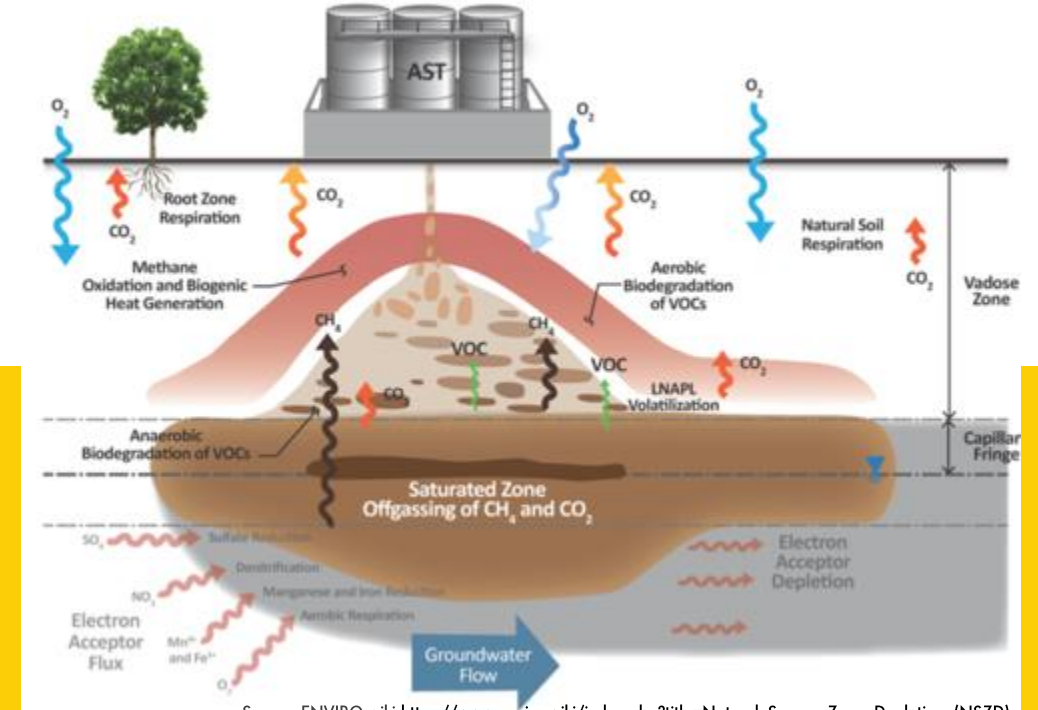




# Evolving conceptual models for Natural Source Zone Depletion

## Methanogenesis, Gas Transport, and Sequenced Biodegradation

Sanjay Garg (Shell Oil Products US)  
Matthijs Bonte (Shell Global Solutions International (NL) BV)  
Jonathan Smith (Shell Global Solutions (UK) Ltd)



Source: ENVIRO.wiki [https://www.enviro.wiki/index.php?title=Natural\\_Source\\_Zone\\_Depletion\\_\(NSZD\)](https://www.enviro.wiki/index.php?title=Natural_Source_Zone_Depletion_(NSZD))

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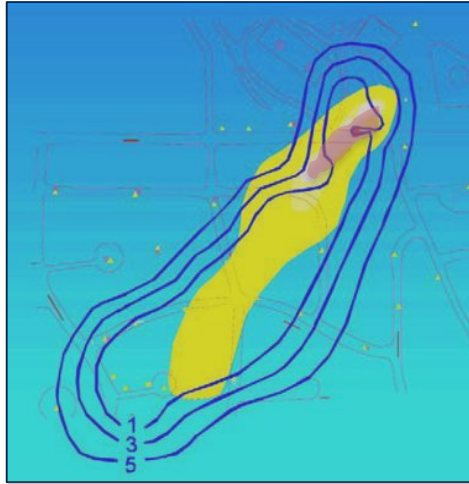
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## Background

