Can Autonomous, High Data Density Sensors Save Time & Costs in Adaptive Management of Hydrocarbon Impacted Sites?

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Saskatoon, SK

remediation technologies symposium 2023

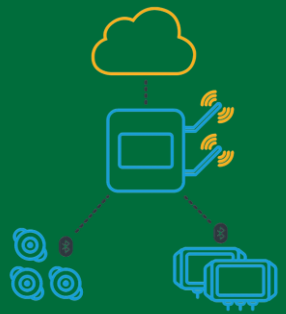
13 October 2023

EMS: Who we are and what we do

Environmental Material Science **(EMS)** has **10 years of R&D of real time monitoring** to improve understanding: **1) contaminated sites**, then **2) soil health and VRT optimization**, now **3) GHG emissions monitoring**.

- Technology can be utilized across all industry sectors

Real-Time Measurement



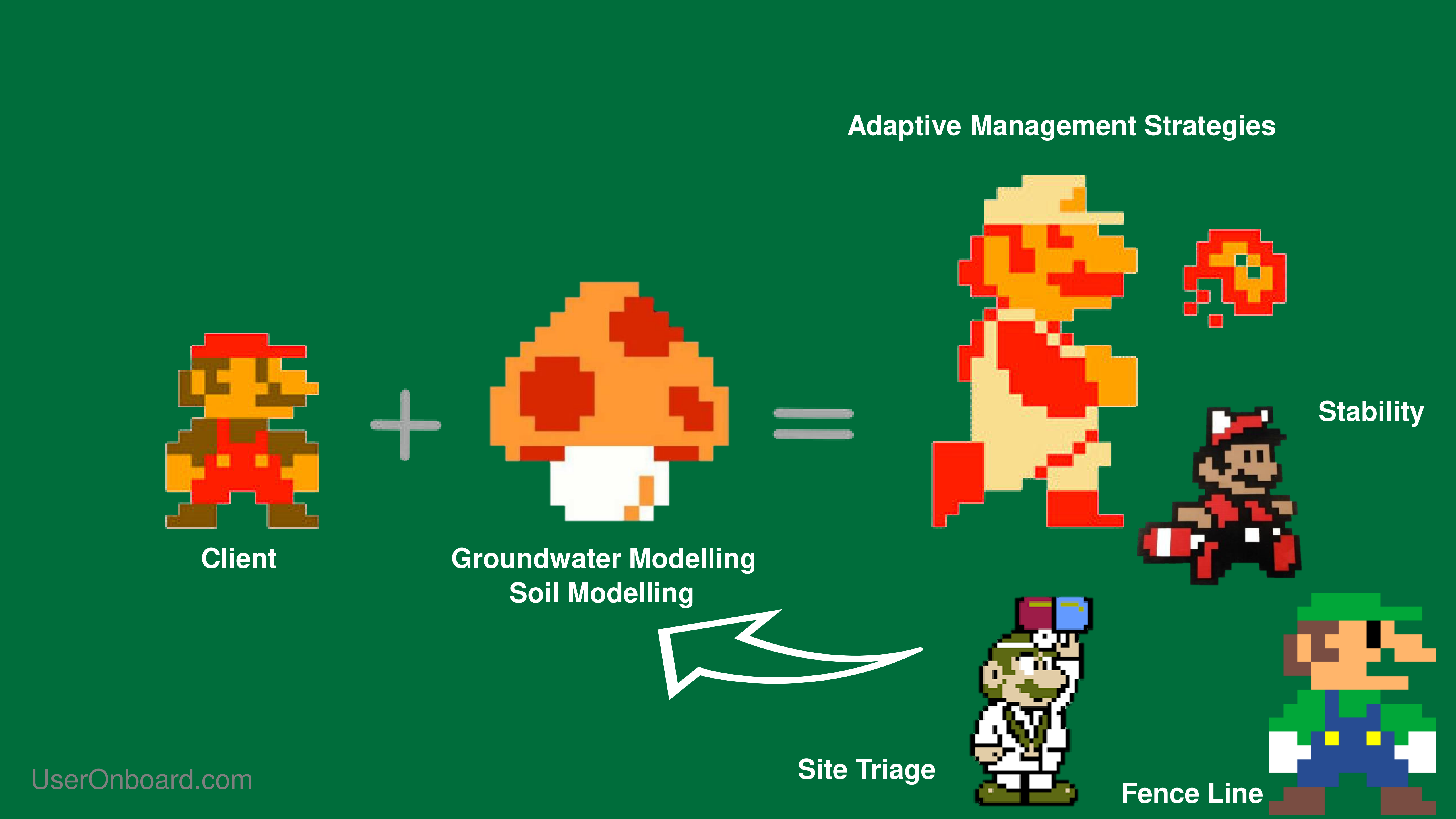
Quantify mass reduction with fringe placement

