BATTELLE 2023 SEDIMENTS CONFERENCE

The Duration of Ebullition Processes in NAPL-Contaminated Sediments and Implications for Remedy Design

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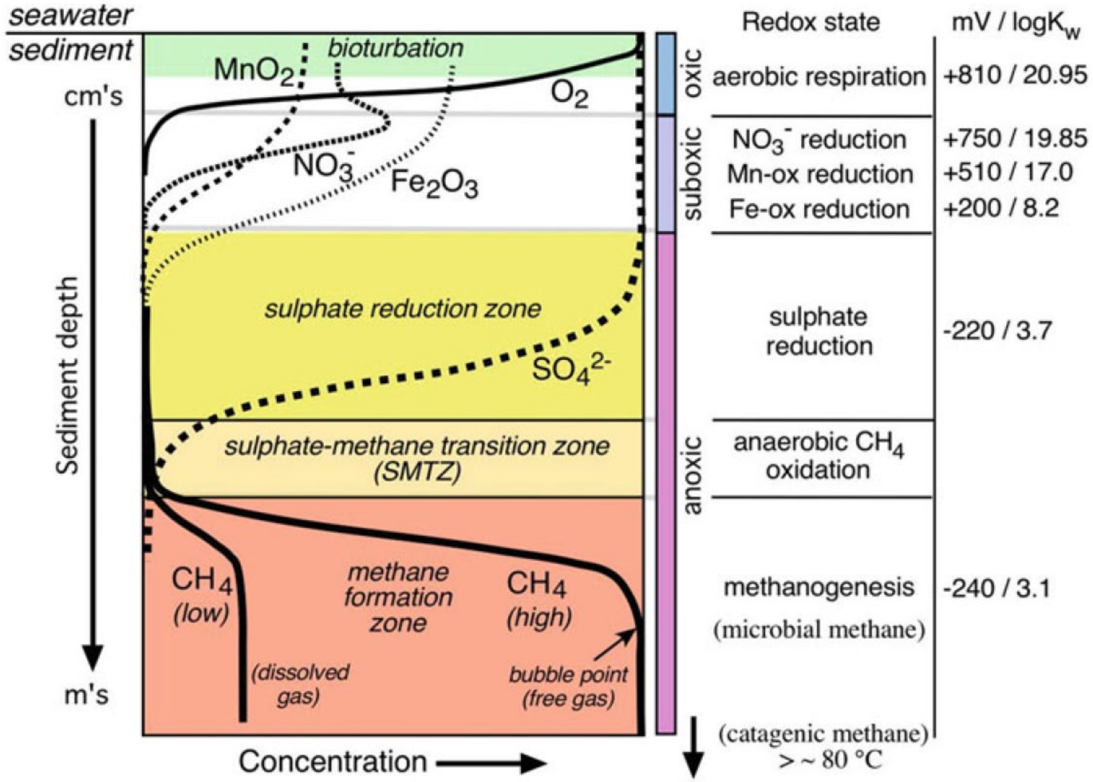
What is Ebullition?

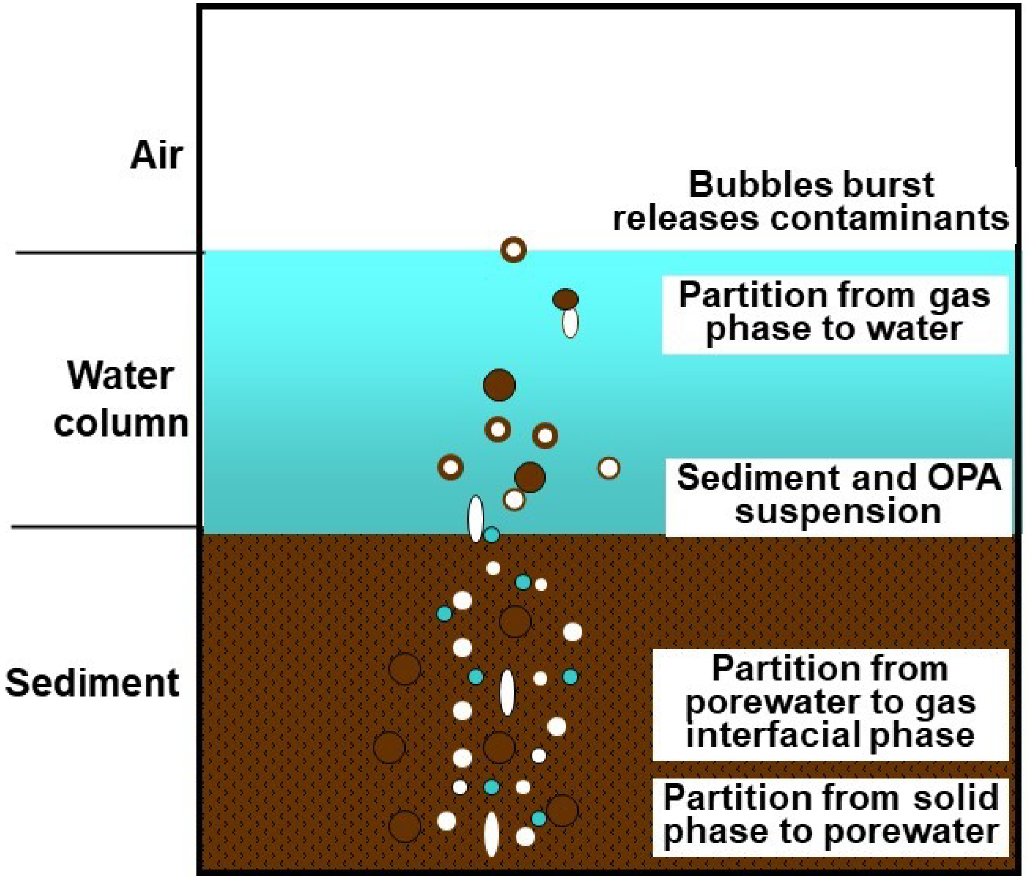
- Production of gas (mainly methane and carbon dioxide = biogas) as a result of microbial decomposition of organic matter
  - Methanogenesis is ultimate terminal electron-accepting process in biogeochemical redox ladder
- Bubbles form when gas solubility is exceeded in porewater
- Sediment fracture and upward bubble migration when buoyancy forces exceed tensile strength



Source: Whiticar 2020

Ebullition-Facilitated Contaminant Transport

- Pathway common to many NAPL-contaminated sediment sites
- NAPL migration as film on rising bubbles
- VOC partitioning into and transport by gas phase
- Resuspension of contaminated particles by stream of rising gas bubbles



Source: Viana and Rockne 2021

What Controls Ebullition?

