# Characterization of Contaminant Evolution and Ketones Accumulation in an Aged DNAPL Source Zone within a Sedimentary Bedrock Aquifer

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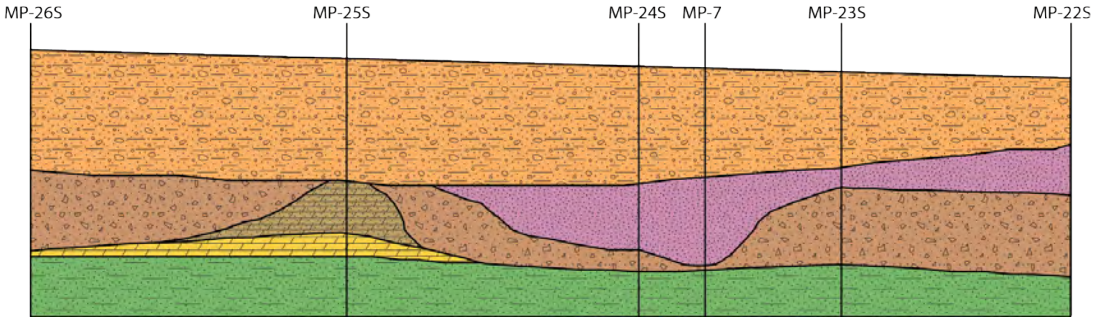
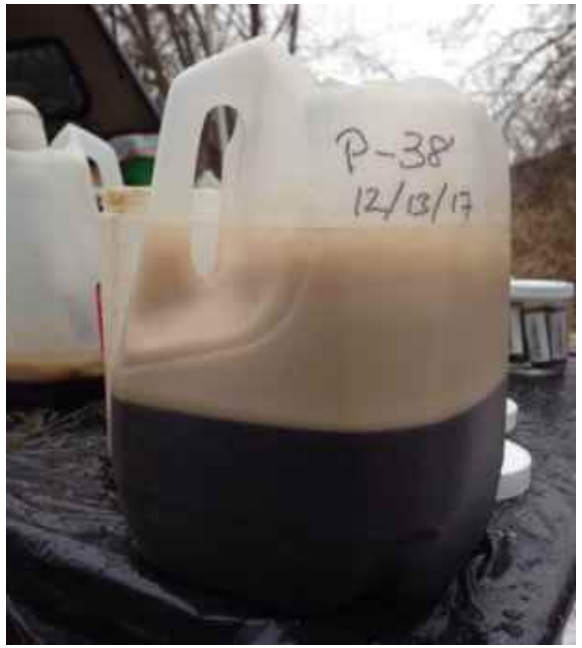
# Ingredients for Biodegradation in a Complex Hydrogeologic Setting

Groundwater Flow in Fractured Sedimentary Rock Water Supply Aquifer

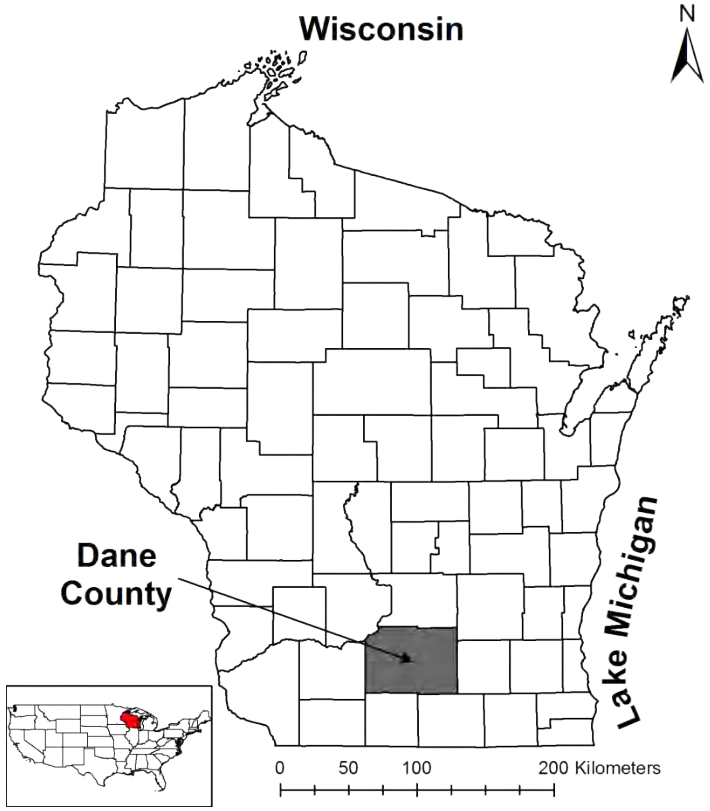
Overlapping Unconformities Create Complex Stratigraphy