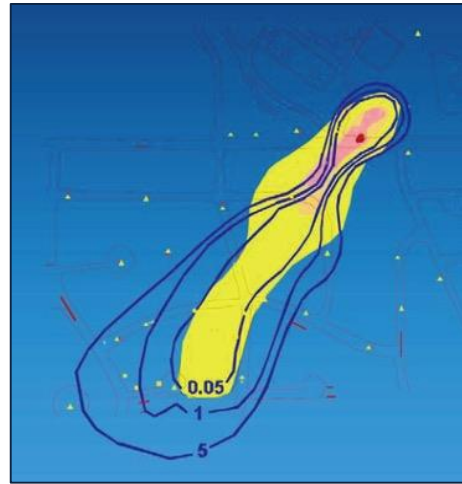
1

What do we usually look for? → Key Electron Acceptors For MNA

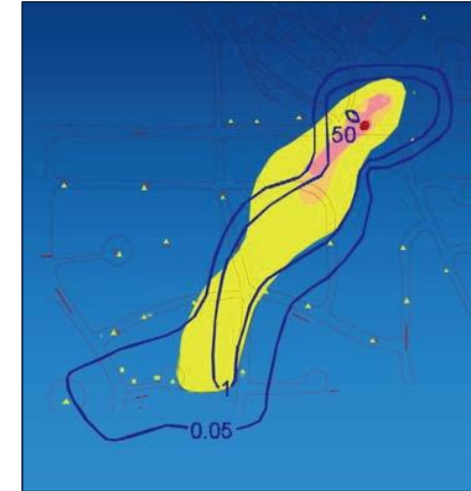
Dissolved Oxygen "Hole"



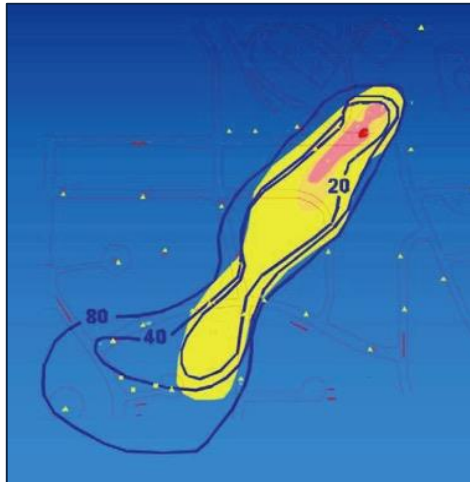
Nitrate "Hole"



Ferrous Iron "Blob"



Sulfate "Hole"



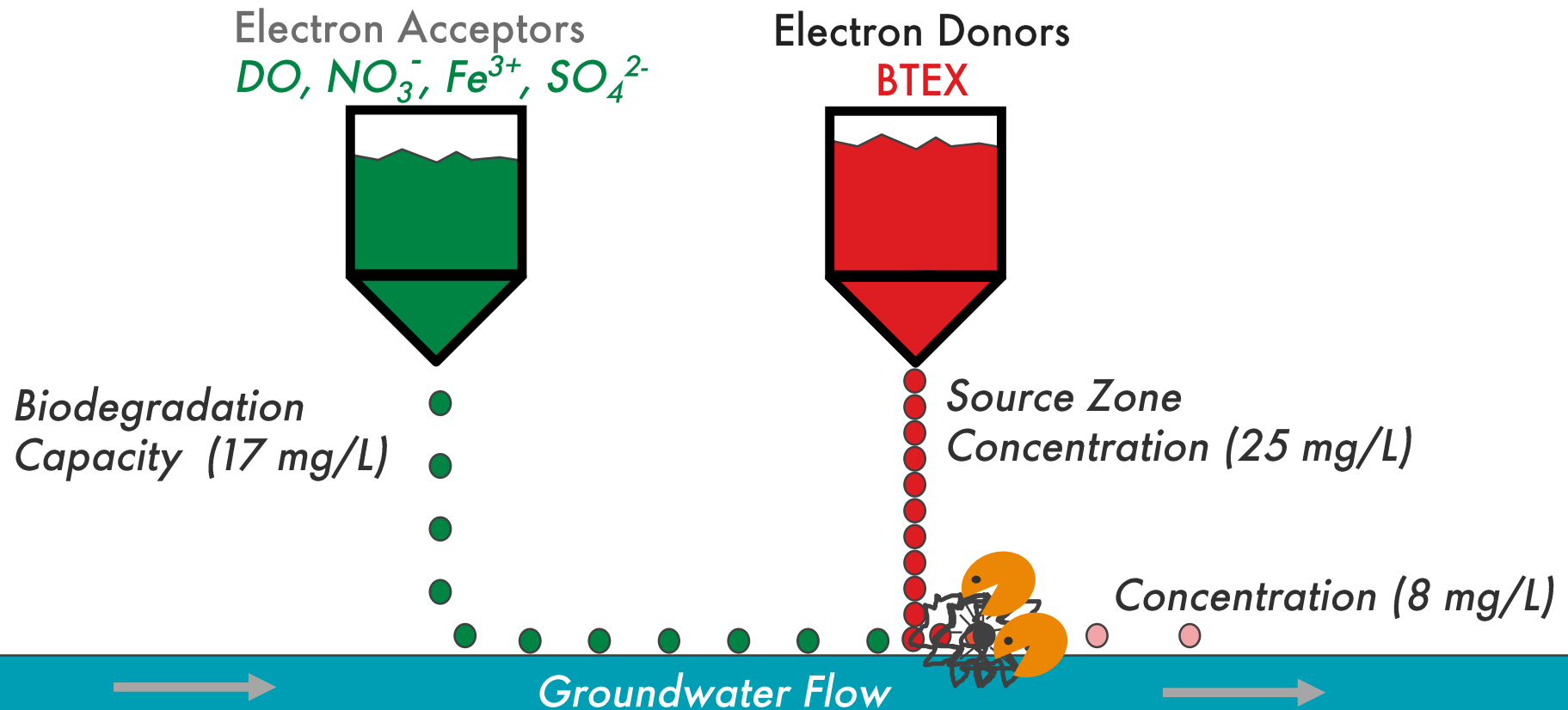
Dissolved Methane "Plume"