- Rate of biogas production and persistence
  - Microbial activity (methanogens, methanotrophs)
  - Availability of biodegradable carbon (hydrocarbons, natural organic matter, sewage)
  - Geochemical conditions (abiotic oxidation of methane)
- Rate of gas bubble formation and migration
  - Solubility depends on temperature, pressure (depth, tidal), and salinity
  - Sediment physical characteristics
- If sediment labile carbon source is finite, then the duration of ebullition will be **finite**

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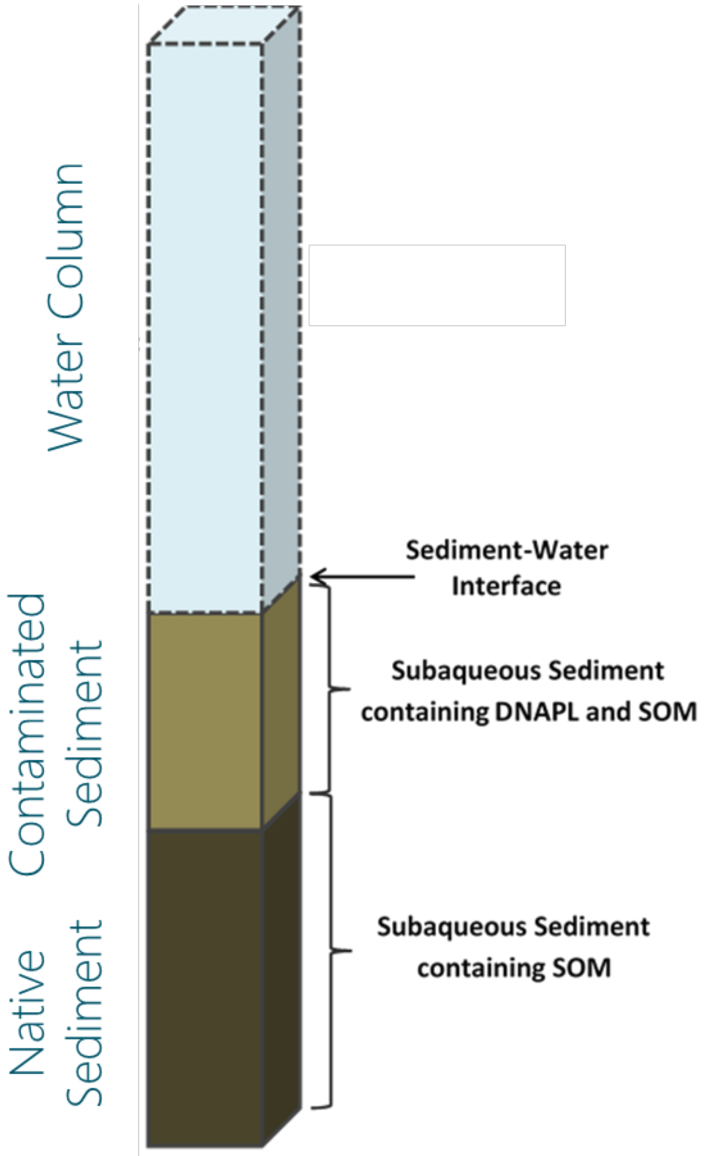
CHALLENGE

At what depths in sediment column are conditions favorable for biogas bubble formation?

How long will conditions remain favorable?

Estimating Ebullition Duration

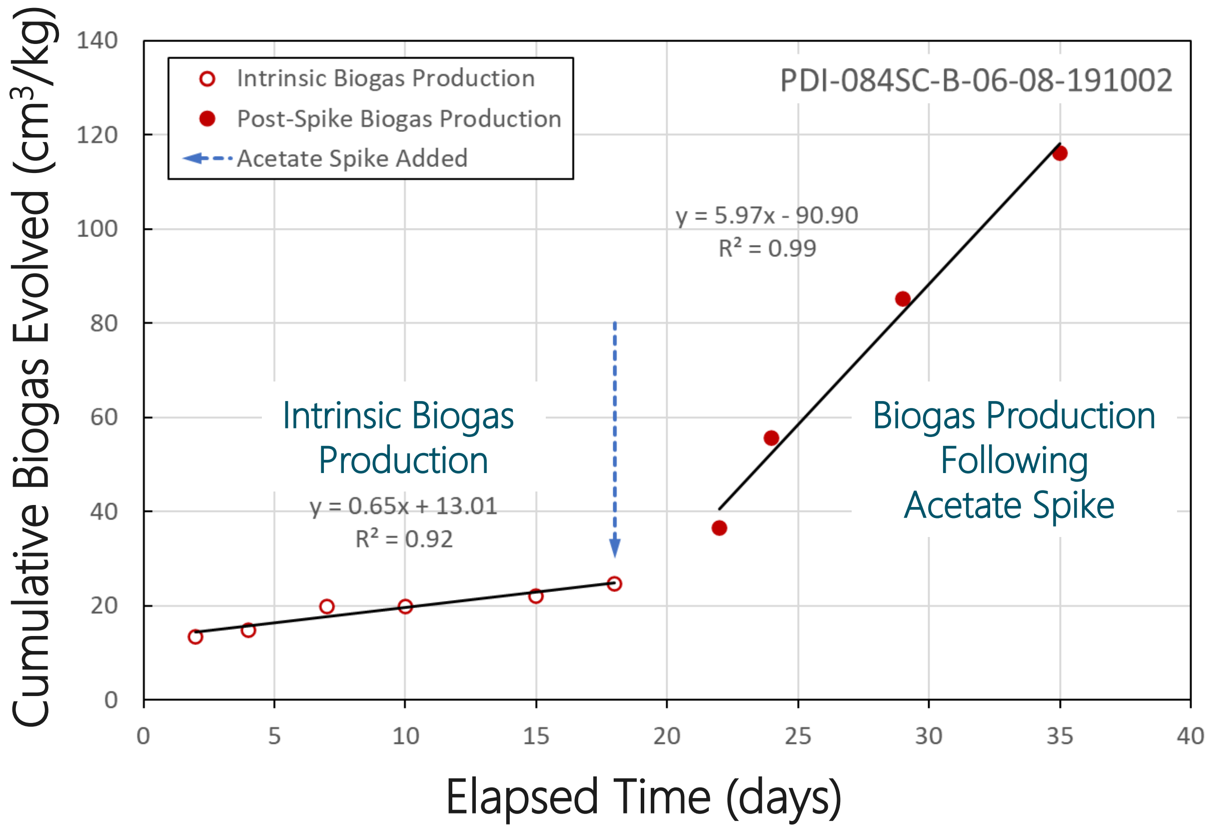
- Process-based biogeochemical sediment-water model supported by site-specific sediment geochemistry and biogas generation data
- Predict ebullition potential over time
  - Balance between depth-dependent rates of methane generation and oxidation
  - Is the vertically integrated biogas production rate net positive?
    - Yes: ebullition is possible
    - No: ebullition is not possible