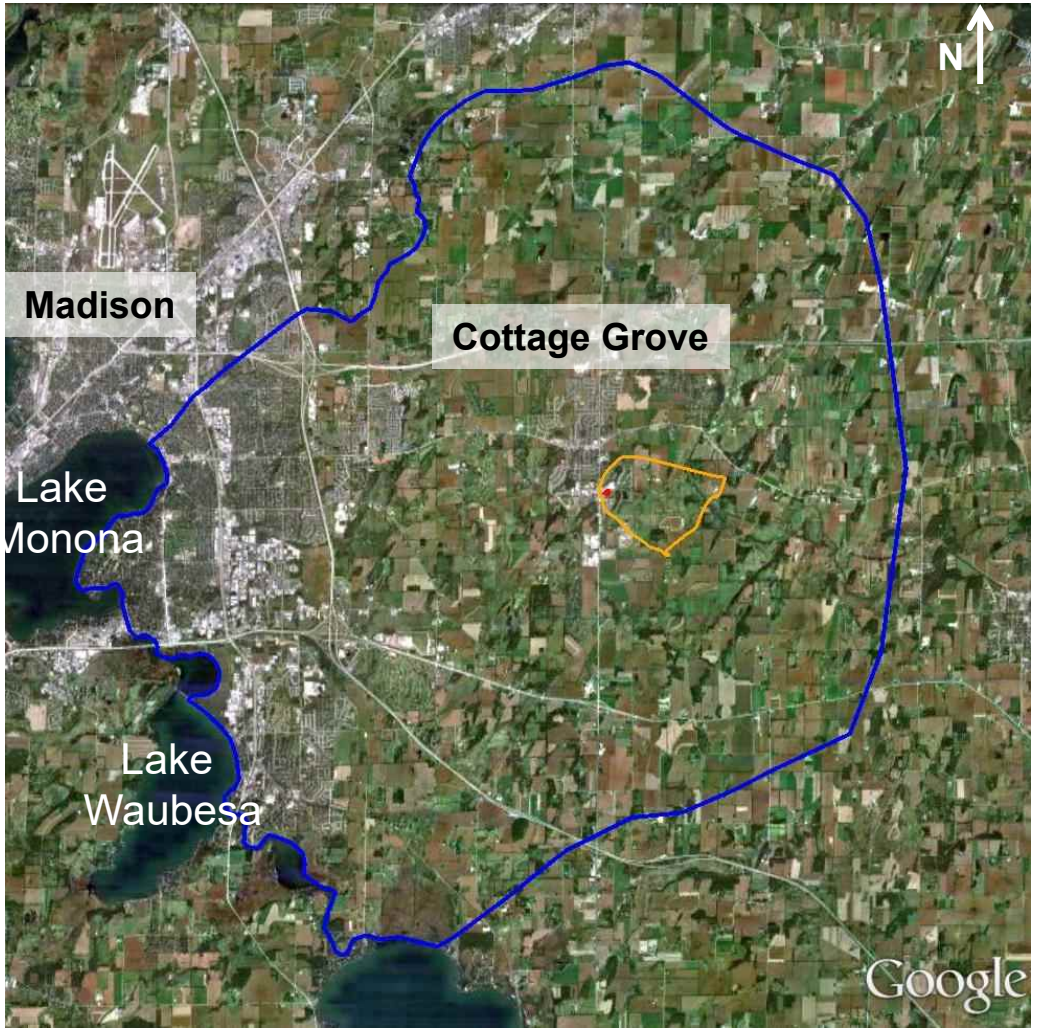



Complex Mix of Contaminants as DNAPL Aged in the Subsurface for > 50 Years



# Site Located in South Central, Wisconsin



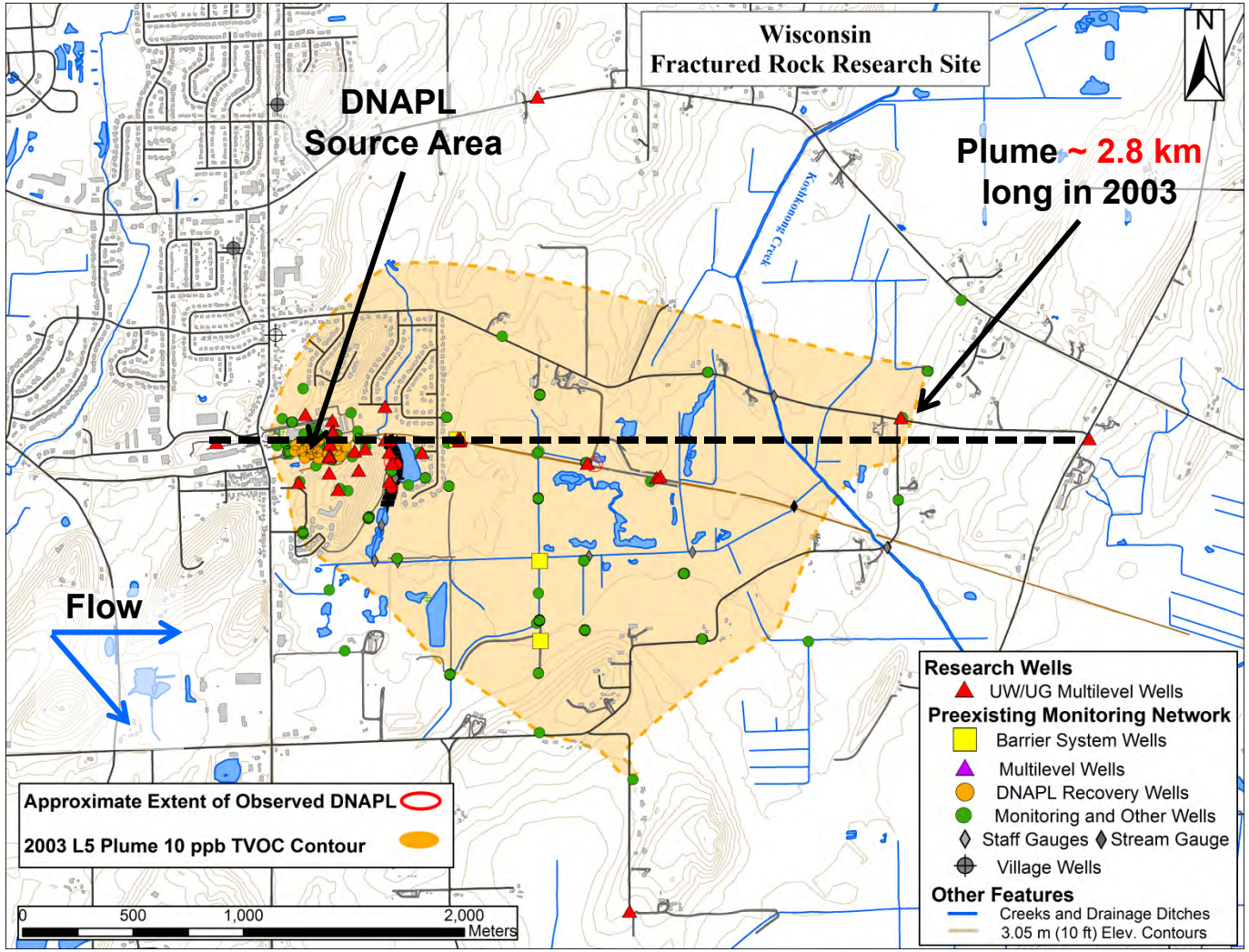




DNAPL source zone

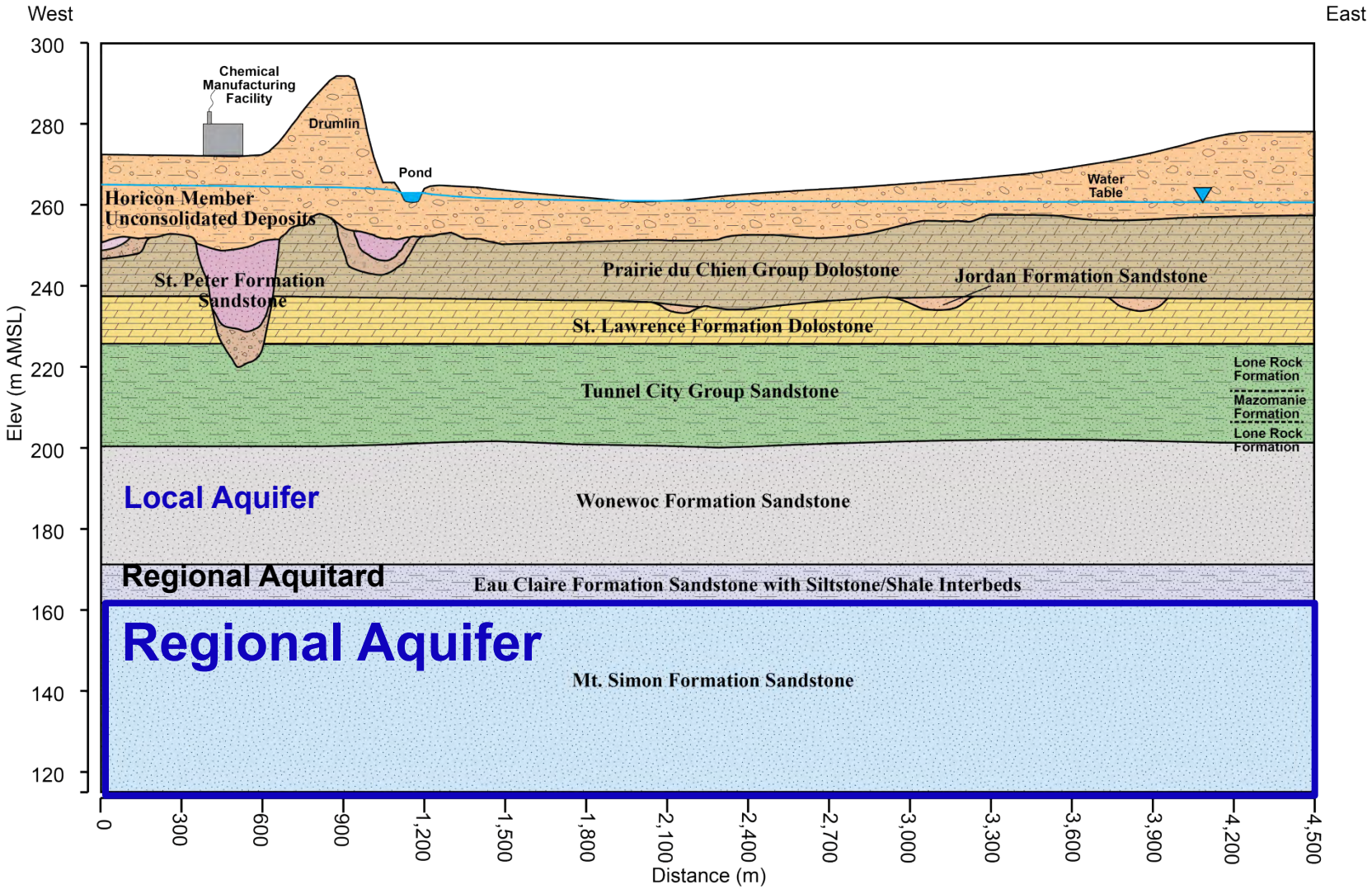
Max extent dissolved phase plume

Flow model domain

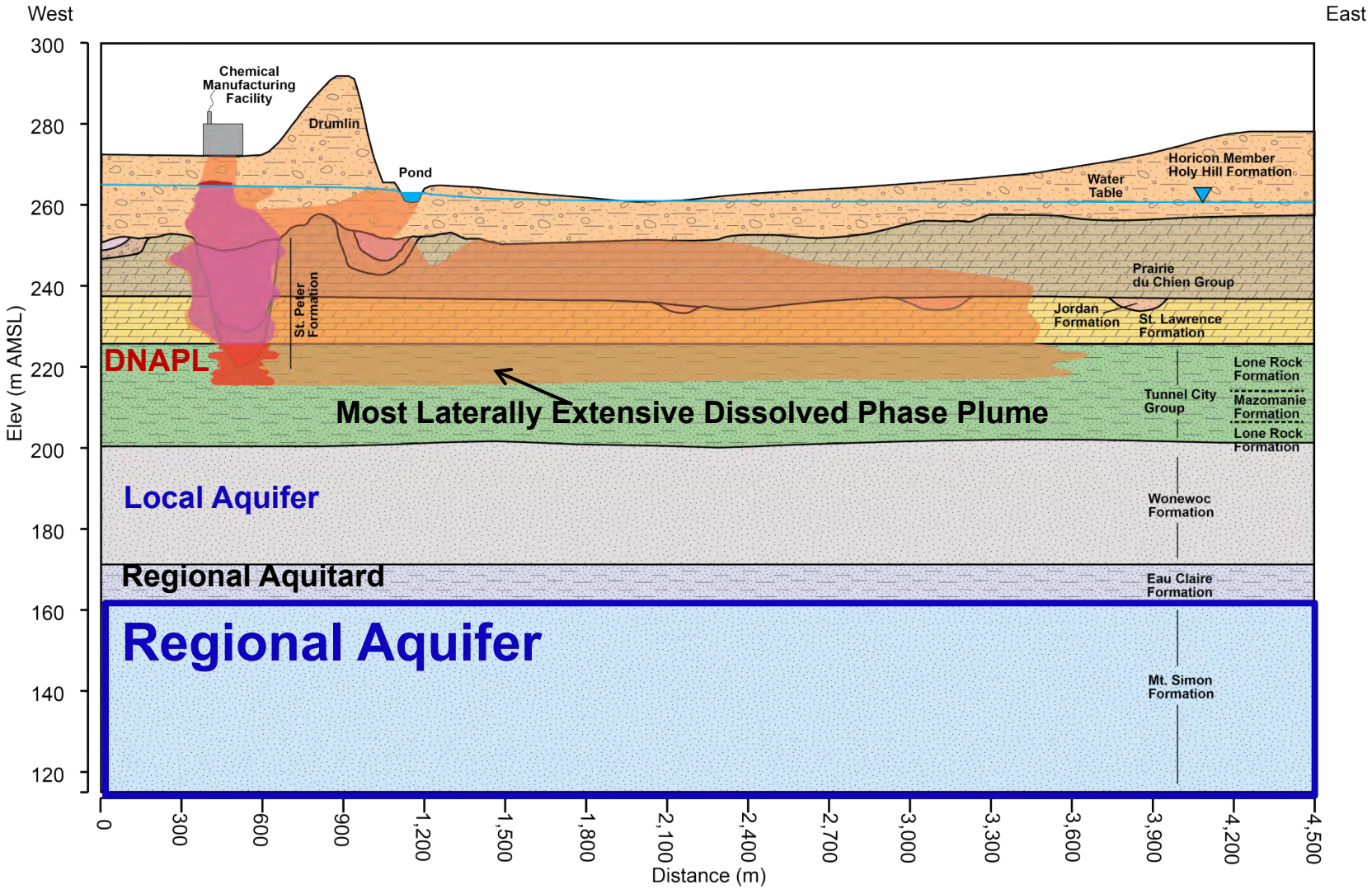
# Mixed Organics DNAPL Source Zone and Large Plume



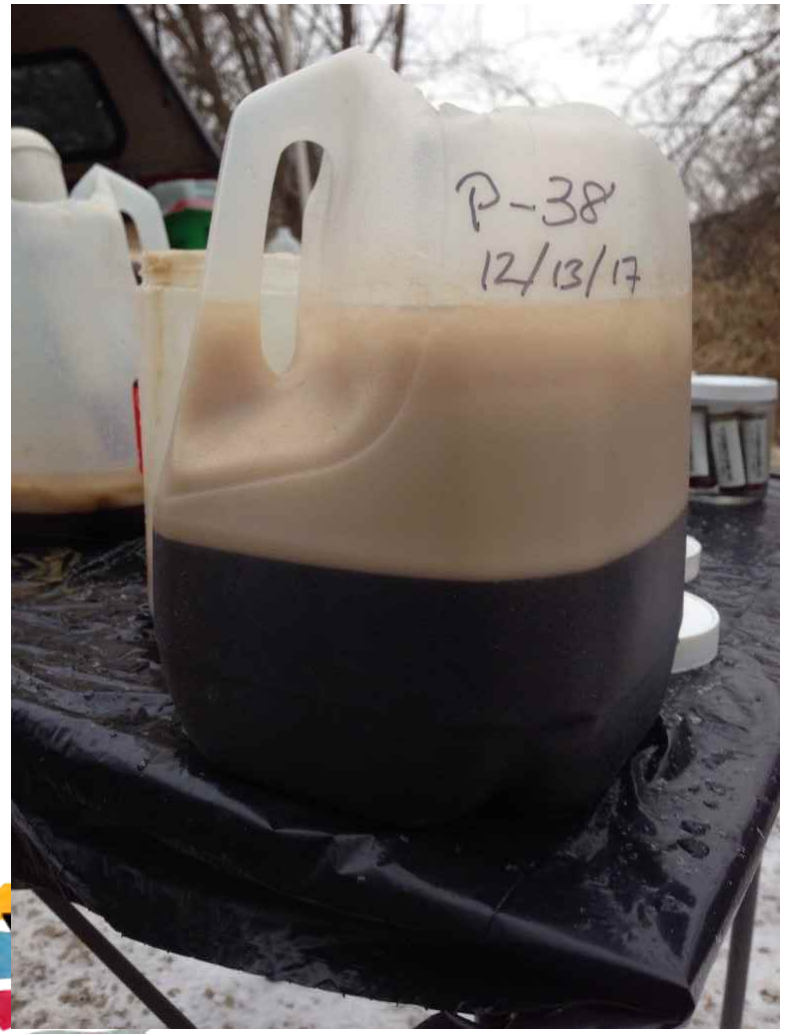
# Lithostratigraphy
# Schematic Cross-Section



