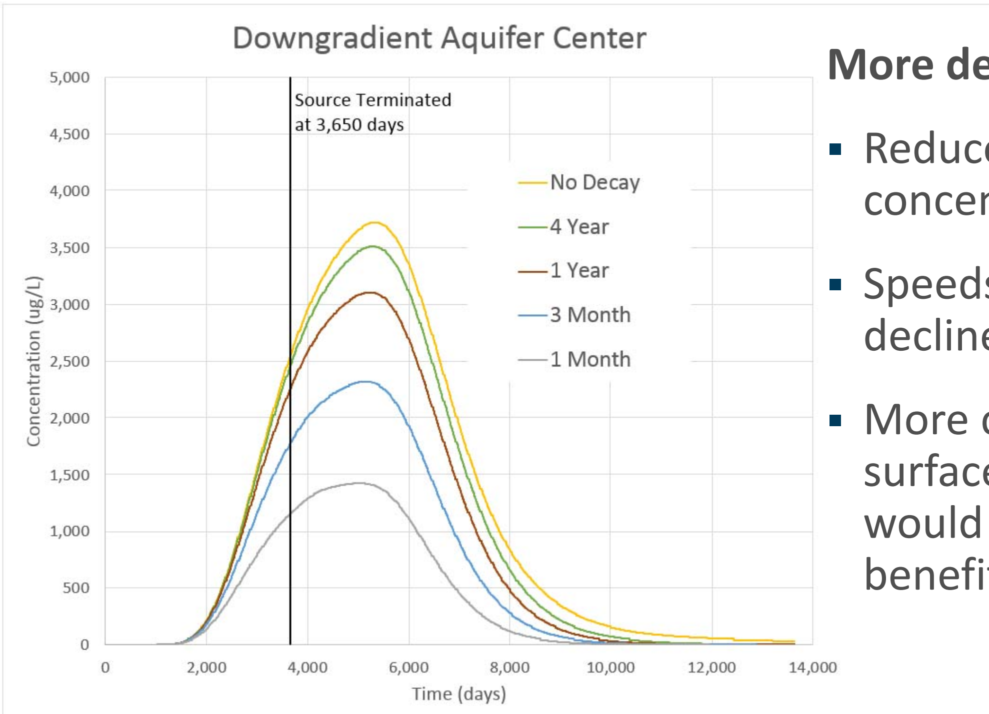
Model Results
Concentration Profile in Clay at Source

CVOCs at 0.25ft at 3650 days of diffusion into clay are:

- No Decay = 3,300 ug/L
- 1 Yr Half-Life = 1,500 ug/L
- 3 Mo Half-Life = 500 ug/L
- 1 Mo Half-Life = 100 ug/L



Model Results
Time Concentration – Downgradient



More decay in clay/matrix:

- Reduces the peak concentration
- Speeds up concentration decline
- More clay, with higher surface area in aquifer would increase these benefits.

Conclusions

1. Abiotic Decay is an essential component of most CSMs.

2. Abiotic Decay properties of clay or fractured rock matrix can result in either:
   - A bad case of back diffusion when no decay is occurring.
   - Reducing (eliminating?) back diffusion problems if abiotic decay is high in the clay/rock matrix and the clay seams are numerous.

3. Greater mass of clay/matrix per volume of aquifer can result in more diffusion and greater mass loss.

4. High % of clay seams in aquifer or porous fractured media can present greater potential for MNA.

5. DFN sampling results can be confusing if decay in the matrix is not considered.

Thank you

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Questions?

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