### KEY POINT

MNA focused on groundwater plume: how far and at what concentration

## Biodegradation Capacity of Saturated- Zone Electron Acceptors



**KEY  
POINT**

Electron Acceptor mass-balance underestimated  
LNAPL source zones biodegradation significantly

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## NSZD Conceptual Model

2

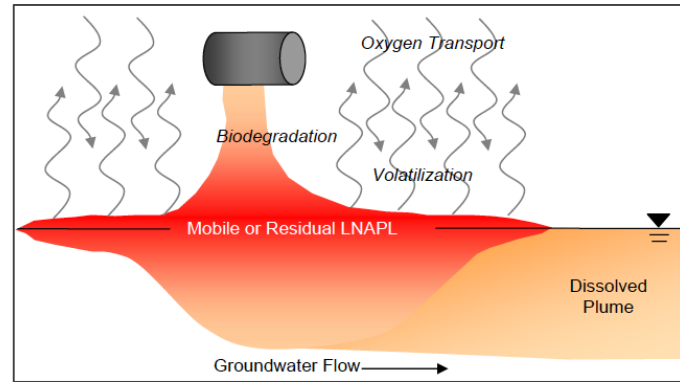
## Vapor Fluxes drive LNAPL loss

Baedecker et al., 1993

Mass transfer calculations indicated that the primary reactions in the anoxic zone are...and **outgassing of  $\text{CH}_4$  and  $\text{CO}_2$**

Molins et al., 2010

*"...the main degradation pathway can be attributed to **methanogenic degradation** of organic compounds ...."*



ITRC, 2009

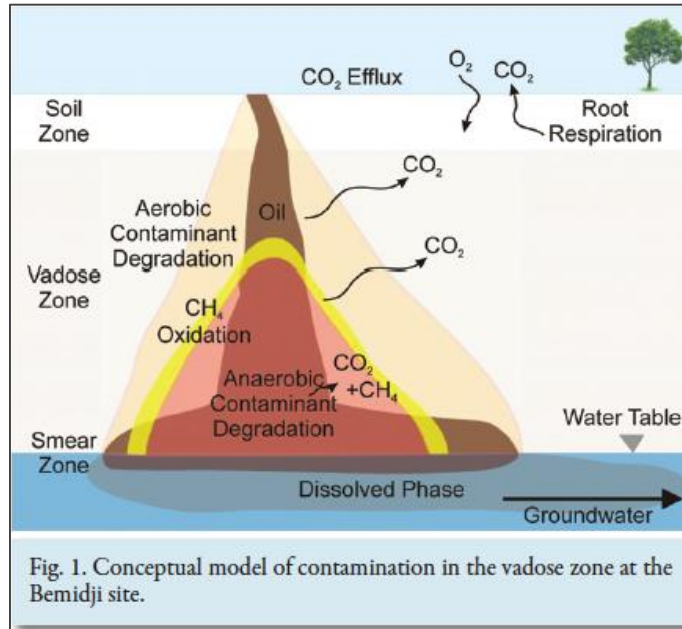
Amos & Mayer, 2006

*transfer of biogenically generated gases from the smear zone provides a major control on carbon balance*