# Schematic Contaminant Distribution



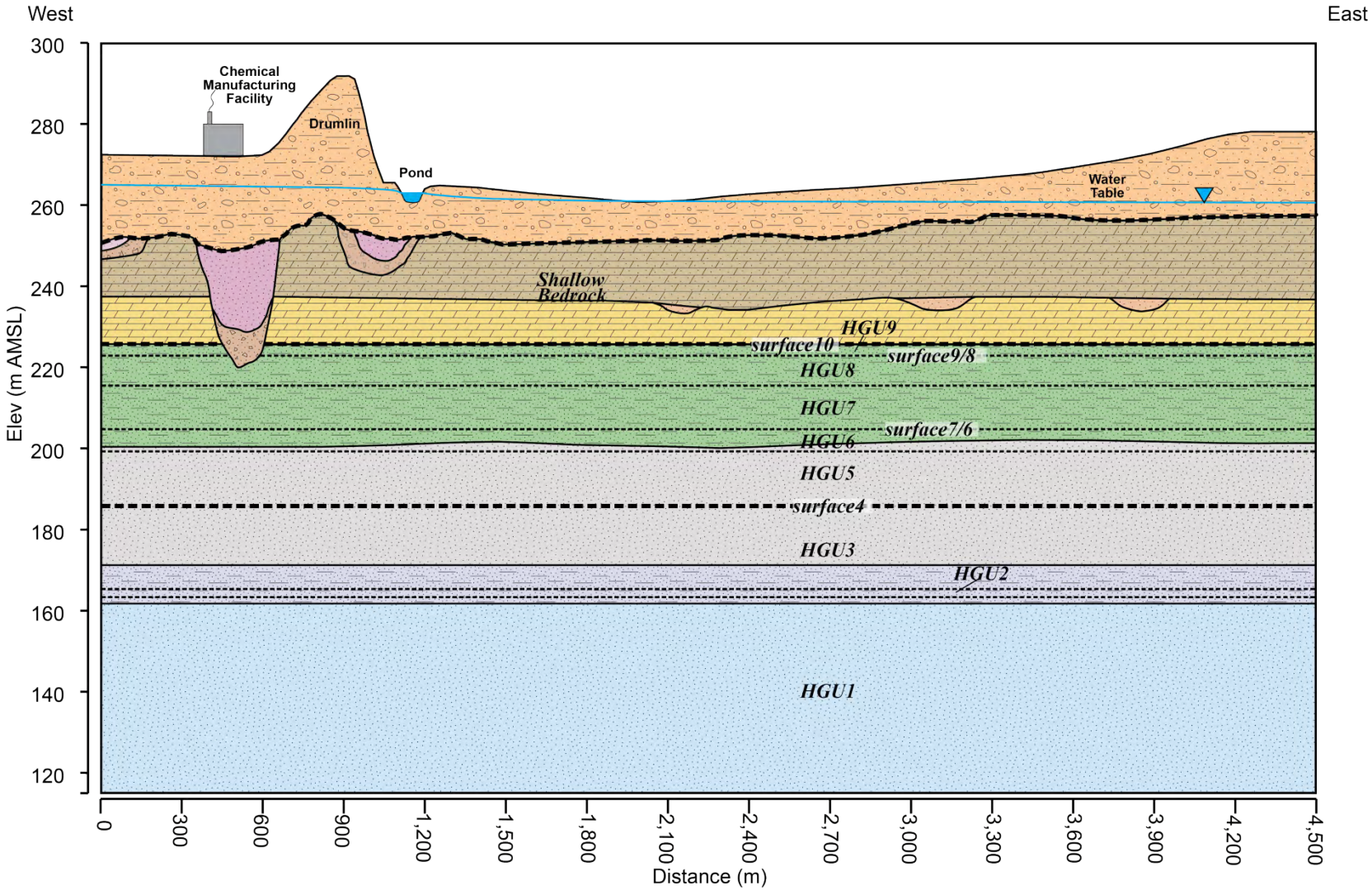
# Complex Mixture of Organic Contaminants Aged in the Subsurface for Over 50 Years



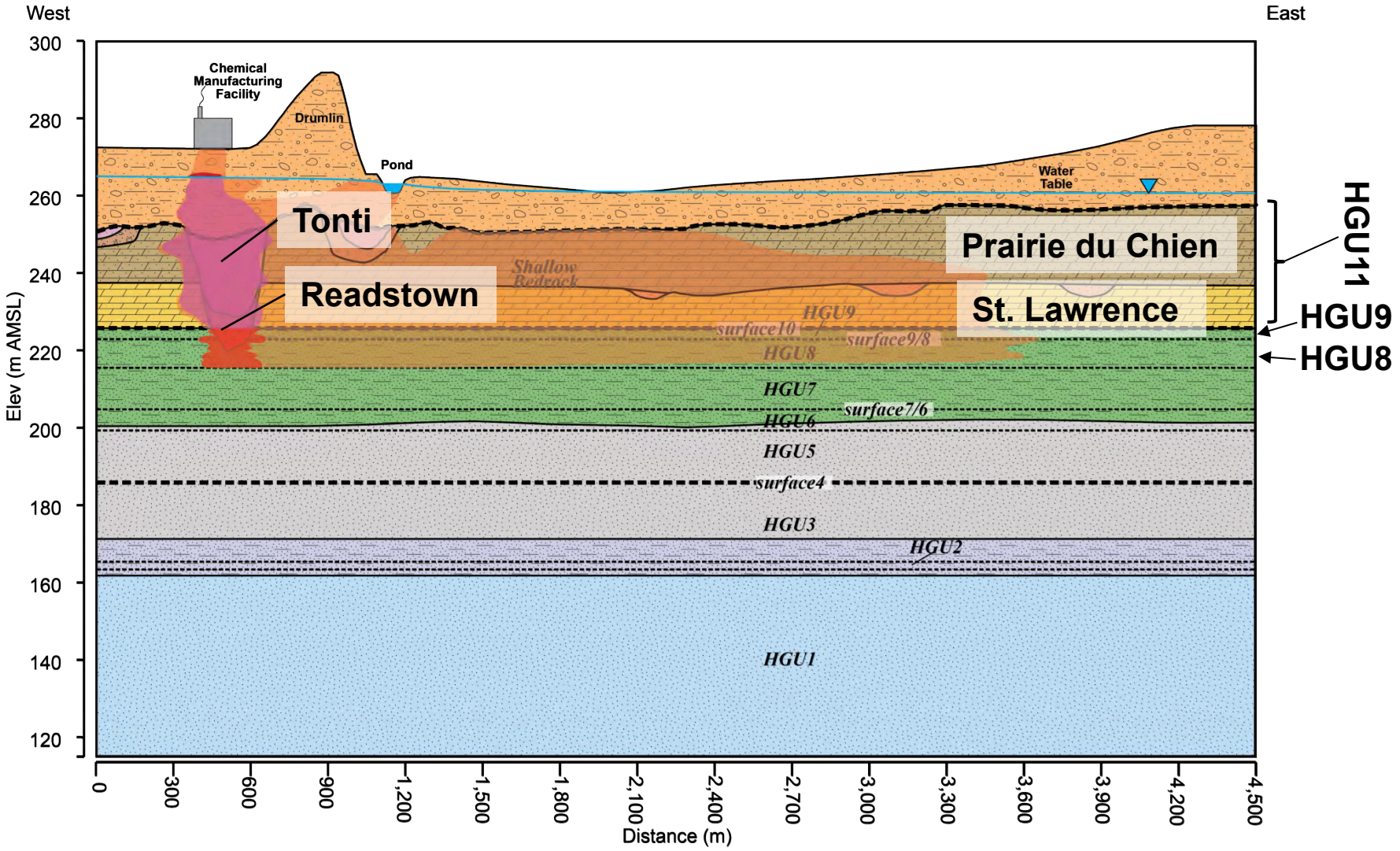

Chlorinated solvents
Benzene, toluene, xylenes
Ketones

Mixture is a *DNAPL*
Dense Non-aqueous Phase Liquid

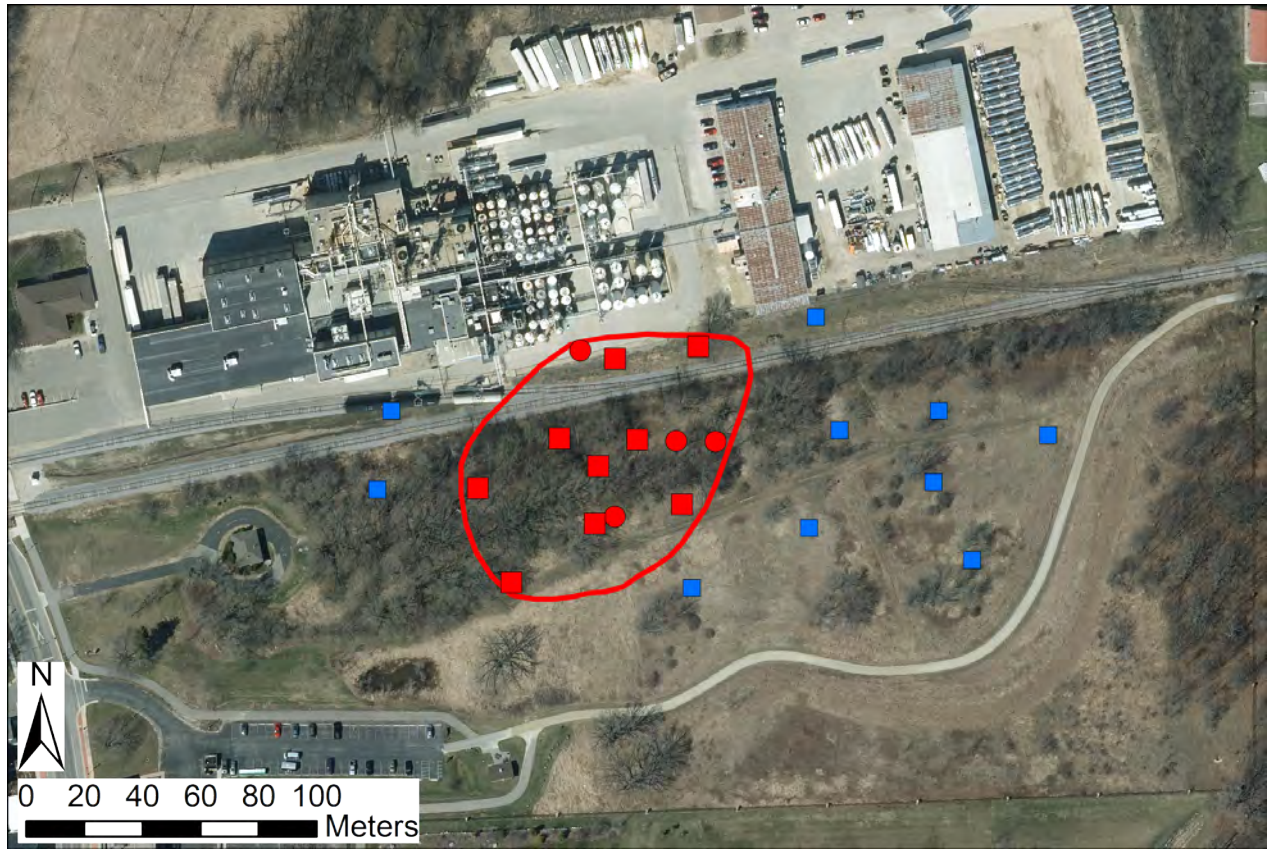
# Bedrock Hydrogeologic Unit Nomenclature



# Bedrock Hydrogeologic Unit Nomenclature



# DNAPL Pumping 1999-2002




Removed ~ 34,000 L of DNAPL

No pumpable DNAPL

Pumpable DNAPL

HSI GeoTrans 1998
HSI GeoTrans 1999
GeoTrans 2000
GeoTrans 2001
GeoTrans 2003

# Research Questions

- How is the mass distributed spatially and between phases (dissolved, sorbed, NAPL)?
- How has the source zone evolved since the DNAPL pumping in the late 1990s?
- What degradation processes are occurring in and near the source zone?