Accuracy

Year-round tracking = more robust site picture than PIT

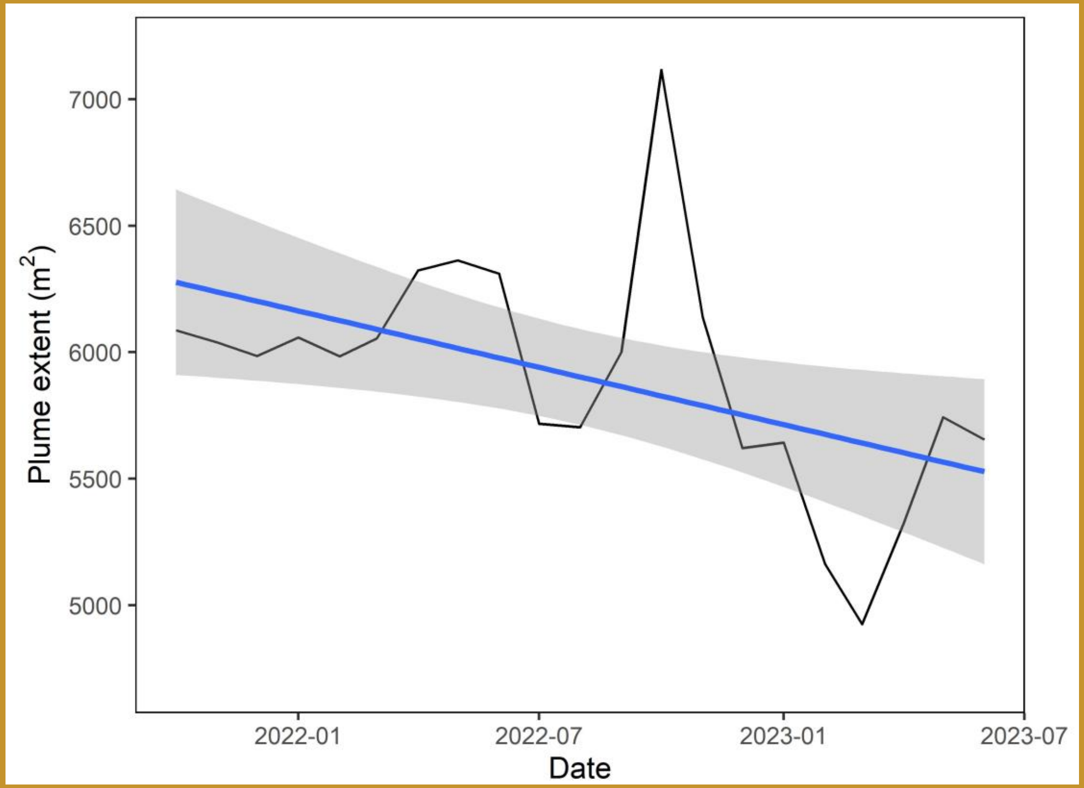
Engagement

Real-time data facilitates better engagement with regulators

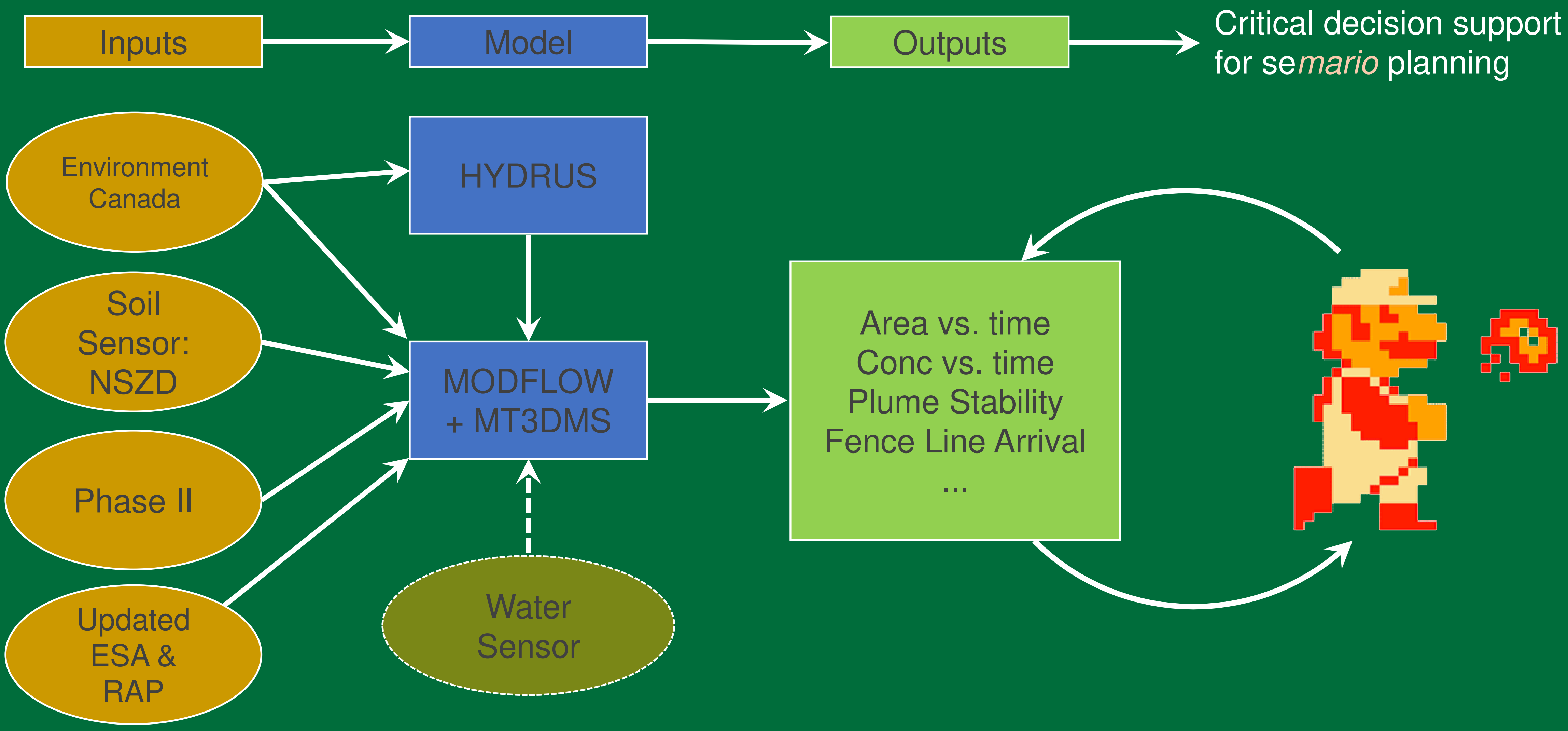


Adaptive Management Strategies
Stability
Client
Groundwater Modelling
Soil Modelling
Site Triage
Fence Line
UserOnboard.com

Groundwater and Soils tell us two different facets of a contaminated site



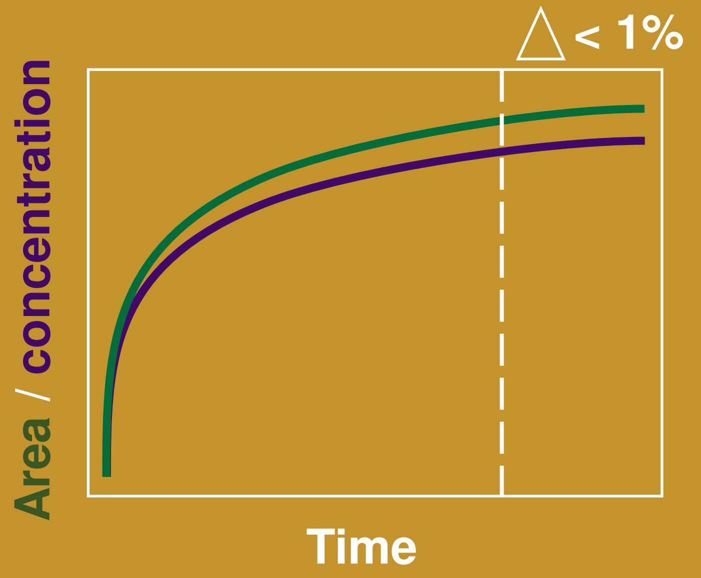
Groundwater Modeling (Benzene)



Groundwater Modeling (Benzene)