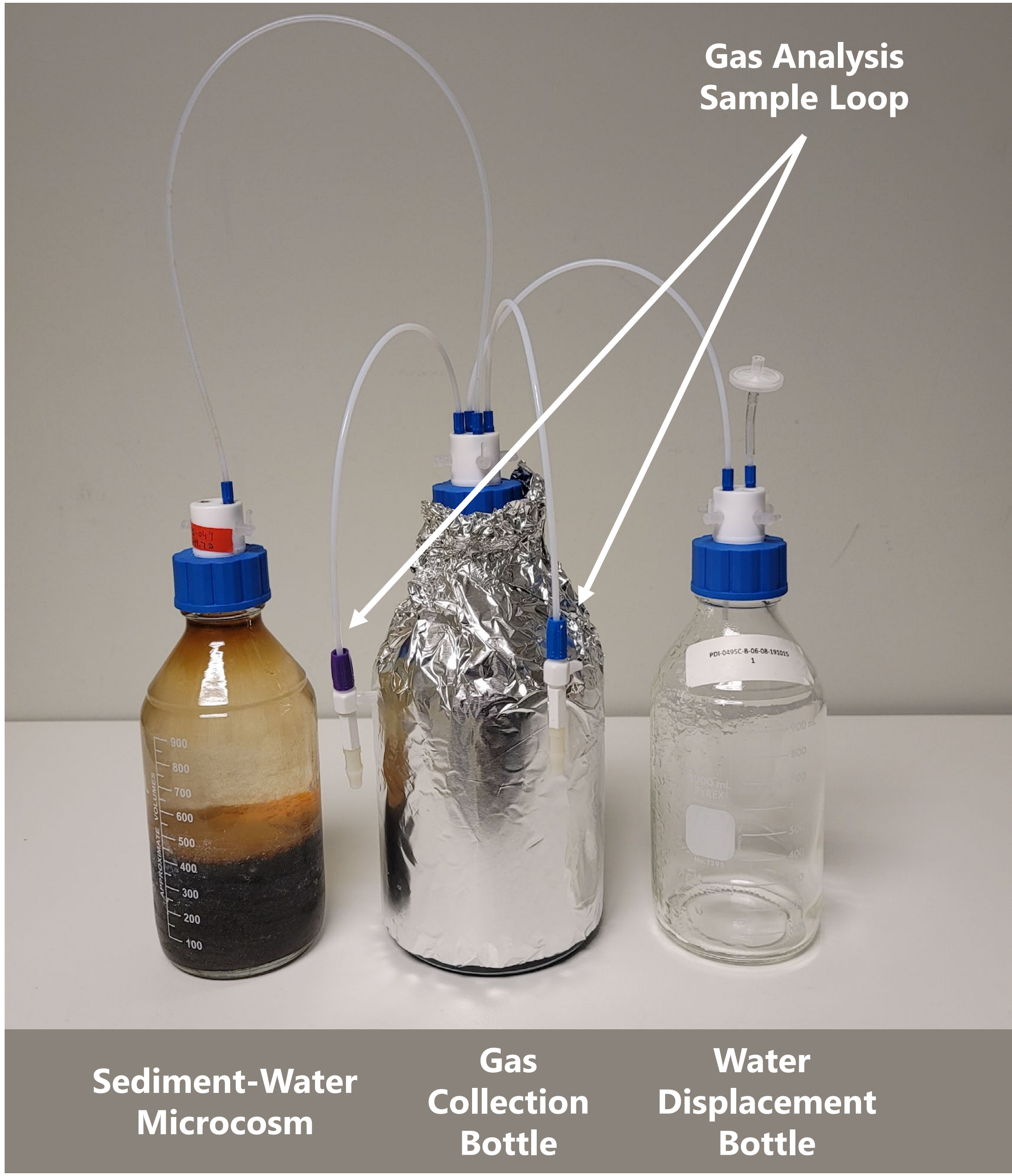


SOM: sediment organic matter

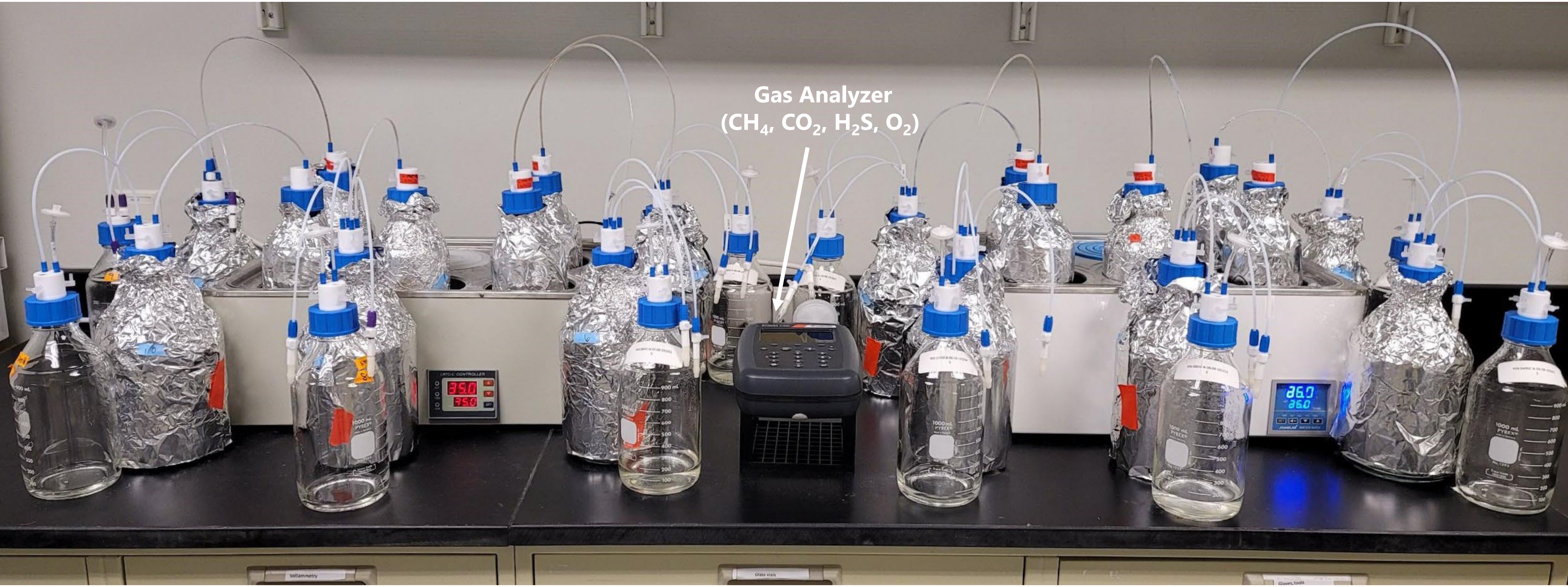
APPROACH + METHODS

Measuring Biogas Production Rates





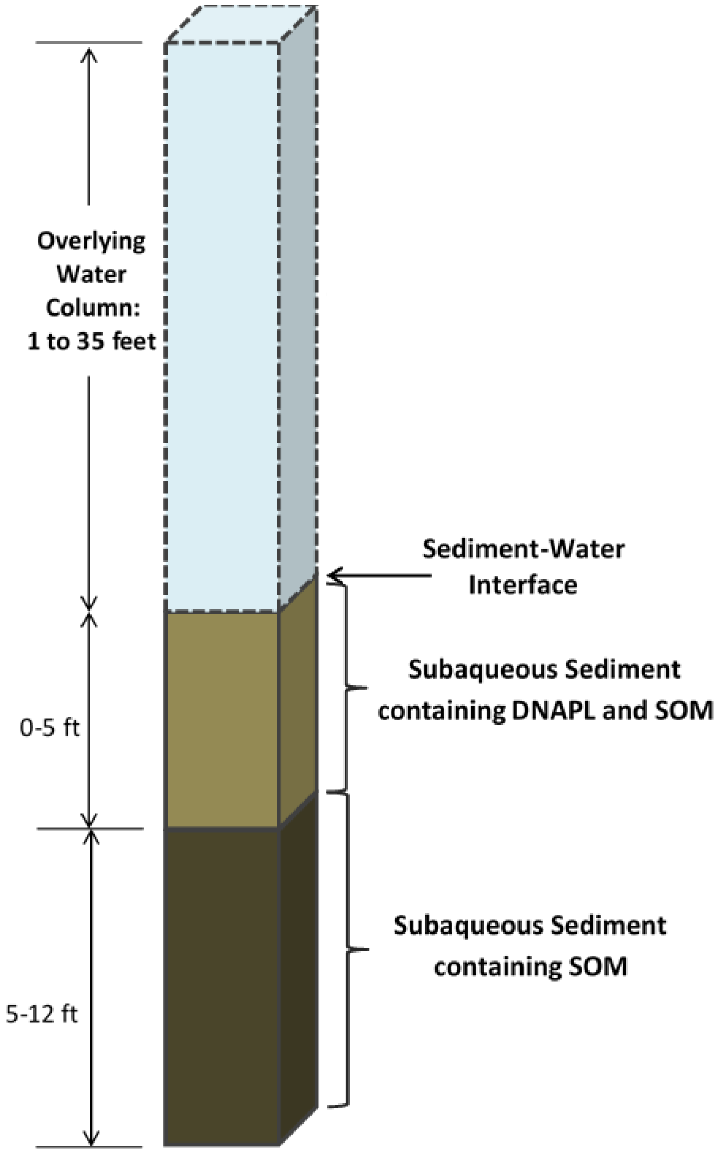
APPROACH + METHODS



Laboratory incubation setup to quantify site-specific biogas production rates and composition

Modeling Approach

- 1D biogeochemical reactive transport model of sediment and overlying water column (PHREEQC)