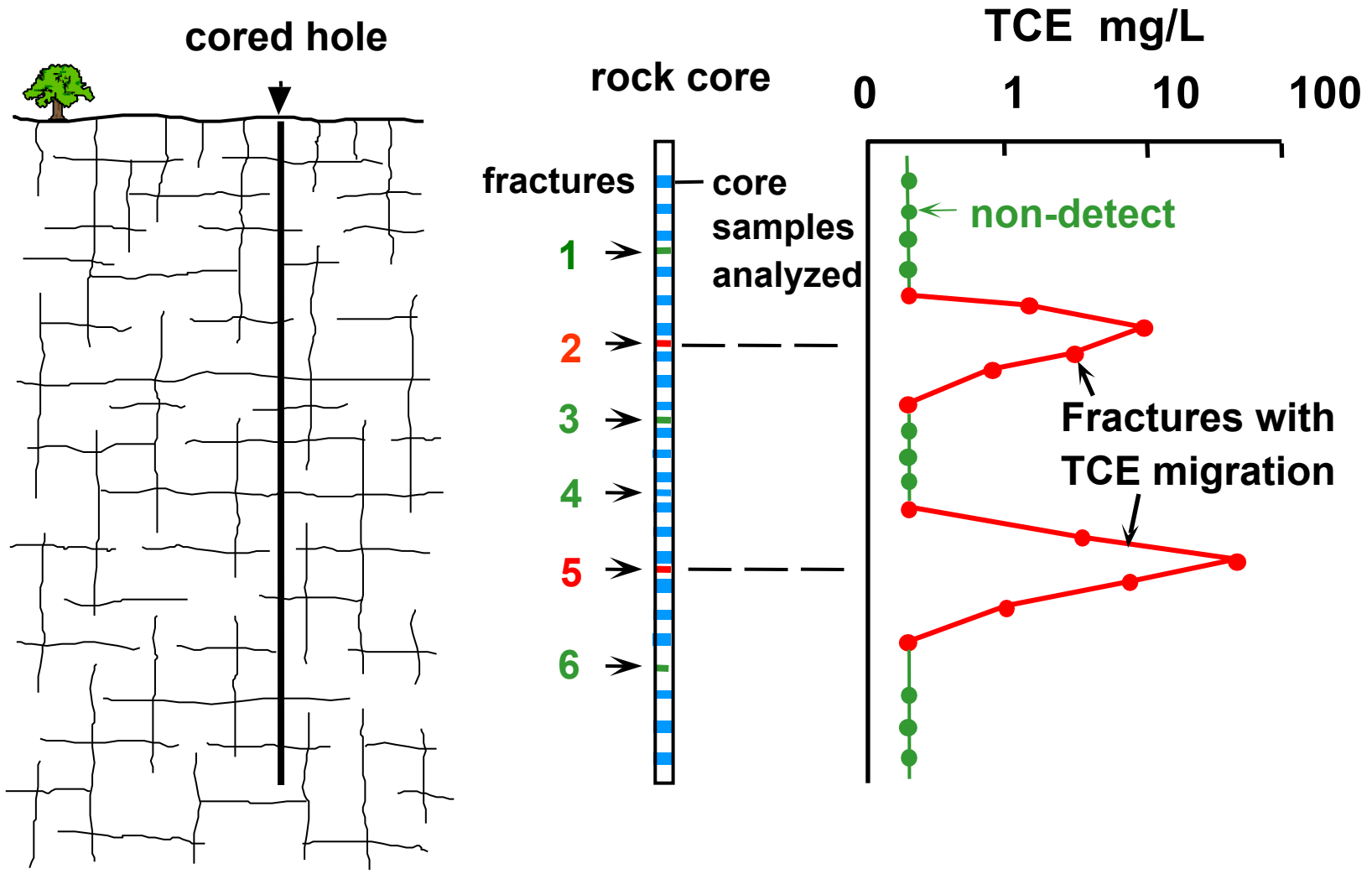
# Approach

Collect high resolution rock core contaminant profiles to characterize the contaminant mass and phase distribution

Use the rock core contaminant profiles to identify depth intervals where DNAPL phase is likely present

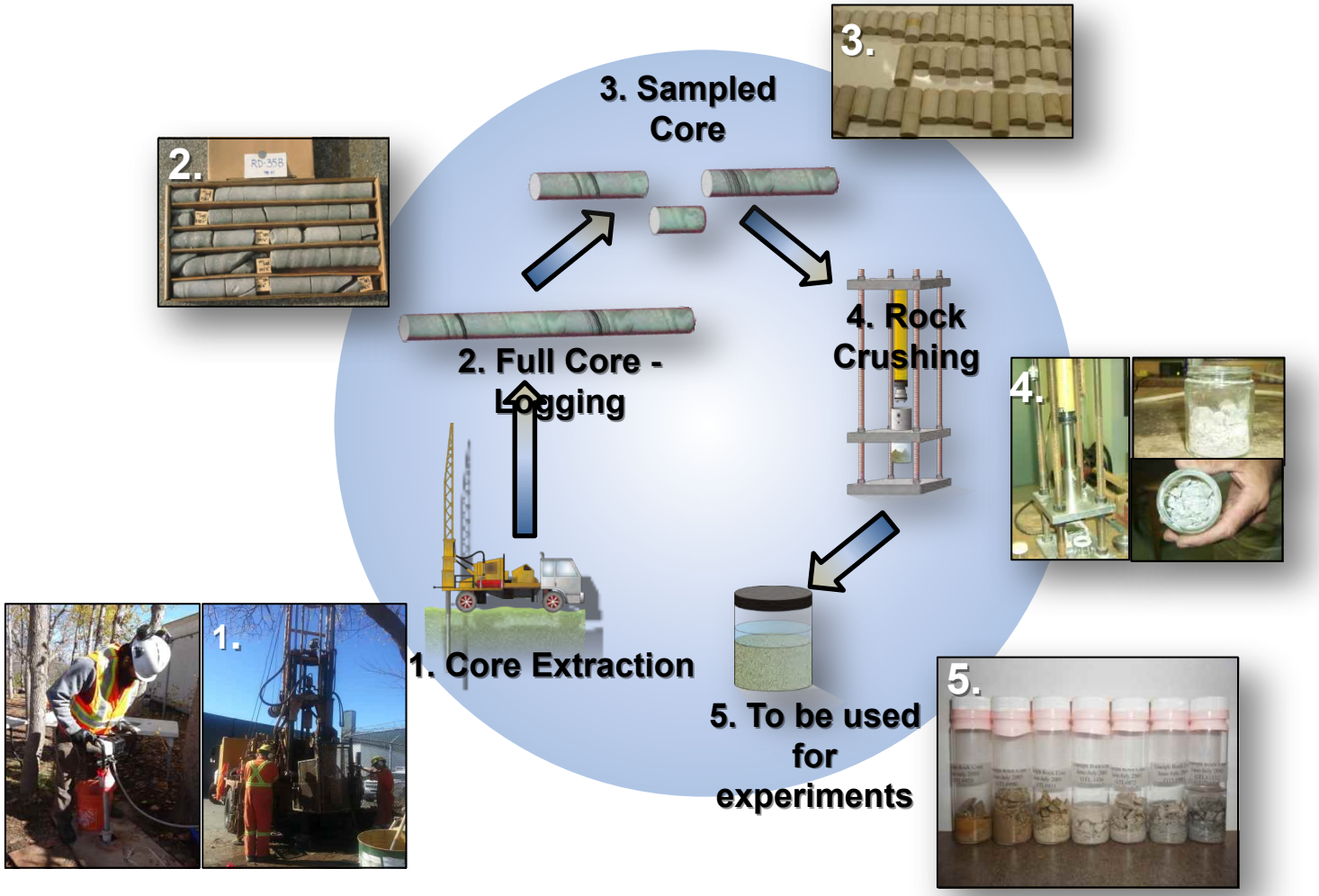
Integrate results from rock core contaminant sampling and multilevel groundwater sampling for a wide variety of parameters to assess degradation processes

# Rock Core Sampling for Total Contaminant Mass



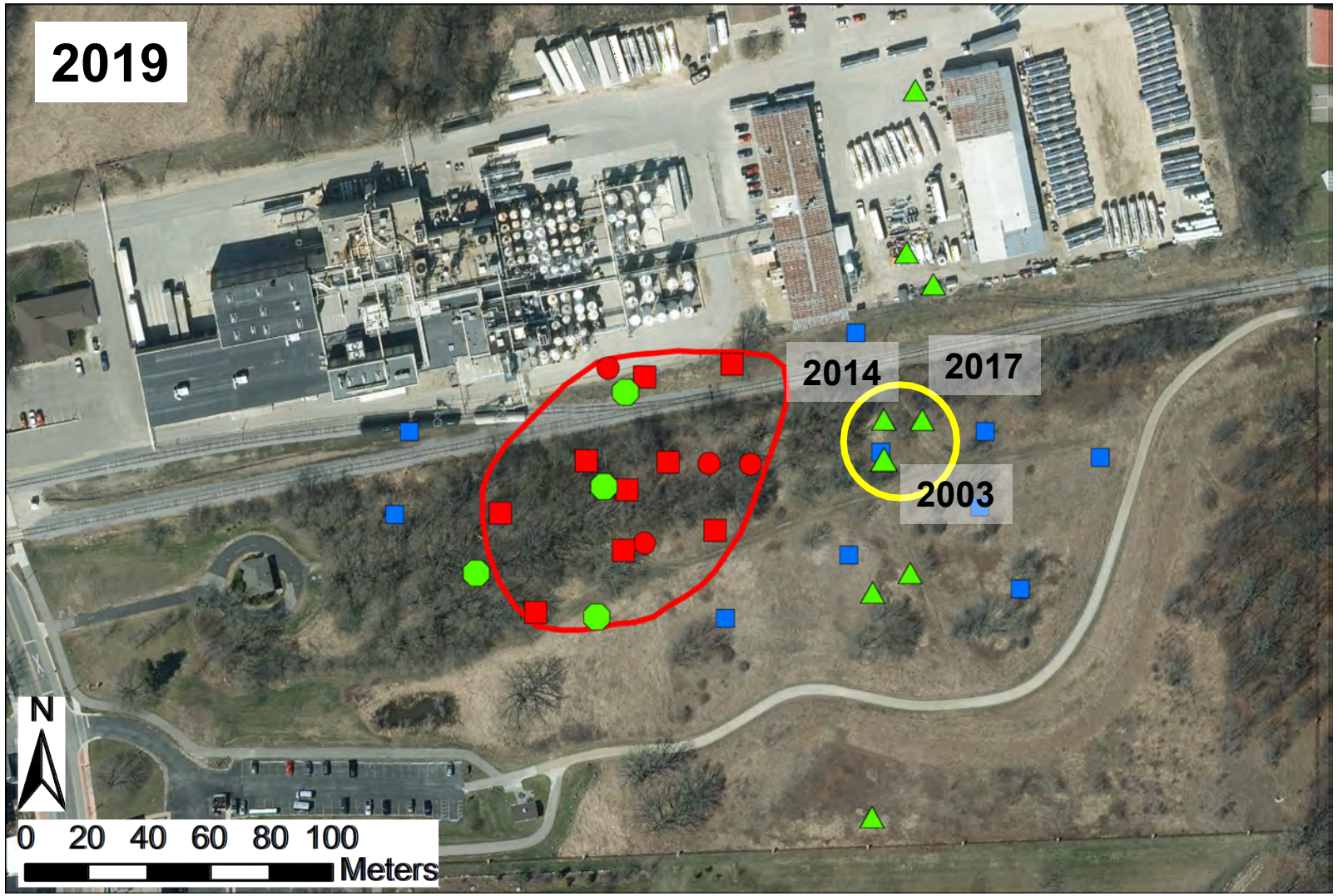

Parker et al. (2012)

# Rock Core Sampling Work Flow




Parker et al. (2012)