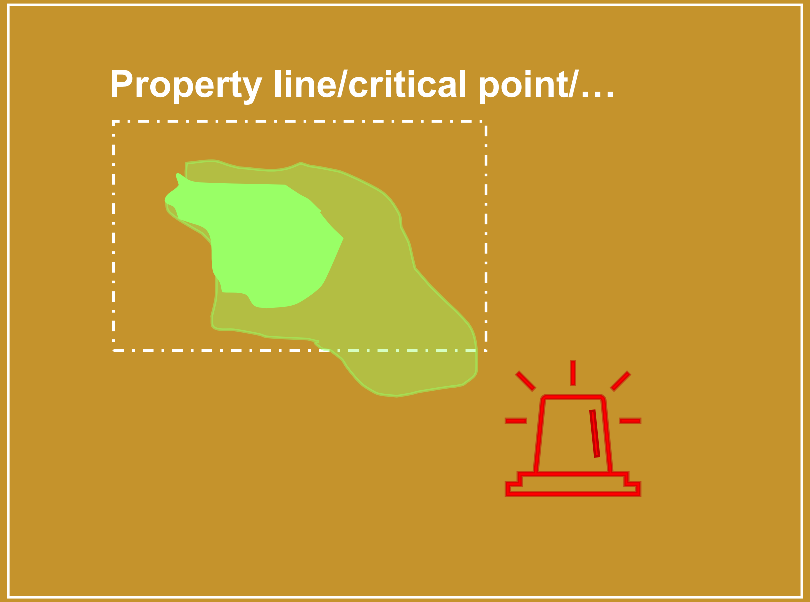
Plume Stability

When does the plume stop expanding and/or moving?



Fence Line Arrival

Does the plume hit a critical receptor?



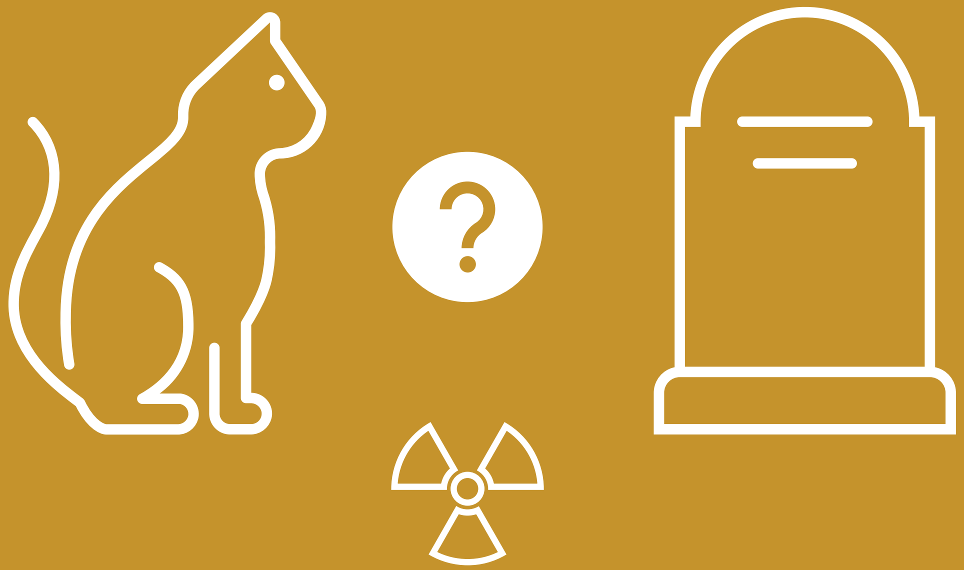
Groundwater Modeling (Benzene)

THREE scenarios

- Do nothing
- NSZD
- Biostimulation

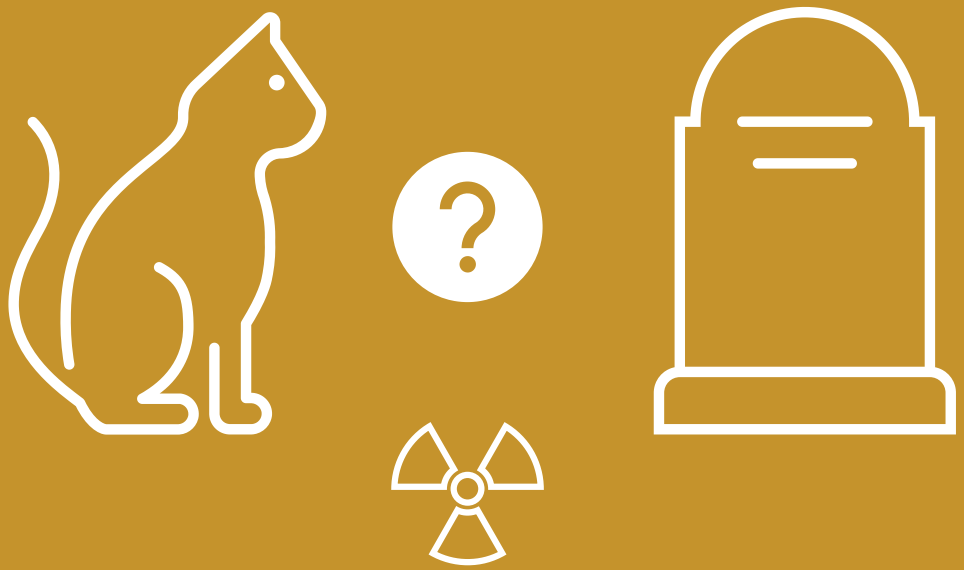
Schrödinger’s Cat

Physics

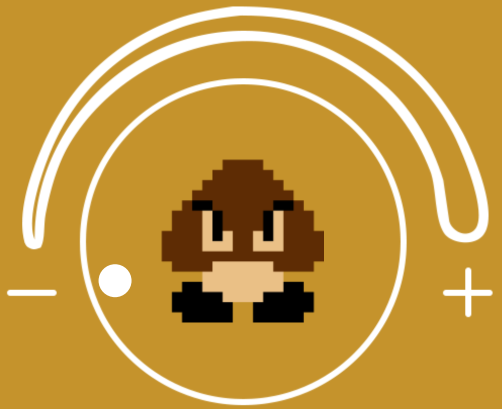


Schrödinger's ~~Cat~~ Goomba (NSZD)