- Transport includes advection-dispersion-diffusion of dissolved components
  - Time-variable upward or downward advection to simulate groundwater-surface water interactions
- Spatially distributed multicomponent DNAPL (BTEX, PAHs, etc.)
  - Kinetic dissolution of DNAPL components
- Sorption of soluble DNAPL components on sediment organic matter (SOM)



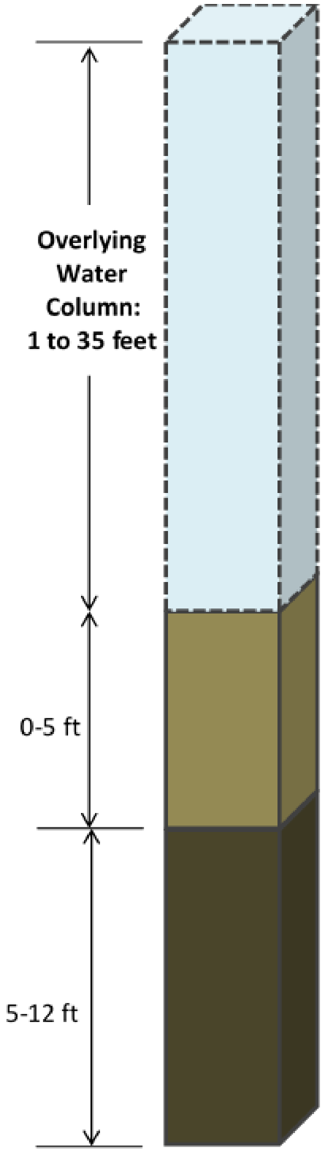
Modeling Approach (cont.)