Lundegard & Johnson  
2006

*mass loss associated with oxygen diffusion through the vadose zone is more significant (2 OOMs) than dissolution and biodegradation in the saturated zone*

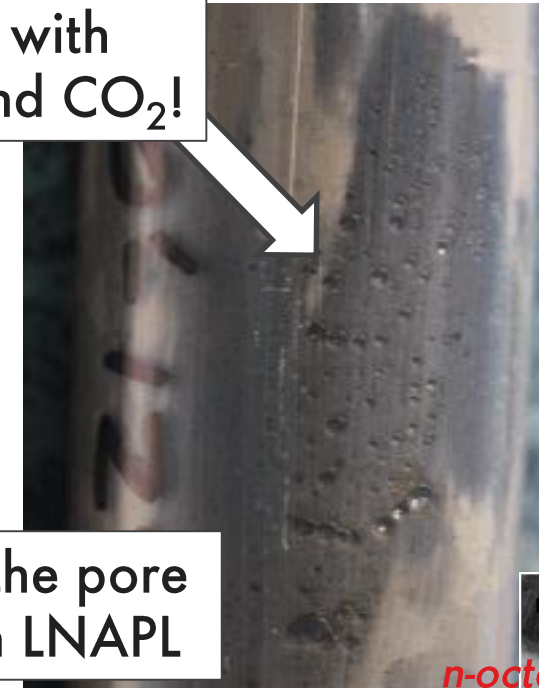
# Natural Source Zone Depletion and sequenced biodegradation



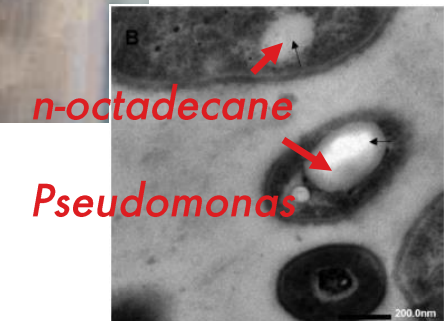
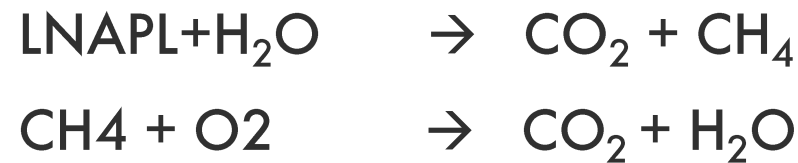
Sihota and Mayer, 2011

Bubbles with methane and CO<sub>2</sub>!

Occurs in the pore space with LNAPL



Source: Tom Sale, CSU



Hua et al., 2014

**KEY  
POINT**

NSZD focuses on source depletion: how long.  
Hydrocarbons don't have to dissolve to biodegrade

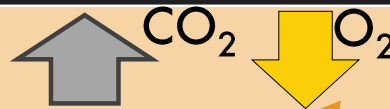
# NSZD Conceptual Model

## KEY PROCESSES

### Surface Efflux



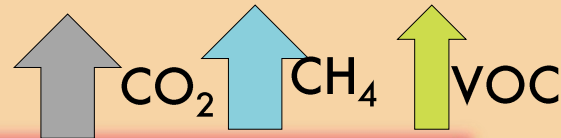
### Aerobic Transport



### Methane & VOC Oxidation

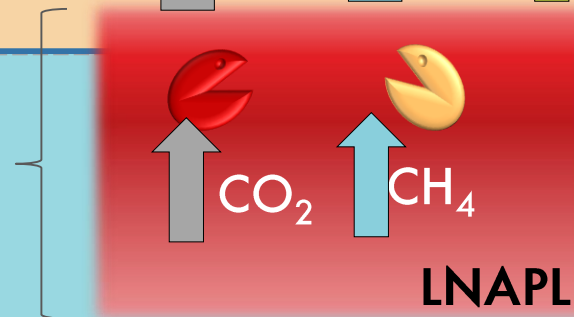


### Anaerobic Transport



### Outgassing, Ebullition

### Methane Generation



## NSZD Rates Being Observed

NSZD Study	Site-wide NSZD Rate	
	(gallons/ acre /year)	(L/Ha/yr)
Six refinery & terminal sites (McCoy et al., 2012)	2,100 – 7,700	20,000 – 73,000
1979 Crude Oil Spill (Bemidji) (Sihota et al., 2011)	1,600	15,200
Two Refinery/Terminal Sites (LA LNAPL Wkgrp, 2015)	1,100 – 1,700	10,500 – 16,000
Five Fuel/Diesel/Gasoline Sites (Piontek, 2014)	300 - 3,100	2,900 - 30,000
Eleven Sites, 550 measurements (Palaia, 2016)	300 – 5,600	2,900 – 53,000
Refinery/distribution depot, France (unpublished Shell data)		15,600
Retail site in Spain (poster @ GQ2019 by Sweeney, Sayas, et al)		260 - 54,000