Physics

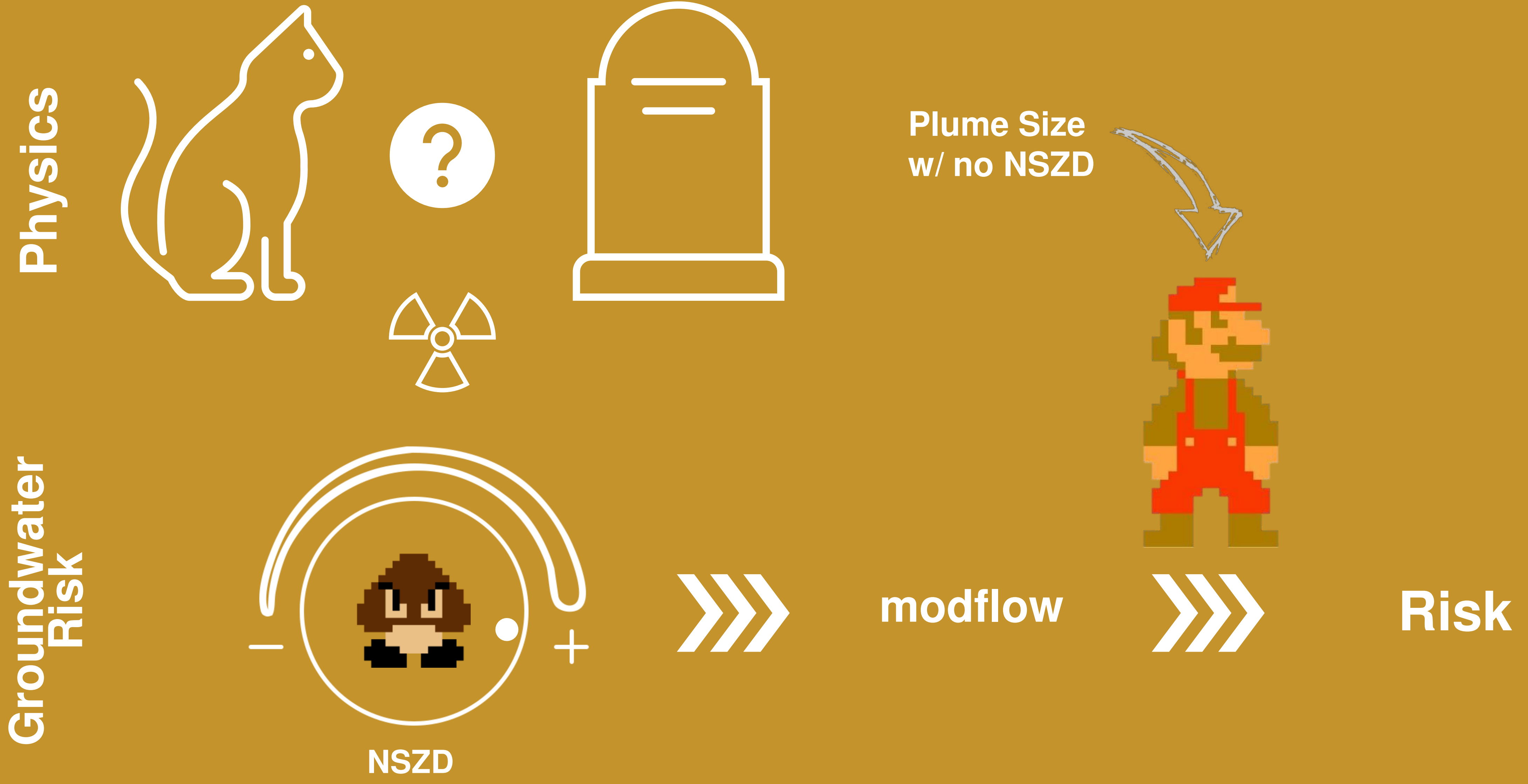


Groundwater Risk



NSZD

Schrödinger's ~~Cat~~ Goomba (NSZD)