- Kinetic biodegradation of dissolved NAPL components and SOM
  - Mineralization of organic compounds to inorganic carbon (CO_2 and/or methane)
  - Sequential electron-acceptor utilization and inhibition terms
- Secondary redox reactions
  - Methane oxidation by O_2, NO_3, Mn(IV), Fe(III), and SO_4
- Gas bubble forms when concentration dissolved gas concentration exceeds solubility in porewater
  - Function of temperature, salinity and hydrostatic pressure
  - Gas bubble composition includes CH_4, CO_2, N_2, and other minor gases

$$
\begin{aligned}
R_i = &\left(K_{ox} * \left(\frac{[C_{org}]}{[C_{org}] + [K_{m,org}]}\right) * \left(\frac{[S_{ox}]}{[S_{ox}] + [K_{m,ox}]}\right)\right) \\
&+ \left(K_{denit} * \left(\frac{[C_{org}]}{[C_{org}] + [K_{m,org}]}\right) * \left(\frac{[S_{nit}]}{[S_{nit}] + [K_{m,nit}]}\right) * \left(\frac{[I_{ox}]}{[I_{ox}] + [S_{ox}]}\right)\right) \\
&+ \left(K_{iron} * \left(\frac{[C_{org}]}{[C_{org}] + [K_{m,org}]}\right) * \left(\frac{[S_{iron}]}{[S_{iron}] + [K_{m,iron}]}\right) * \left(\frac{[I_{ox}]}{[I_{ox}] + [S_{ox}]}\right) \right. \\
&\left. * \left(\frac{[I_{nit}]}{[I_{nit}] + [S_{nit}]}\right)\right) \\
&+ \left(K_{sulf} * \left(\frac{[C_{org}]}{[C_{org}] + [K_{m,org}]}\right) * \left(\frac{[S_{sulf}]}{[S_{sulf}] + [K_{m,sulf}]}\right) * \left(\frac{[I_{ox}]}{[I_{ox}] + [S_{ox}]}\right) \right. \\
&\left. * \left(\frac{[I_{nit}]}{[I_{nit}] + [S_{nit}]}\right) * \left(\frac{[I_{iron}]}{[I_{iron}] + [S_{iron}]}\right)\right) \\
&+ \left(K_{ferm} * \left(\frac{[C_{org}]}{[C_{org}] + [K_{m,org}]}\right) * \left(\frac{[I_{ox}]}{[I_{ox}] + [S_{ox}]}\right) * \left(\frac{[I_{nit}]}{[I_{nit}] + [S_{nit}]}\right) \right. \\
&\left. * \left(\frac{[I_{iron}]}{[I_{iron}] + [S_{iron}]}\right) * \left(\frac{[I_{sulf}]}{[I_{sulf}] + [S_{sulf}]}\right)\right)
\end{aligned}
$$

Example Application

- Former MGP site, upper 5 feet of sediment contaminated by tar
- Simulate effect of groundwater-surface water interaction regimes on vertical distribution and evolution of biogas production zone over time
  - No advection (diffusion only)
  - Upwelling
  - Downwelling



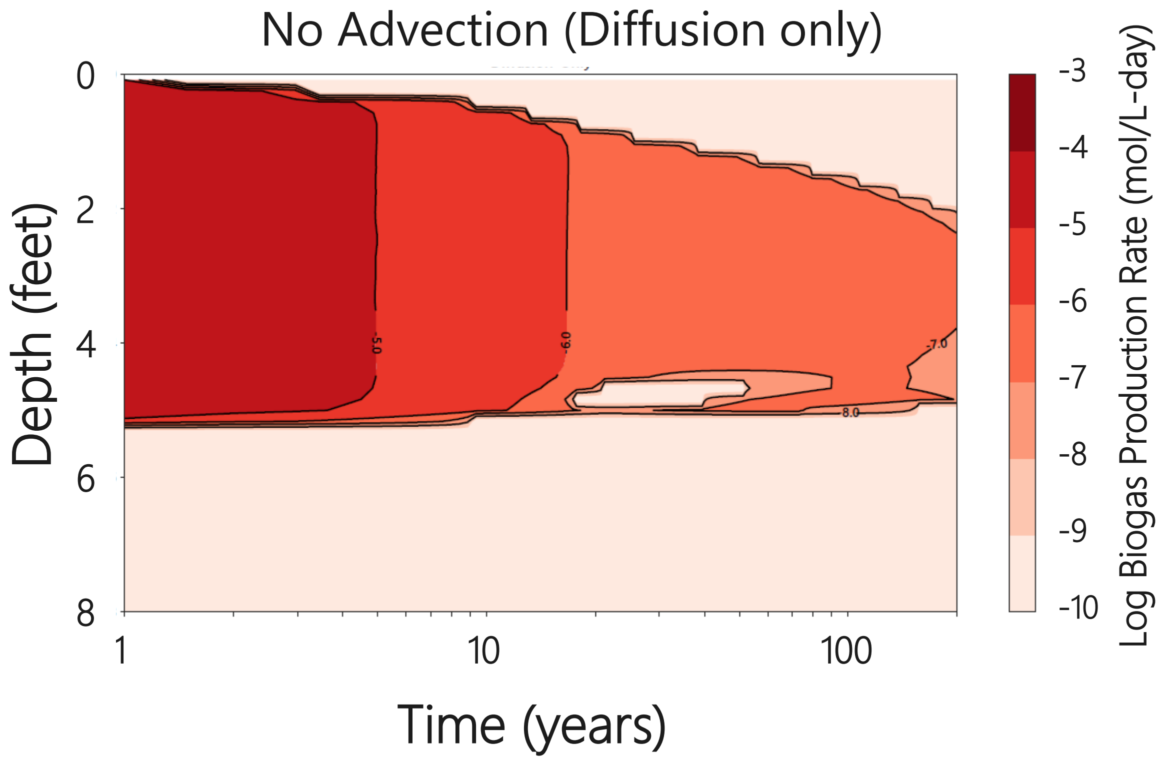
River Water Chemistry		
Parameter	**Value**	**Units**
Temperature	11	°C
pH	7.5	
Dissolved Oxygen	16	mg/L
Dissolved Inorganic Carbon	12.5	
Calcium	6.0	
Chloride	7.2	
Iron(III)	0.084	
Nitrate, as N	0.49	
Sodium	4.4	
Sulfate, as SO_4^{2-}	3.0	