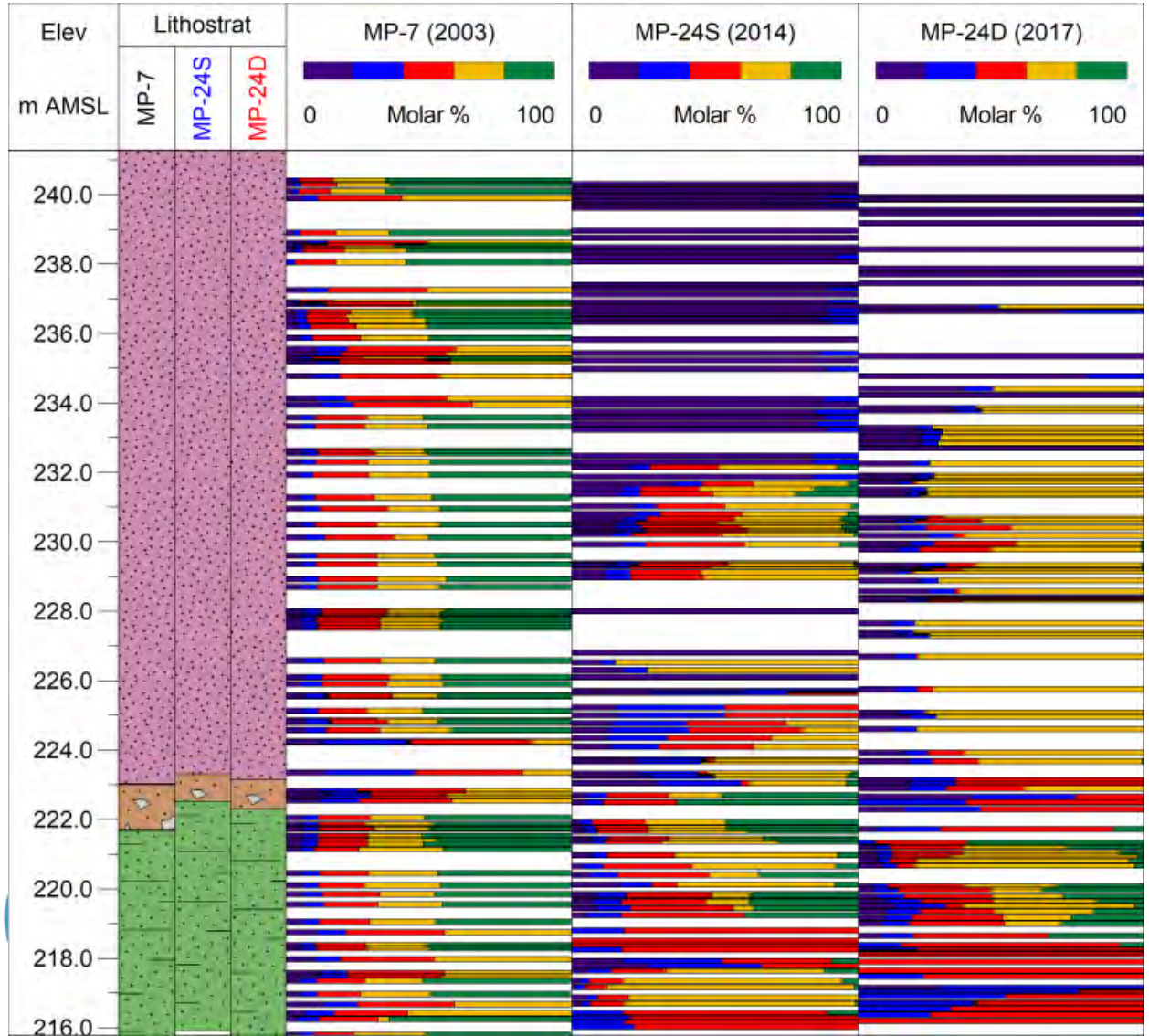
# Collect Rock Core Contaminant Profiles at Multiple Locations Between 2003 and 2019




Core and multilevel system

Core

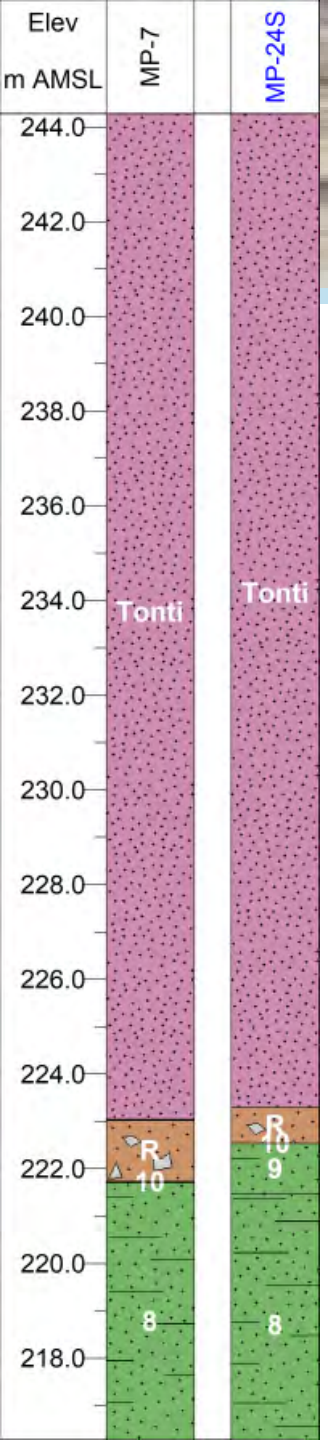
# Temporal Variation of Organic Composition




- Similar composition at all elevations in 2003
- More variability in composition with depth in recent years

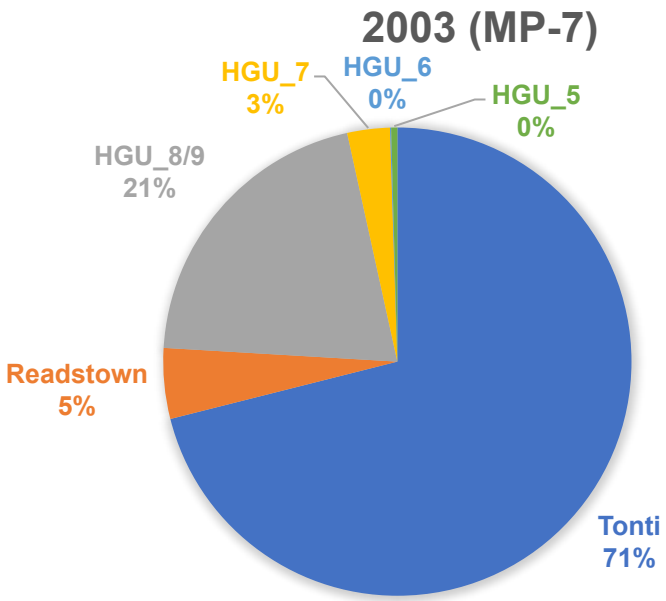
Ethenes
Ethanes
BTEX
Ketones
Methanes

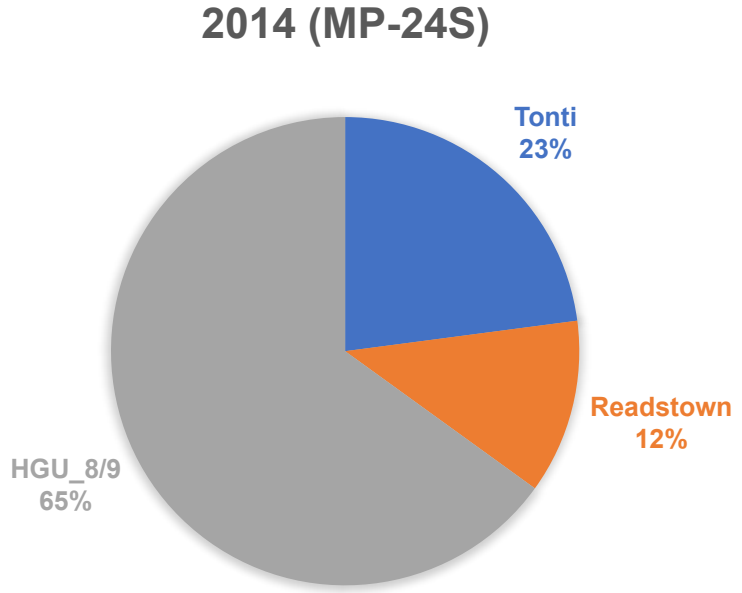
# Vertical Distribution of Contaminant Mass Evolves Through Time (2003-2014)




In 2003 (MP-7), 70% of the molar mass is located within the Tonti Mbr.

In 2014 (MP-24S), 65% of the molar mass is located within HGUs 8 and 9



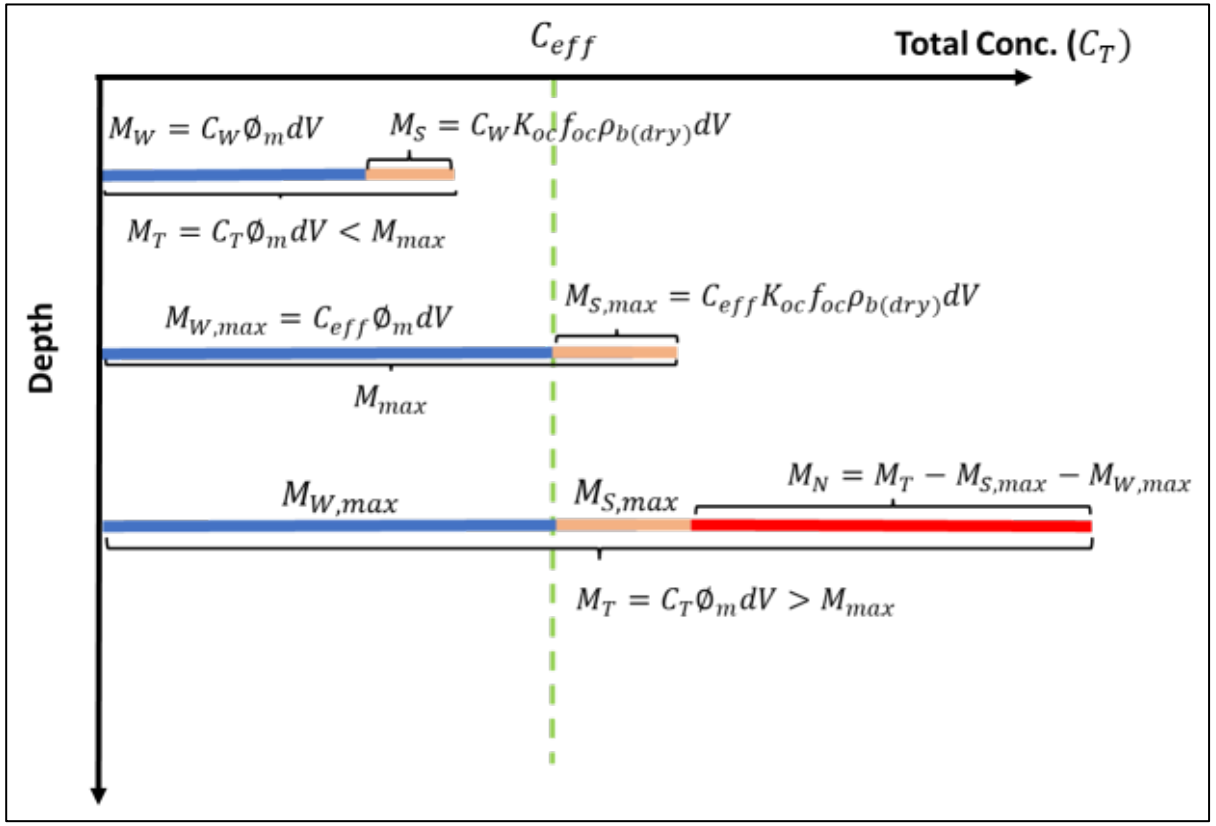
# Contaminant Mass Partitioning Approach

Total contaminant mass from rock core samples is partitioned into the dissolved, sorbed, and NAPL phases

Supports:

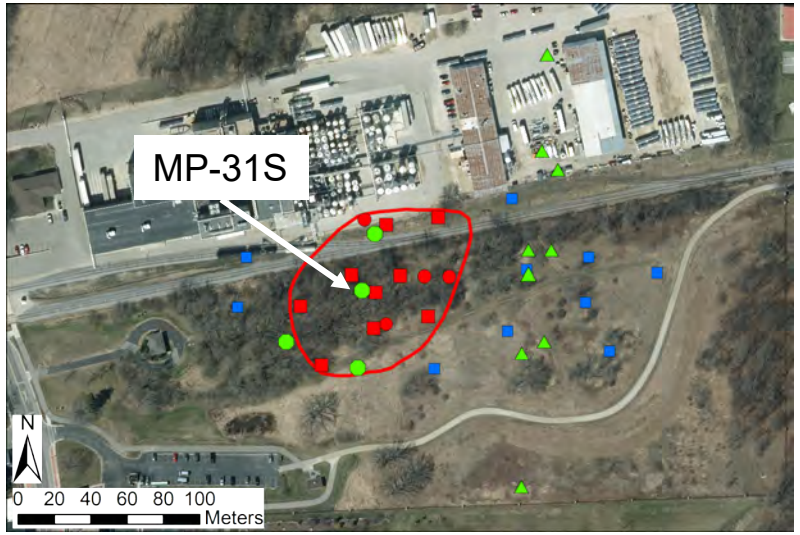
- Characterization of remaining residual and mobile DNAPL

- Estimates of total mass remaining in source zone

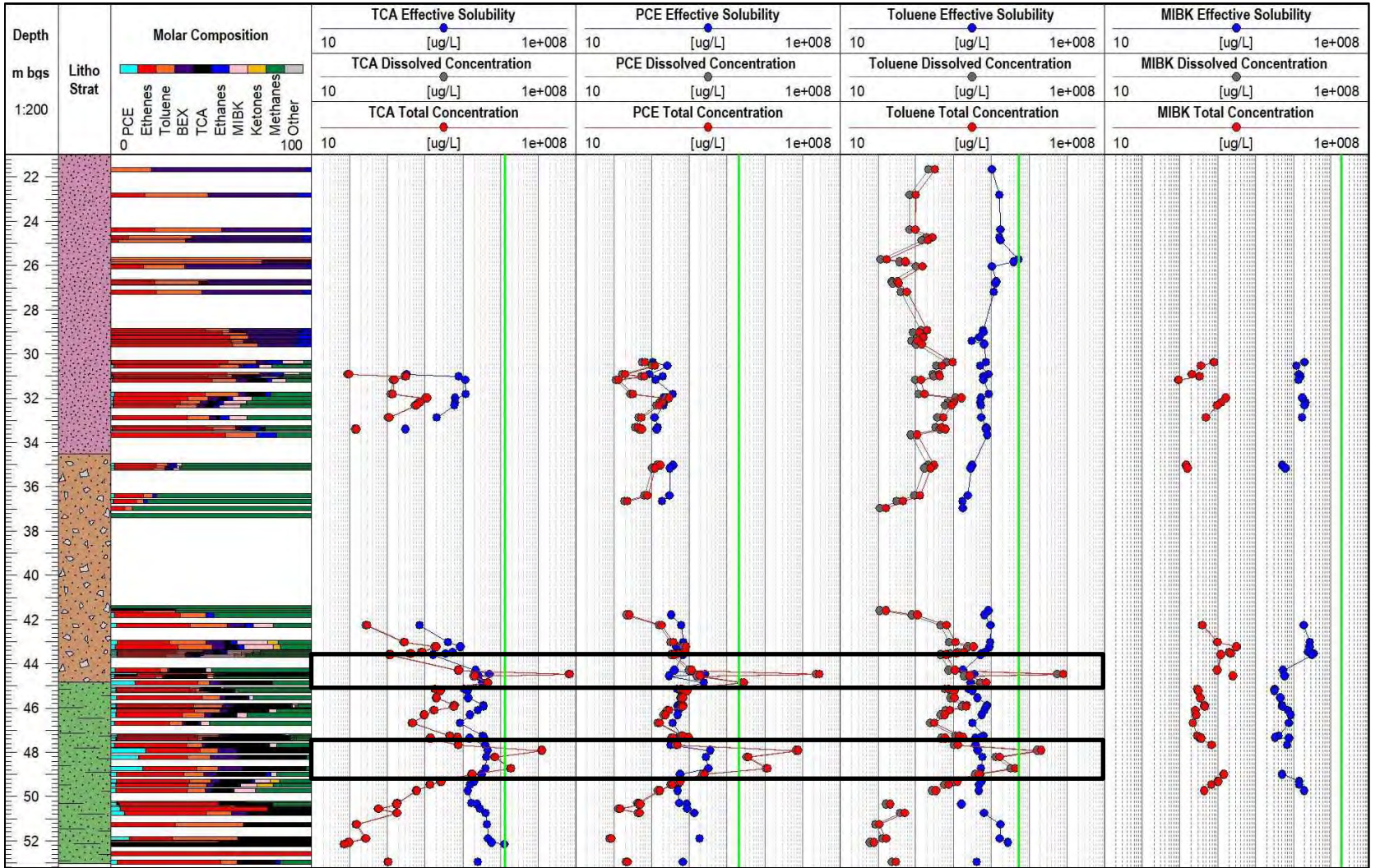


# Porewater Concentrations vs Effective Solubilities

Pore water concentrations higher than estimated effective solubilities suggest the presence of DNAPL

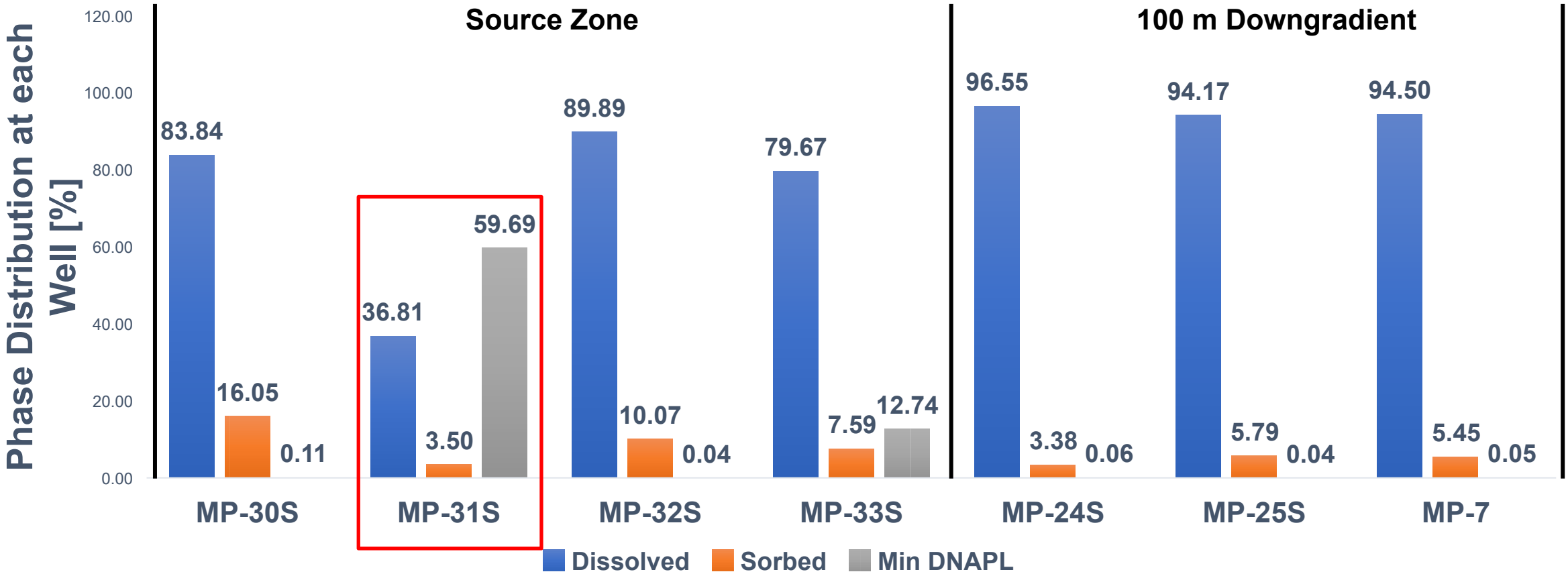



## MP-31S



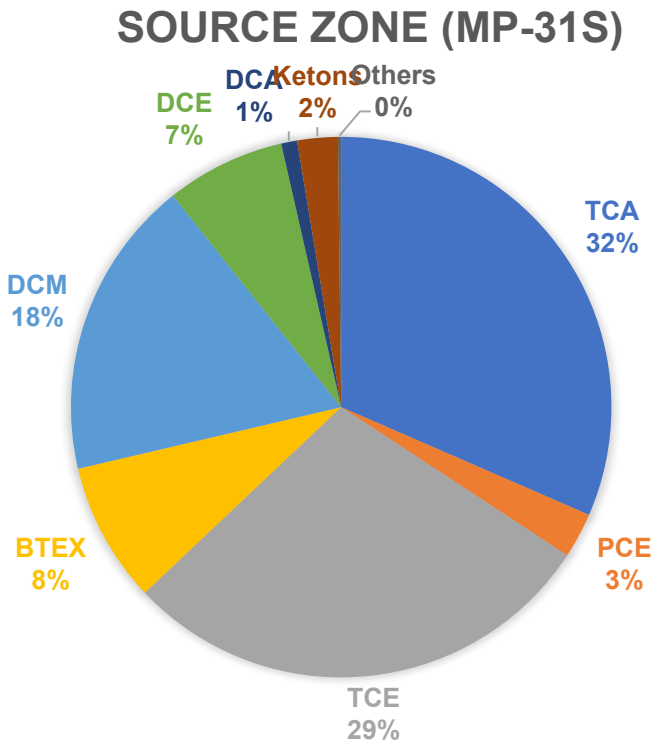
# Phase Distribution

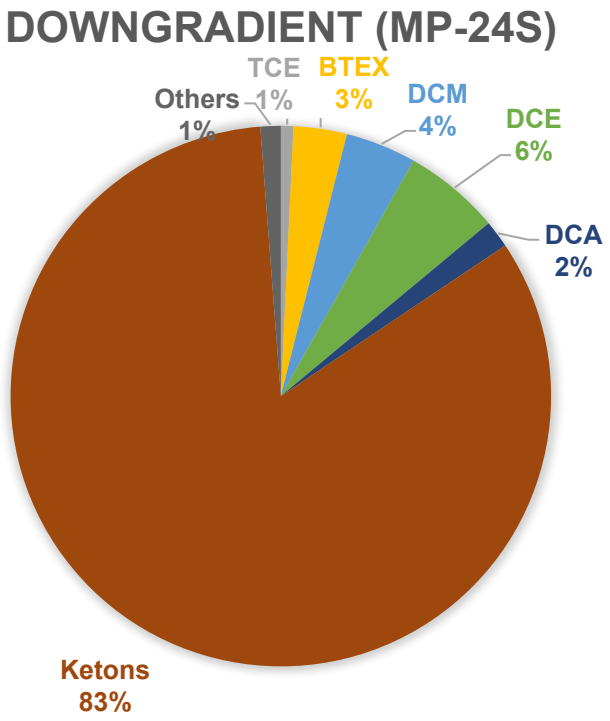
- DNAPL present in the center of the source zone (MP-31S)
- Nearly all mass downgradient of the source zone is in the dissolved phase