**KEY  
POINT**

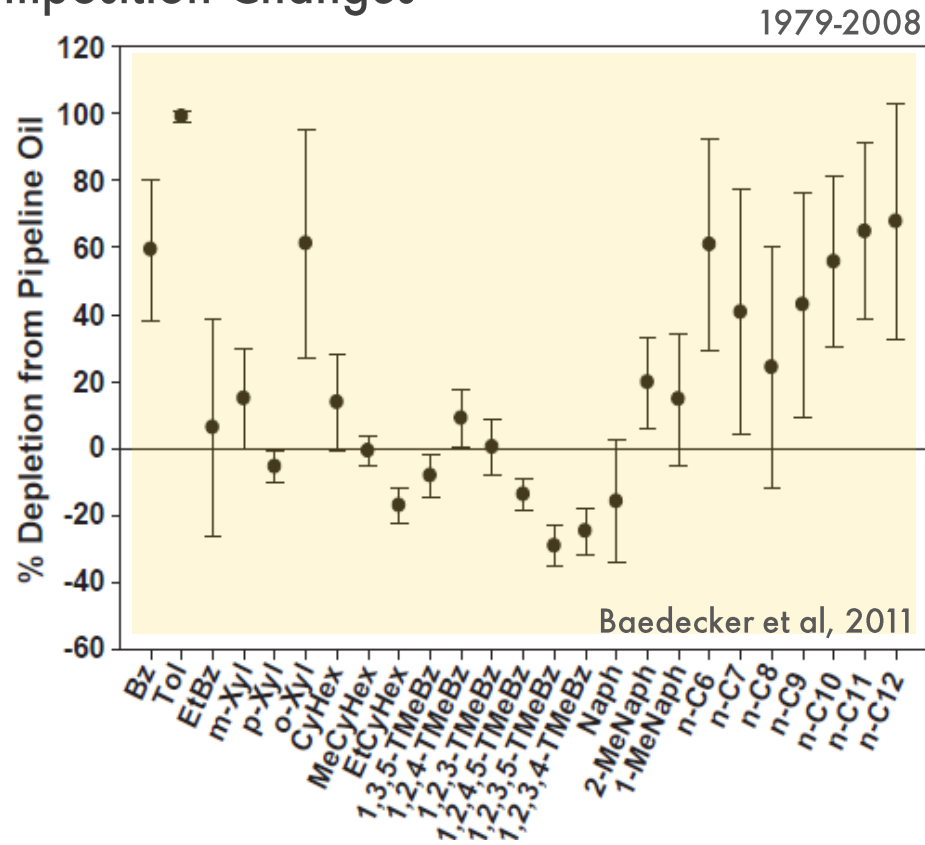
NSZD rates are in the range of 1000s – 10,000s  
L/Ha/yr [100s to 1000s of gallons/acre/year]

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## NSZD and LNAPL Composition Change: What degrades?