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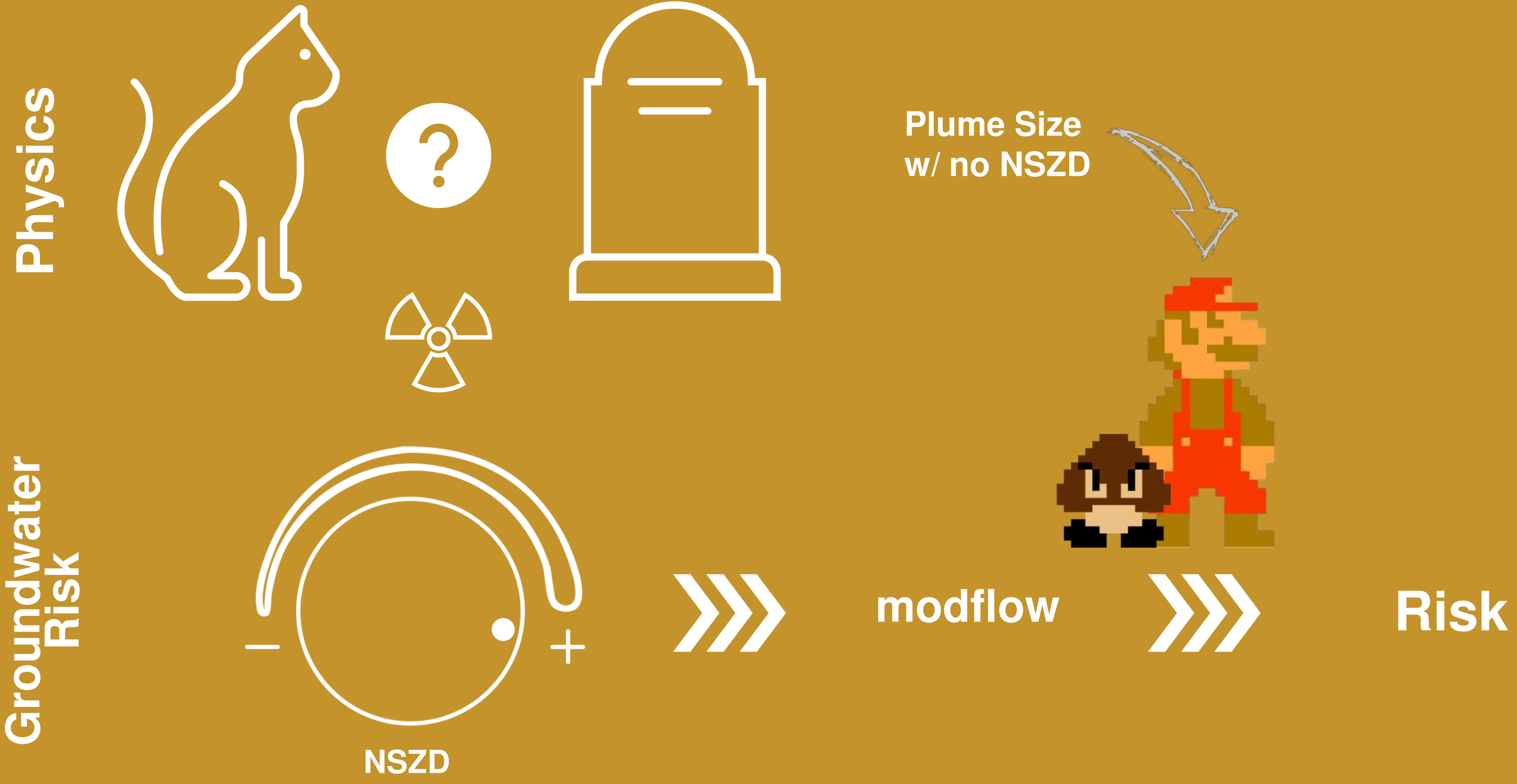
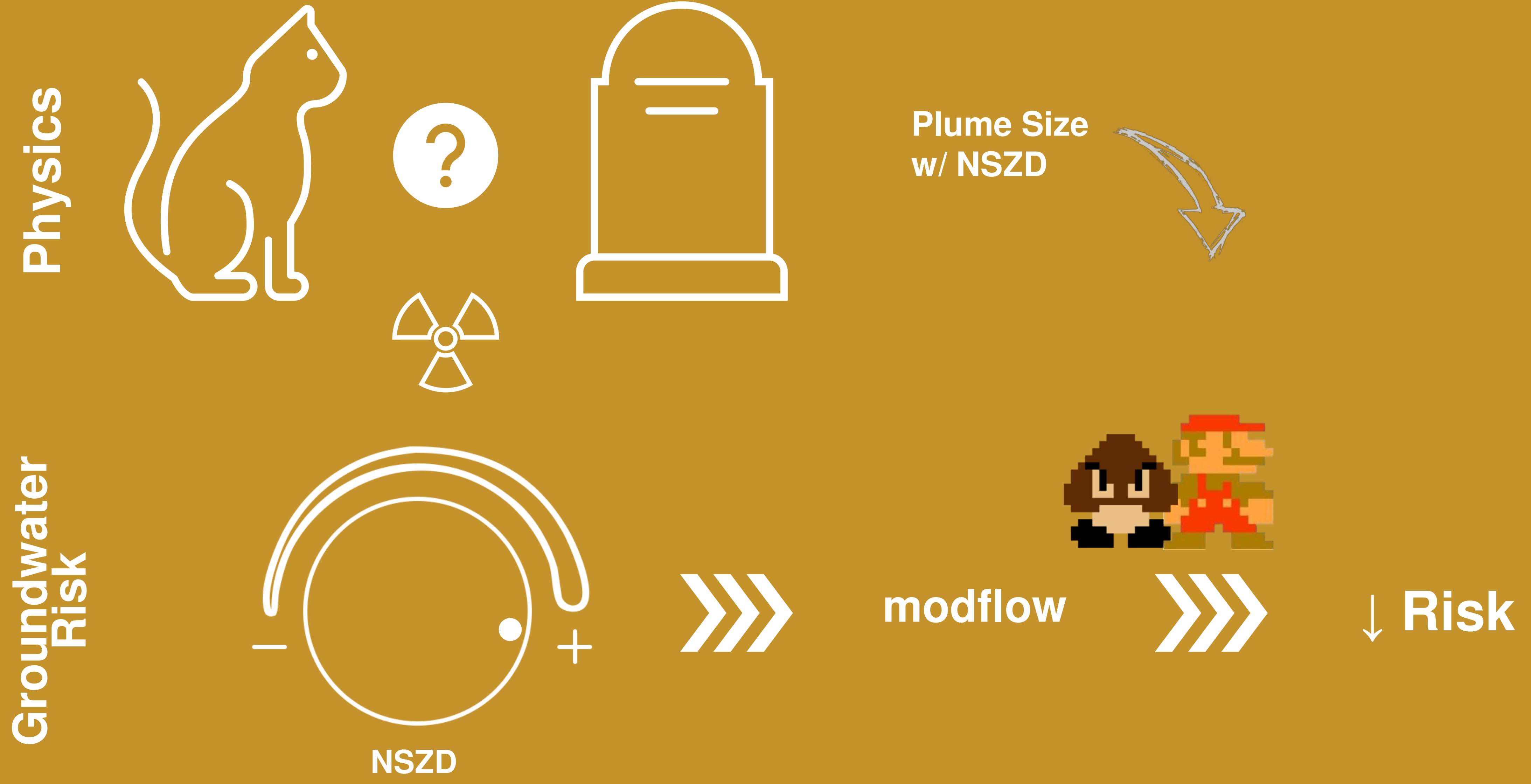
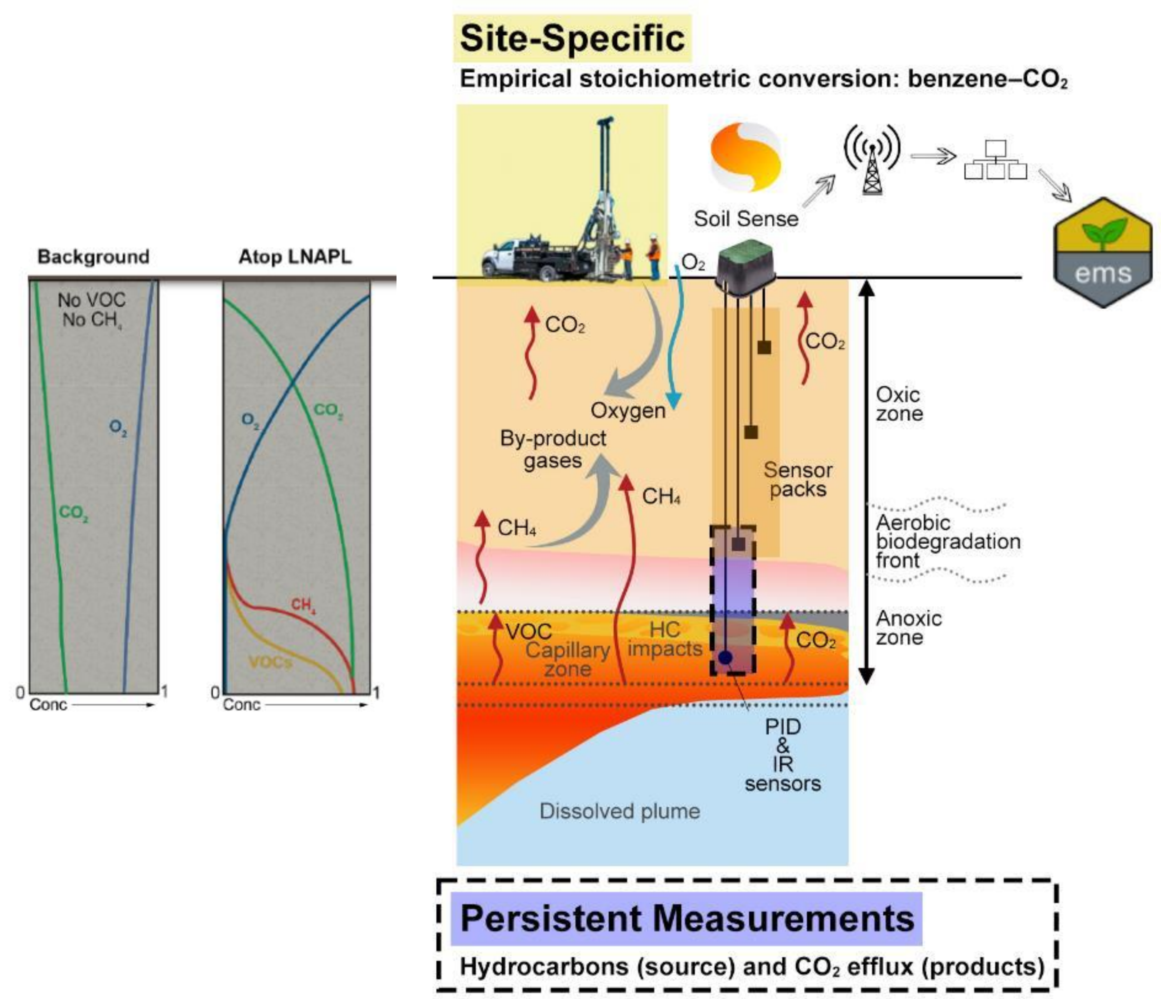