Sediment Chemistry		Average Concentration (mol/L_w) 0-5 ft	5-12 ft
Volatile Organic Compounds (VOCs)	Benzene	3.33E-05	0
	Toluene	8.28E-06	0
	Ethylbenzene	1.05E-04	0
	m,p-Xylene	5.62E-05	0
	o-Xylene	3.30E-05	0
Polycyclic Aromatic Hydrocarbons (PAHs)	Naphthalene	3.25E-03	0
	1-Methylnaphthalene	6.05E-04	0
	2-Methylnaphthalene	9.76E-04	0
	Acenaphthene	1.09E-03	0
	Phenanthrene	2.77E-03	0
	Fluoranthene	1.19E-03	0
	Pyrene	1.47E-03	0
	Recalcitrant (inert) NAPL	2.84E-03	0
Sediment Organic Matter (SOM)		1.0	1.0

Model Results: Evolution of Biogas Production Rates

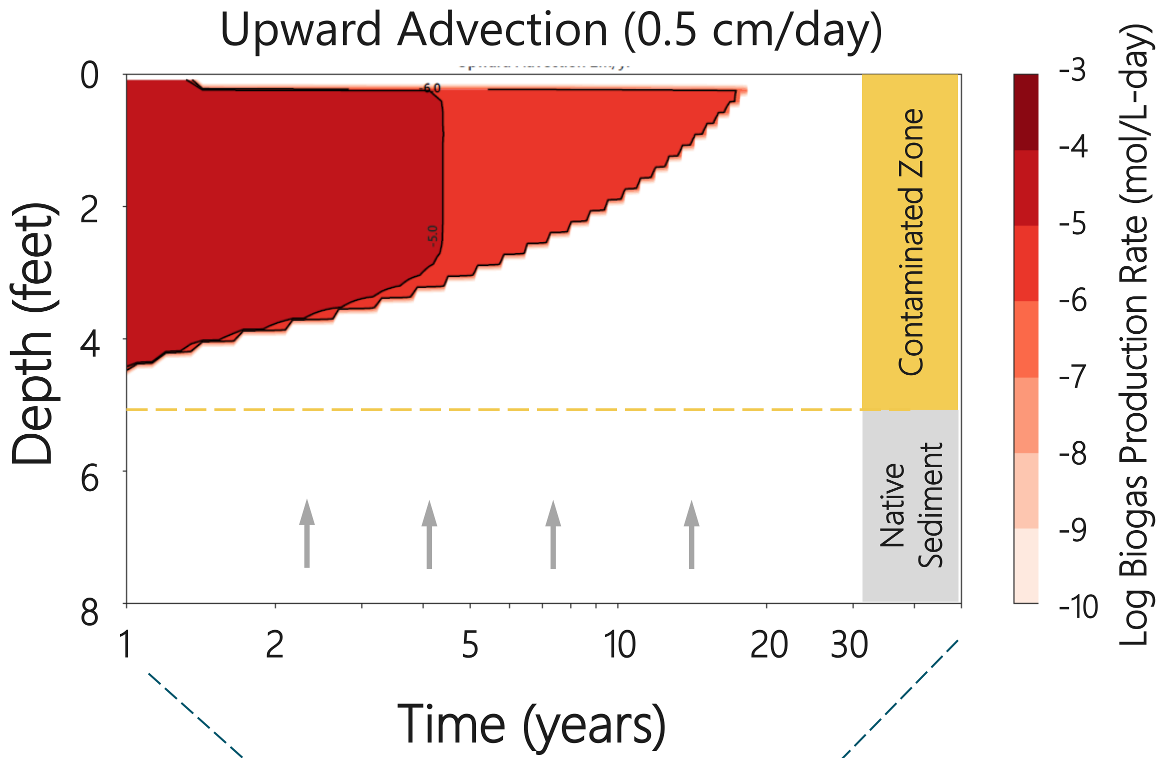
Diffusion Only Scenario

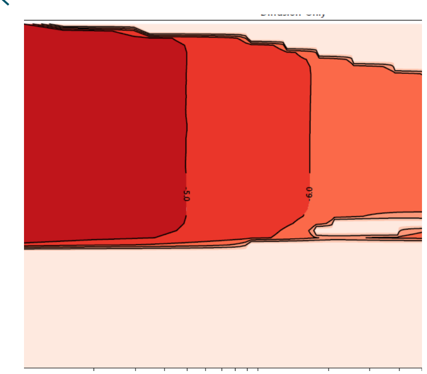
- 200-year simulation
- Intense biogas production across contaminated sediment zone gradually decreases as more labile DNAPL constituents are depleted via dissolution and biodegradation
- Gradual retreat of the upper limit of biogas production due to diffusion of dissolved oxygen from overlying surface water



Upwelling Scenario

- 50-year simulation
- Intense biogas production across contaminated zone
- Biogas production zone shrinks from the bottom up as soluble DNAPL constituents are transported out of the sediment by upwelling porewater
- Biogas production predicted to cease after approximately 20 years as the biodegradable carbon pool is depleted