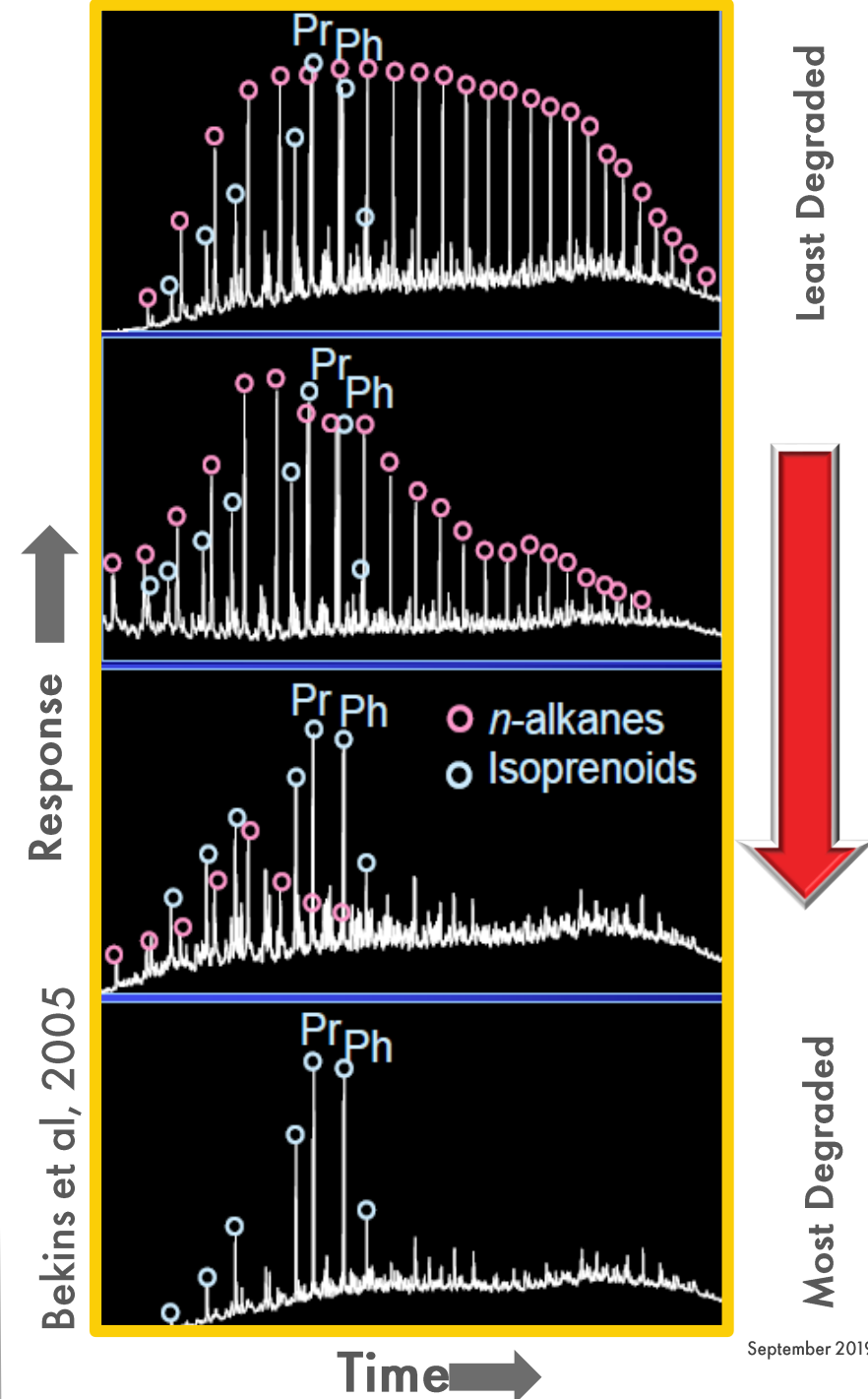
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## LNAPL Composition Changes