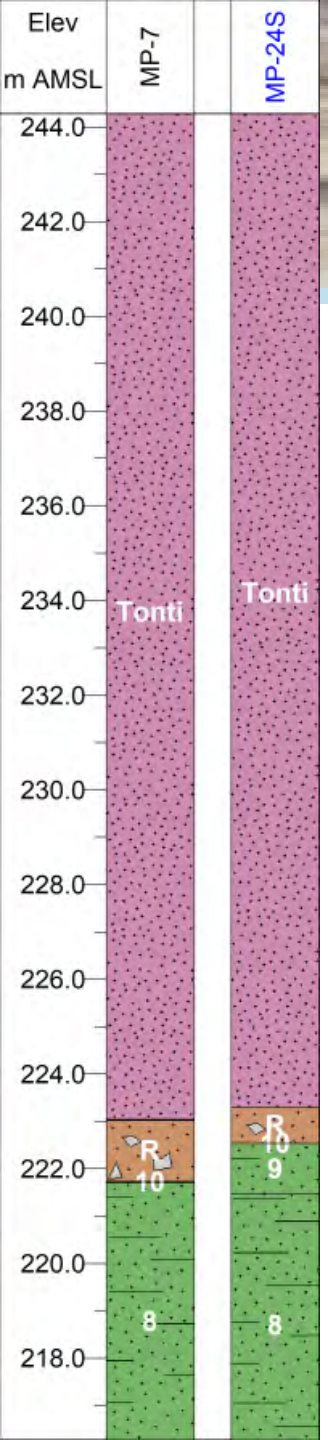
# Porewater Composition in Source Zone vs Downgradient

Pore water composition in source zone is composed of parent organic compounds while downgradient composition is composed primarily of degradation products

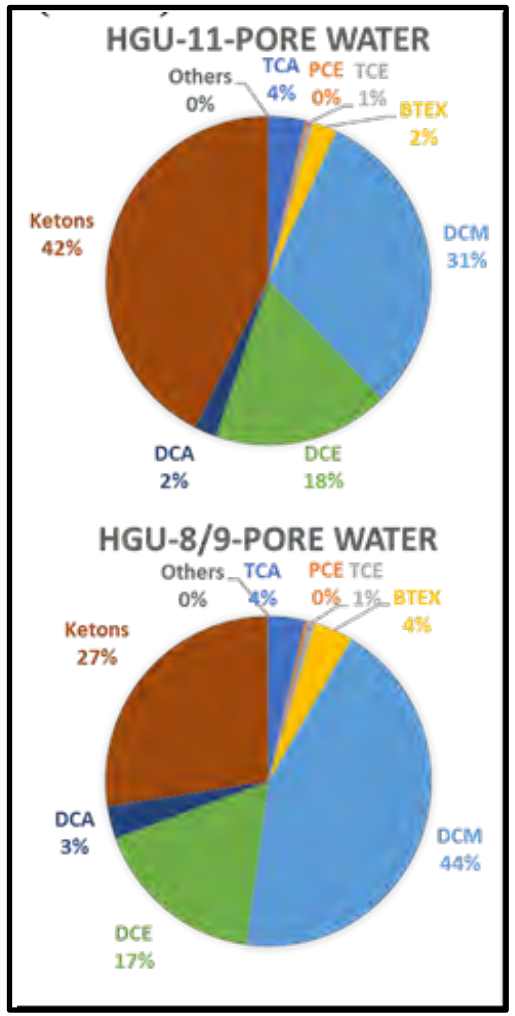


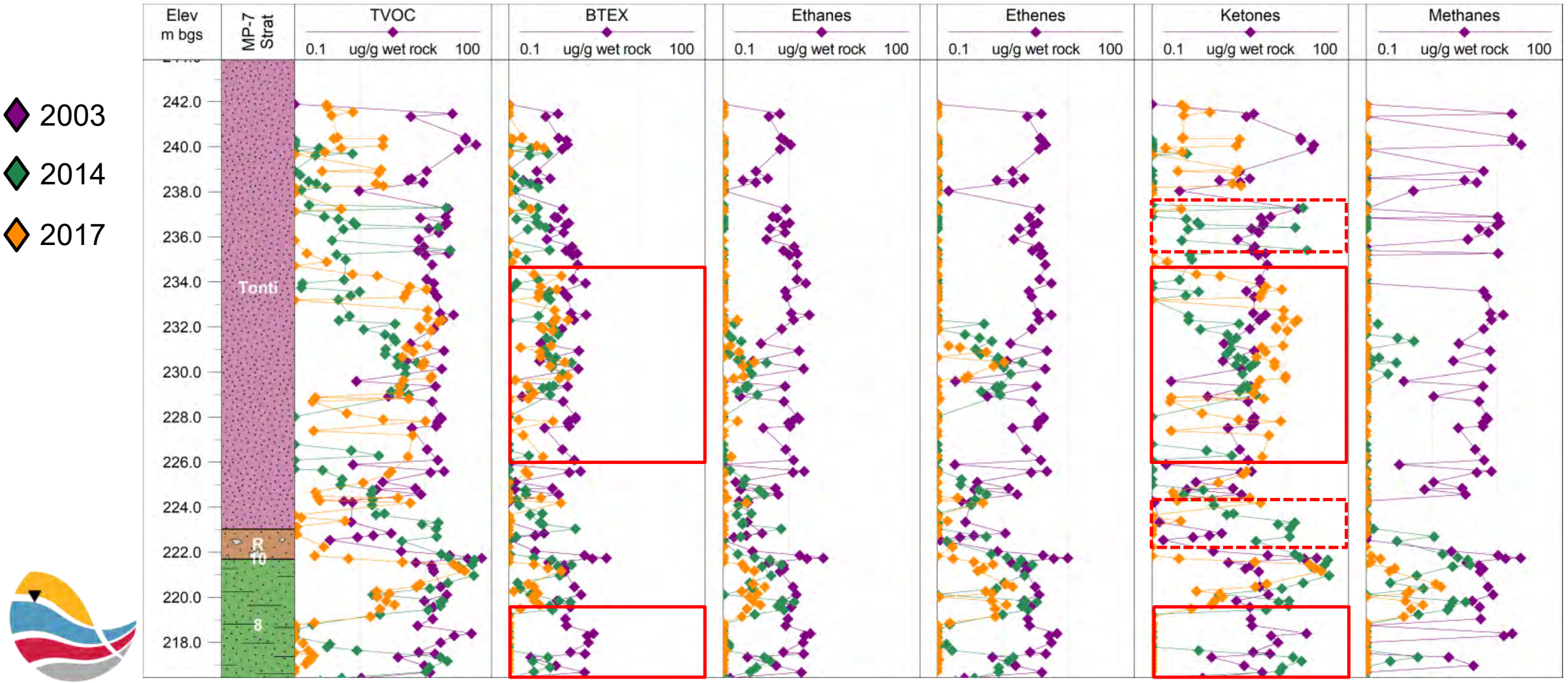
# Are Ketones Being Generated in the Rock Matrix?




2003 (MP-7)

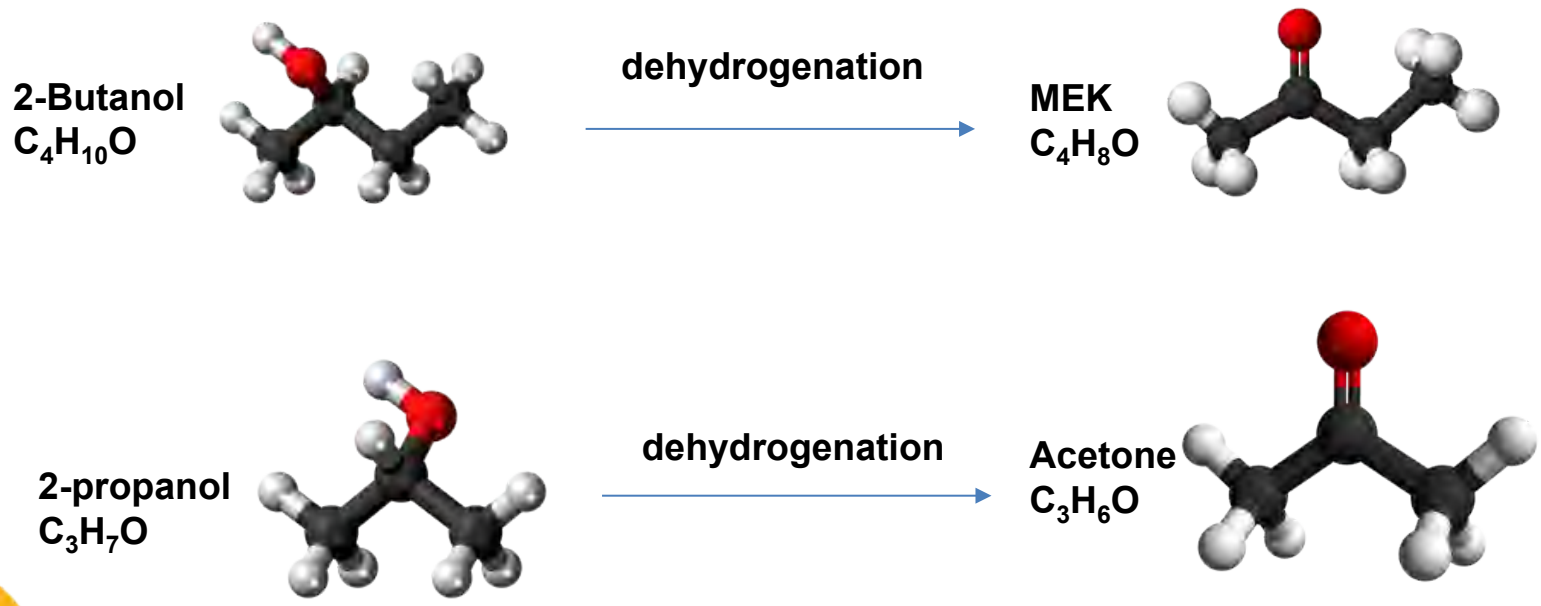


# Increasing Ketone Concentrations in Rock Matrix Through Time



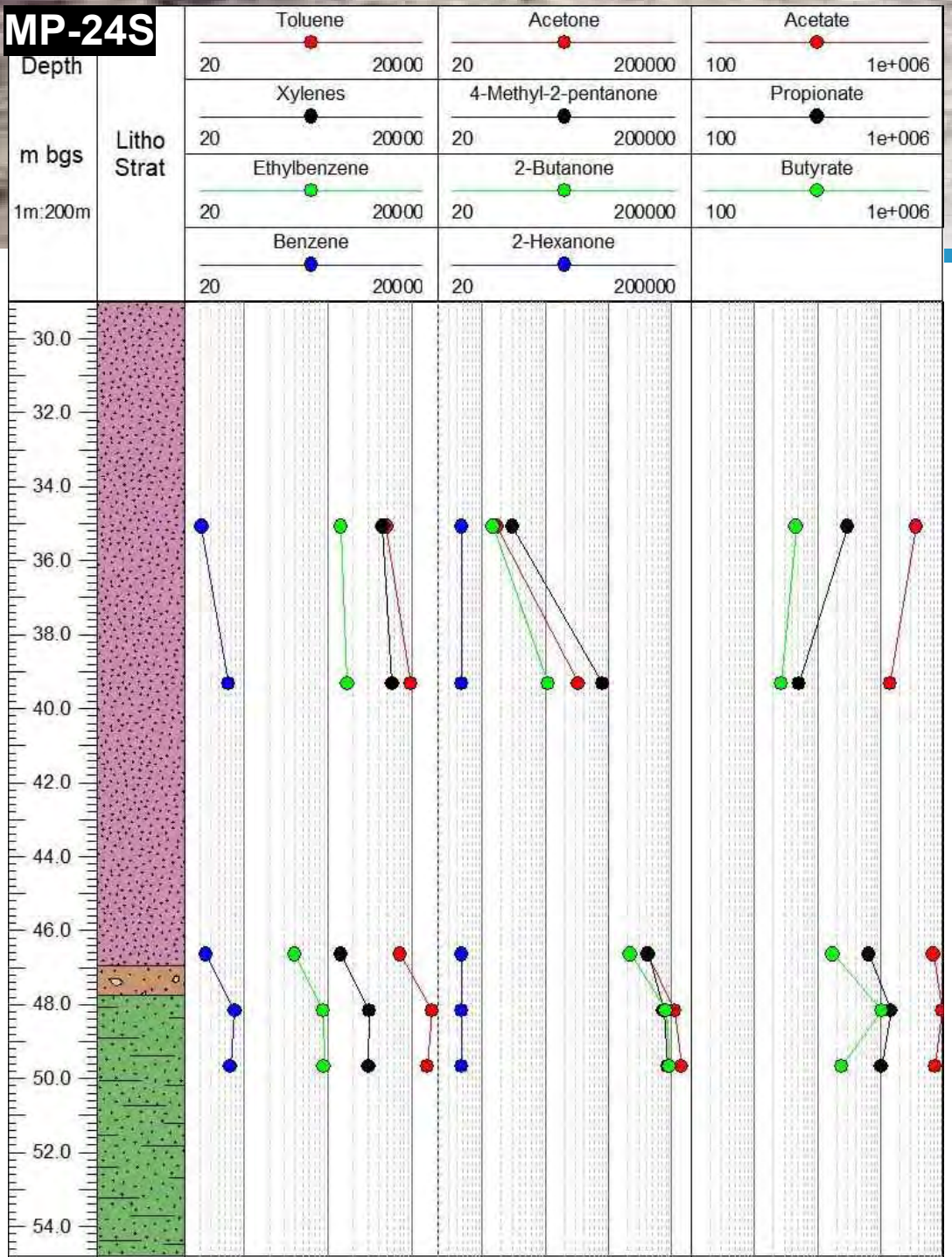
# Possible Reaction Pathways for Ketone Generation