Schrödinger’s ~~Cat~~ Goomba (NSZD)



NSZD: Concentration Gradient Method



CRC Care 2018

1. $J = D_v^{eff}\left(\frac{dC}{dZ}\right)$

J = steady state diffusive flux (g/m²-soil/s)
D_v^{eff} = effective vapour diffusion coefficient (m²/s)
$\frac{dC}{dZ}$ = soil gas concentration gradient (g/m³-m)

2. $J_{impacted} - J_{background} = J_{corrected}$

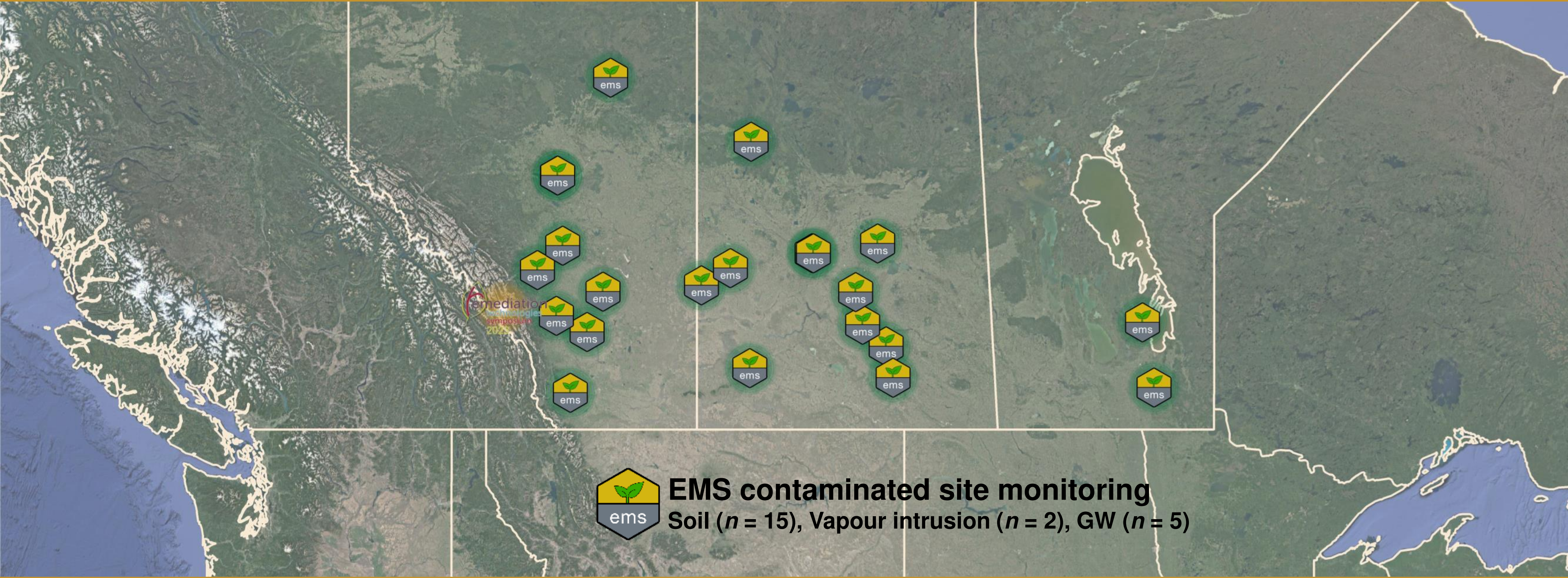
3. **Theoretical stoichiometric conversion: benzene–CO_2**
$2C_6H_6 + 15O_2 \rightarrow 12CO_2 + 6H_2O$
$2C_6H_6$: 2*(12.011 g/mol*6 + 1.008 g/mol*6) = 156.223 g/mol
$12CO_2$: 12*(12.011 g/mol + 15.999 g/mol*2) = 528.096 g/mol

When 156 g of C_6H_6 are consumed, 528 g CO_2 are produced
$Stoich_{CO_2}$ = 156 / 528

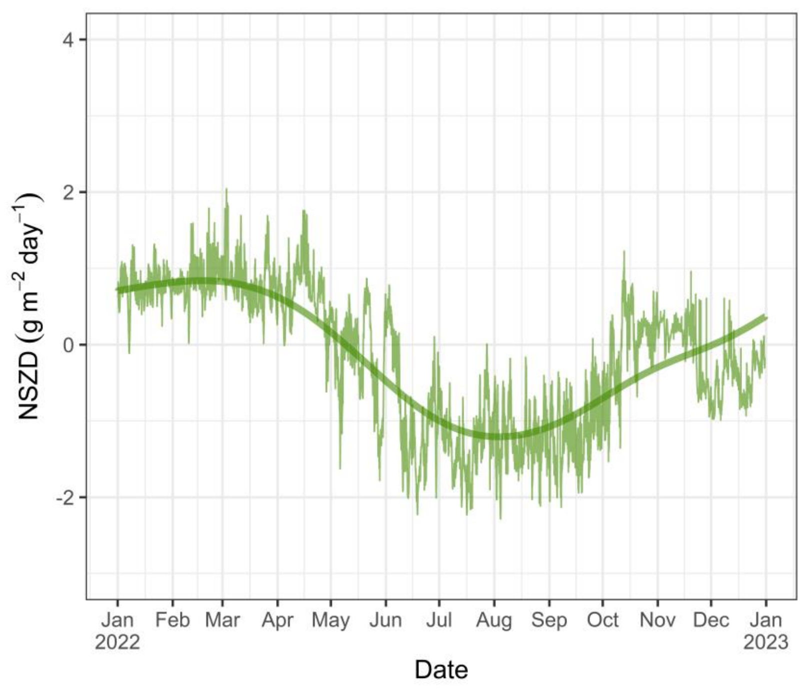
4. **Natural Source Zone Depletion**
NSZD = $J_{corrected} * Stoich_{CO_2}$