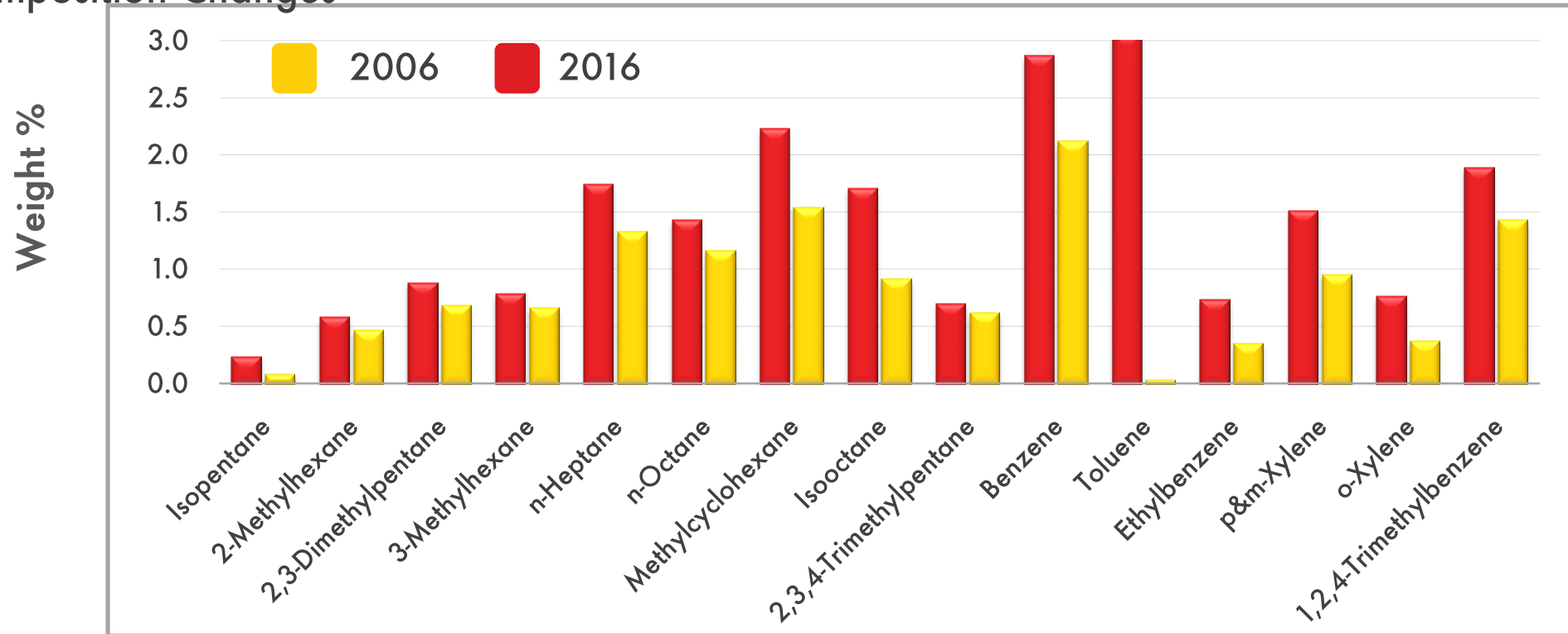


### KEY POINT

- Different constituents degrade at different rates
- Methanogenesis depletes high MW alkanes faster

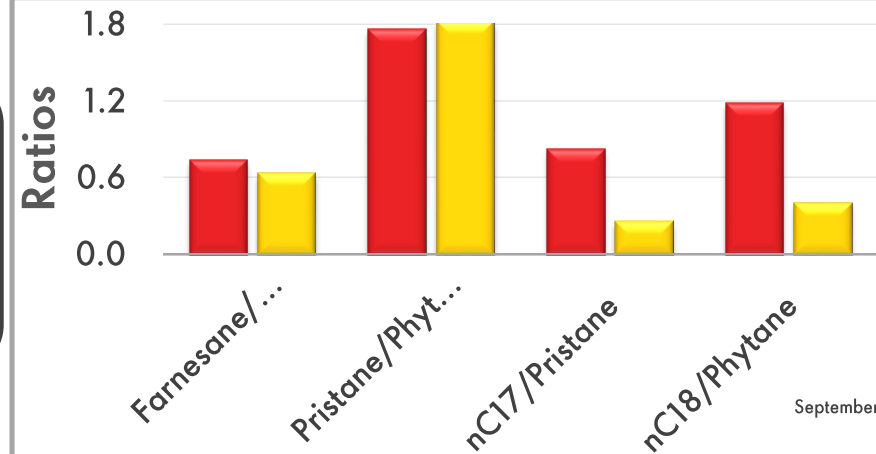


## LNAPL Composition Changes



### KEY POINT

- Different constituents degrade at different rates
- Poorly soluble compounds degrade as well



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## Implications for Practitioners

# 4

# The NSZD Journey

- NSZD being recognized
- Variability in measurement
- Bulk rates

- Focus on dissolved phase
- Ignoring attenuation of LNAPL itself

- Standard method(s)
- Understand compositional & risk change
- Cost-effectively increase NSZD rates
- Fit into regulatory framework

## Questions and more information

### More information:

- Garg et al (2017) Overview of Natural Source Zone Depletion: Processes, Controlling Factors, and Composition Change.

<https://doi.org/10.1111/gwmr.12219>



- CLAIRE-UK (2019) An Introduction to Natural Source Zone Depletion at LNAPL Sites

<https://www.claire.co.uk/component/phocadownload/category/17-technical-bulletins?download=681:tb-20-an-introduction-to-natural-source-zone-depletion-at-lnapl-sites>