- Fermentation of Toluene can produce alcohols and fatty acids
- The alcohols can be converted to ketones through dehydrogenation




| Alcohol | Generated compound |
|---|---|
| Ethanol | Acetate |
| 1-propanol | Propionate |
| 2-propanol | Acetone |
| 1-butanol | Butyrate |
| 2-Butanol | MEK |

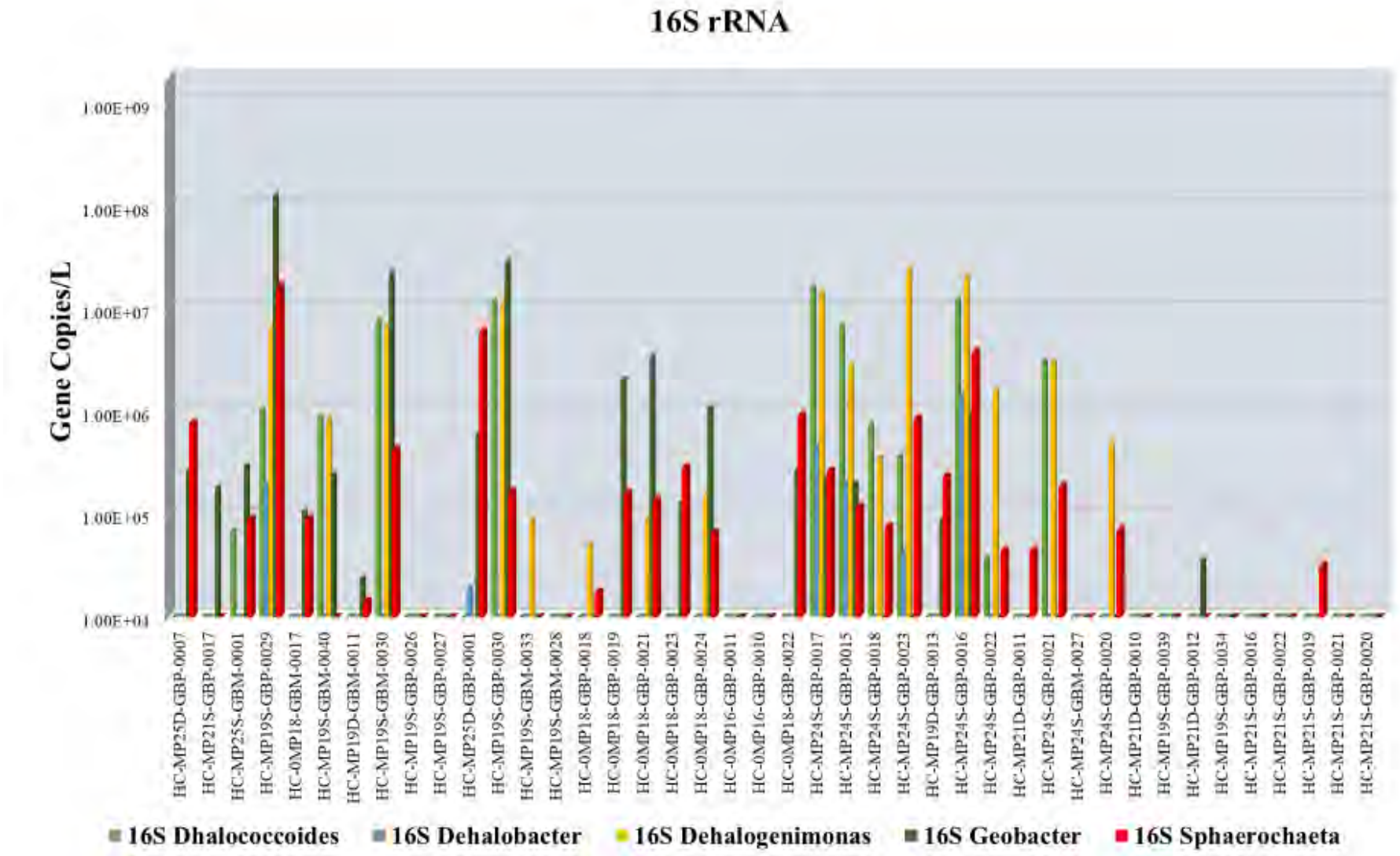
Widdle, 1986; Zellner, 1987




# Fatty Acids in Groundwater Downgradient of Source

- Westbay multilevel system used to collect groundwater samples from select ports
- Analyzed for contaminants of concern and fatty acids
- Fatty acids co-occur with BTEX and ketones

# *Sphaerochaeta*, Iron Reducers, and Dechlorinators are Dominant at the Study Site



# *Sphaerochaeta* May Be Involved in Ketone Generation

Bidzhieva et al. (2018) suggested *Sphaerochaeta* species consume fermentation products (i.e., alcohols) and produce ketones

ISSN 0026-2617, Microbiology, 2018, Vol. 87, No. 6, pp. 757–765. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © S.Kh. Bidzhieva, D.Sh. Sokolova, T.P. Tourova, T.N. Nazina, 2018, published in Mikrobiologiya, 2018, Vol. 87, No. 6, pp. 849–858.

EXPERIMENTAL ARTICLES

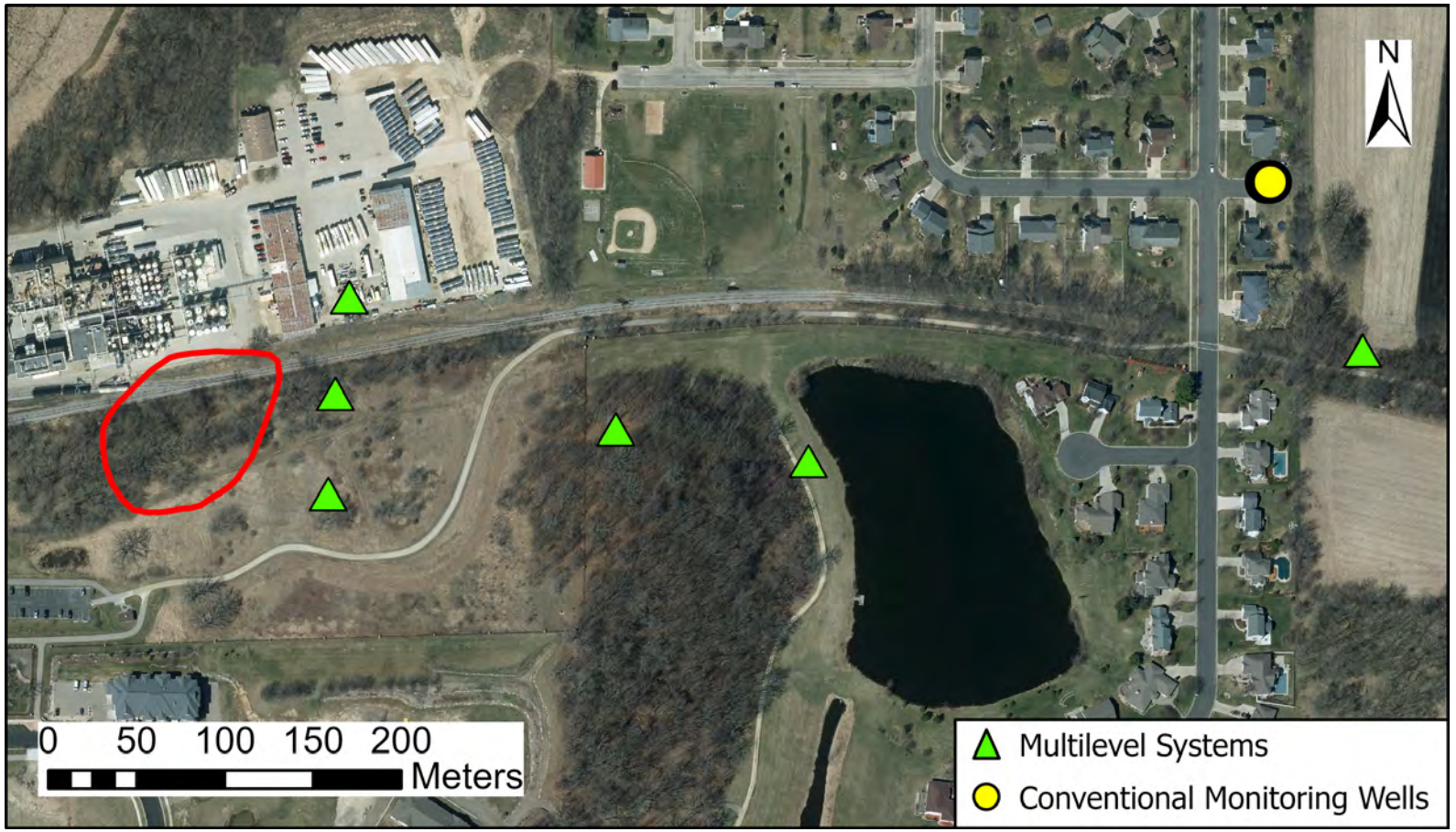
## Bacteria of the Genus *Sphaerochaeta* from Low-Temperature Heavy Oil Reservoirs (Russia)

S. Kh. Bidzhieva[a], D. Sh. Sokolova[a], T. P. Tourova[a], and T. N. Nazina[a, *]
[a] *Winogradsky Institute of Microbiology, Research Center of Biotechnology, Russian Academy of Sciences, Moscow, Russia*
*e-mail: nazina@inmi.ru

Received June 13, 2018

# Further Work Needed to Distinguish Ketones as Degradation Products

- 30 samples collected from 6 multilevel systems and 2 conventional wells
- Fatty acid/alcohols analysis
- Ketone CSIA analyses (TBD)
- Microbial analyses to evaluate possible pathways for ketone generation



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- Groundwater sampling by Glen Hook and Jessica Bulova
- Microbial analyses by Frank Löeffler and Cindy Swift (University of Tennessee)

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Westbay Instruments

# Thank You

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