CRC CARE Technical Report no. 46
The role of natural source zone depletion in the management of light non-aqueous phase liquid (LNAPL) contaminated sites

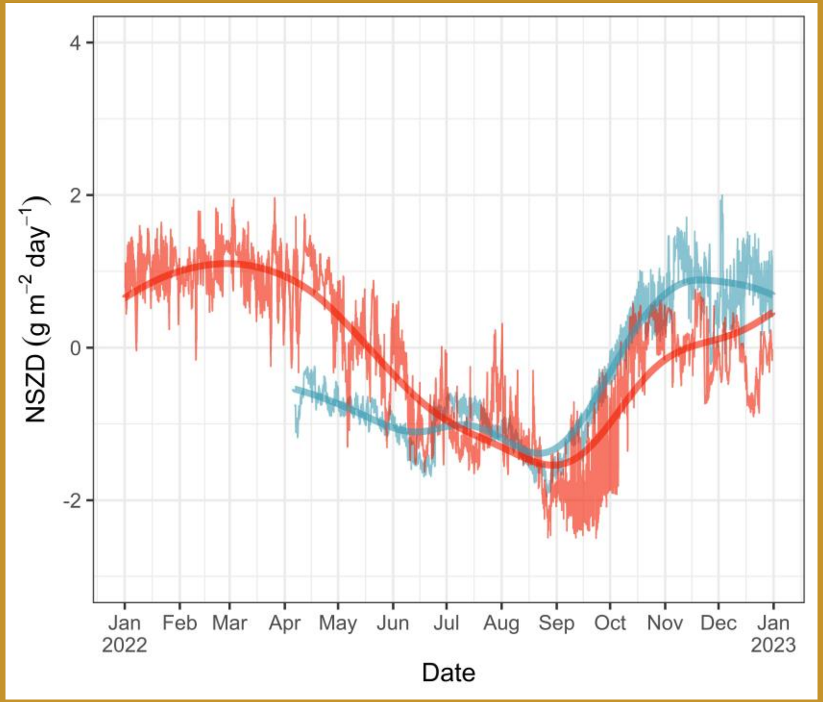
NSZD: Concentration Gradient Method



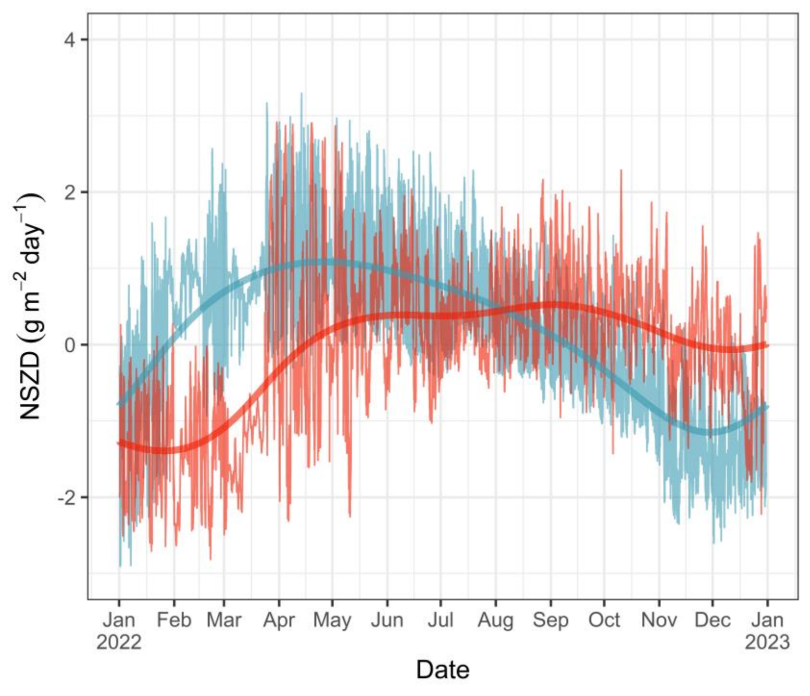
NSZD: Seasonal Patterns



Regional mean (normalized)