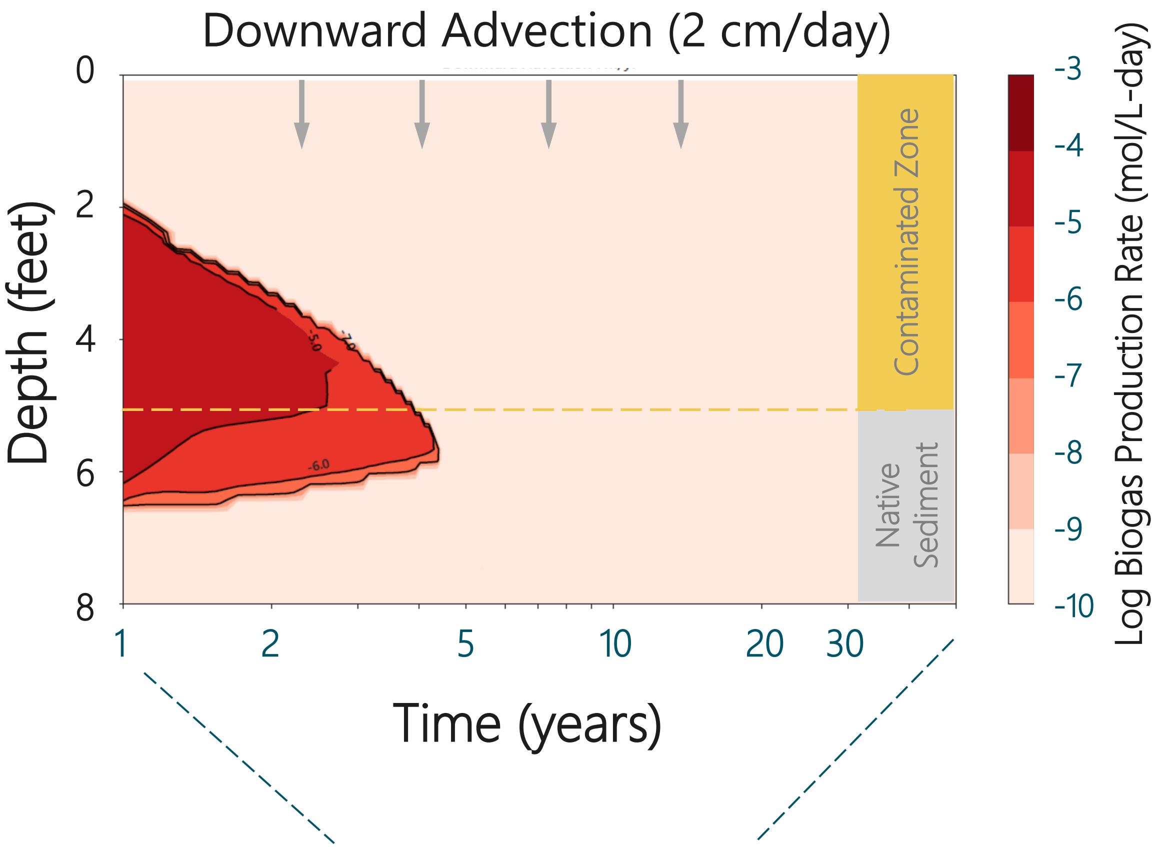


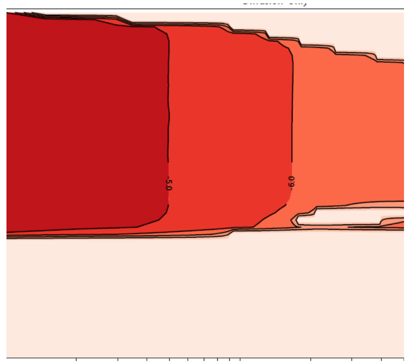


Compare to diffusion-only scenario

Downwelling Scenario

- 50-year simulation
- Intense biogas production limited to the deeper section of the contaminated interval
- Aerobic conditions in the upper section due to surface water infiltration
- Biogas production zone shrinks over time from the top down
- Biogas production predicted to cease within approximately 5 years

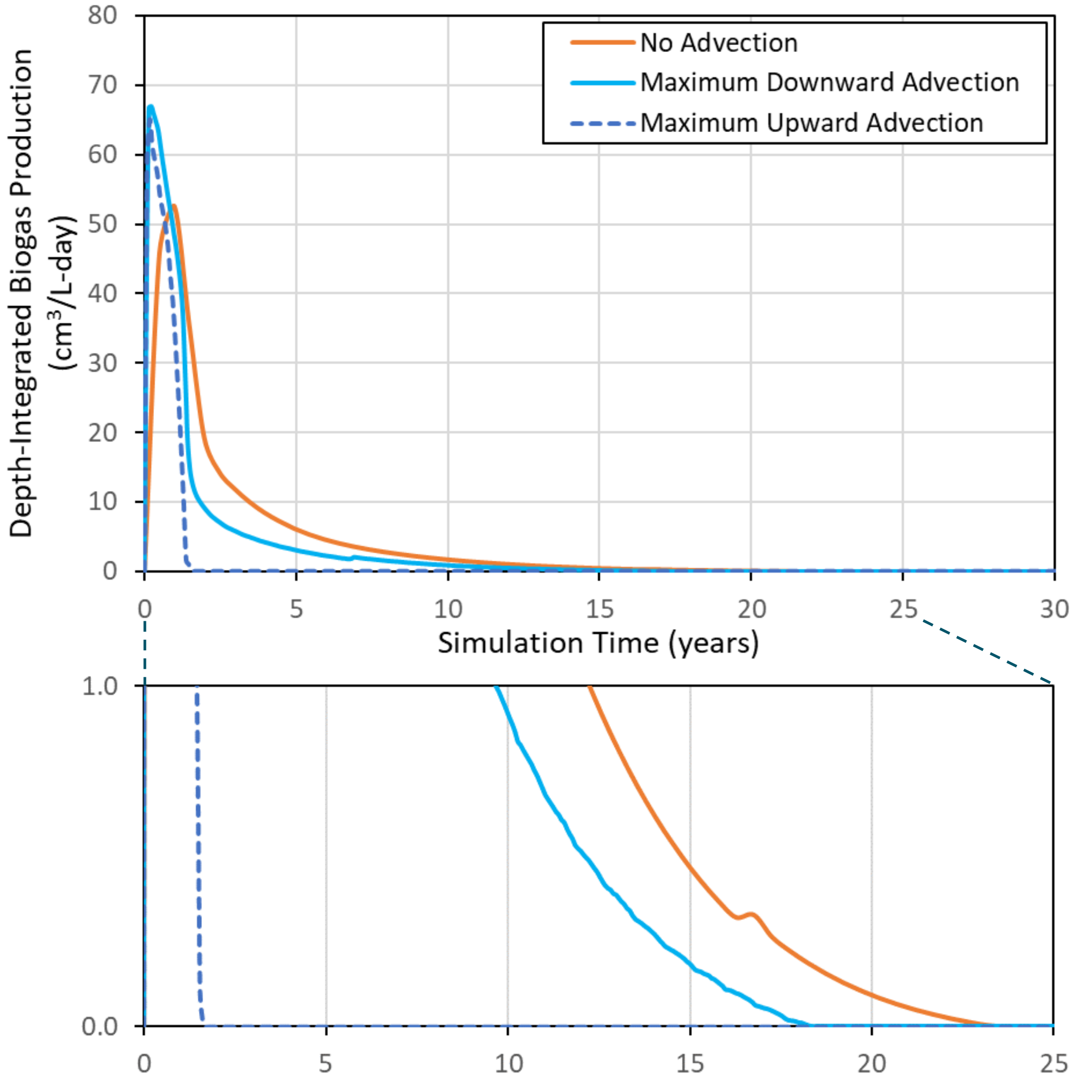




Compare to diffusion-only scenario

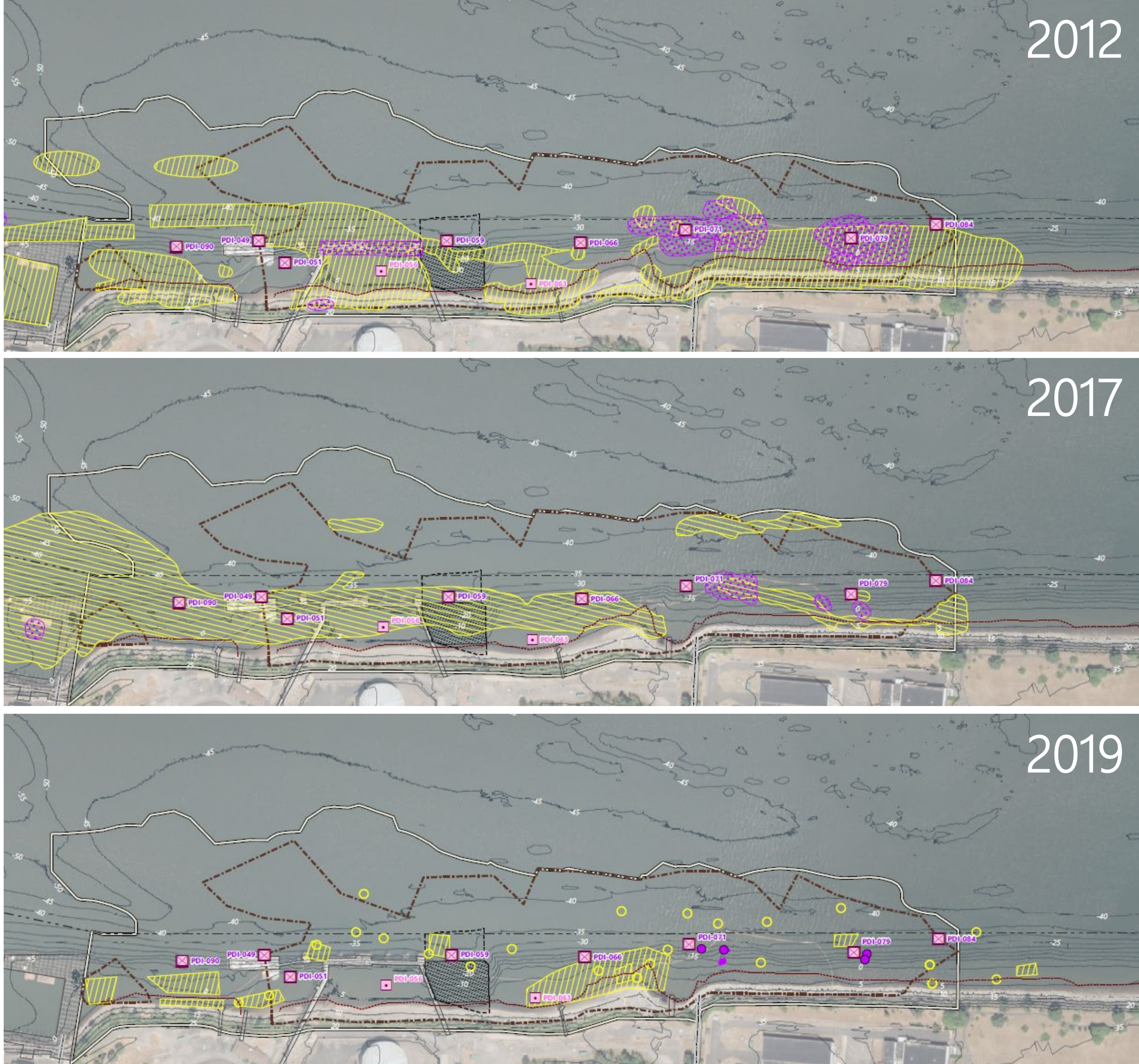
Net Biogas Production and Duration of Ebullition

- Net biogas production in sediment can be used to predict ebullition potential over time
  - Vertical integration of methane generation and oxidation rates over sediment column (calculated by model)
  - Net positive values indicate ebullition is possible
  - Ebullition predicted to cease when vertically integrated biogas production is less than or equal to 0
- Model results show that duration of ebullition is sensitive to direction of advective porewater flux



Reality Check

- Upland source control (hydraulic capture and containment) installed in 2012
- Induced surface water downwelling into sediment
- Ebullition (yellow) and sheening (violet) areal extents diminished significantly over a period of 7 years



Summary

- Ebullition-facilitated contaminant transport is an issue of concern for remediation at many NAPL-contaminated sediment sites
- If sources of biodegradable organics are controlled, ebullition process is expected to be of finite duration
- Site-specific sediment geochemistry, biogas testing, and biogeochemical reactive transport modeling can be used to estimate the duration of ebullition-facilitated contaminant transport and inform remedial design (e.g., organoclay dosing in engineered cap)

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THANK YOU

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Whiticar, M.J., 2020. The Biogeochemical Methane Cycle. In: Wilkes, H. (eds) *Hydrocarbons, Oils and Lipids: Diversity, Origin, Chemistry and Fate*. Springer, https://doi.org/10.1007/978-3-319-54529-5_5-1.

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