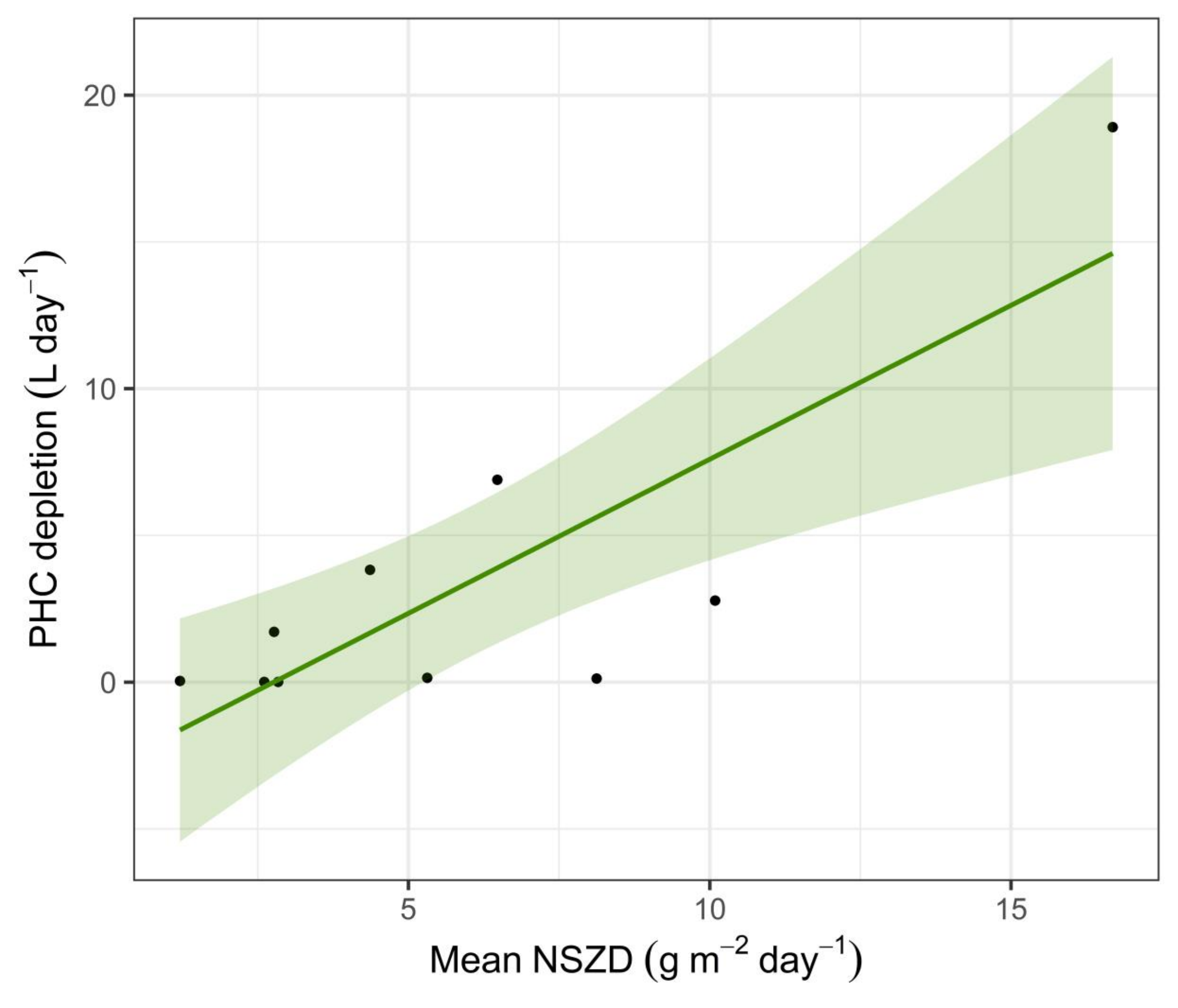
Some sites follow regional mean



Others, not so much

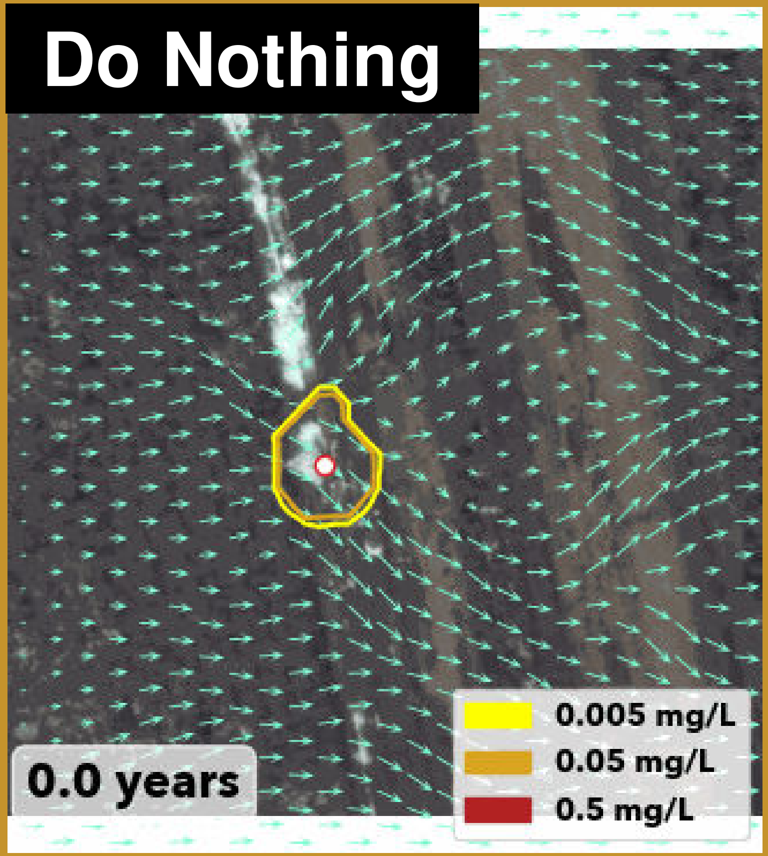
NSZD meets PHC depletion

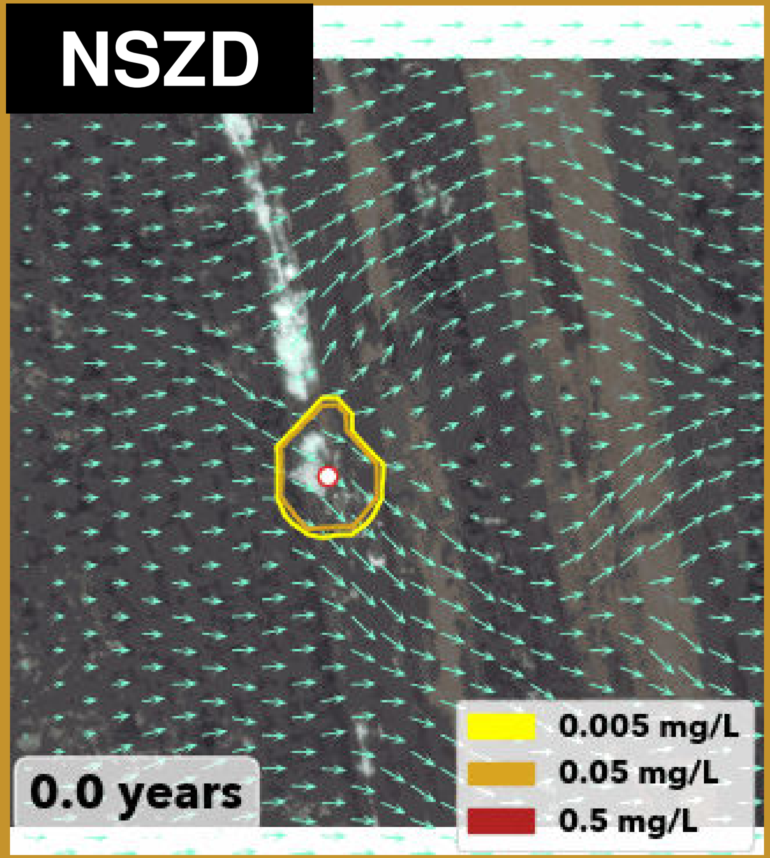
Estimated measuring hydrocarbons directly

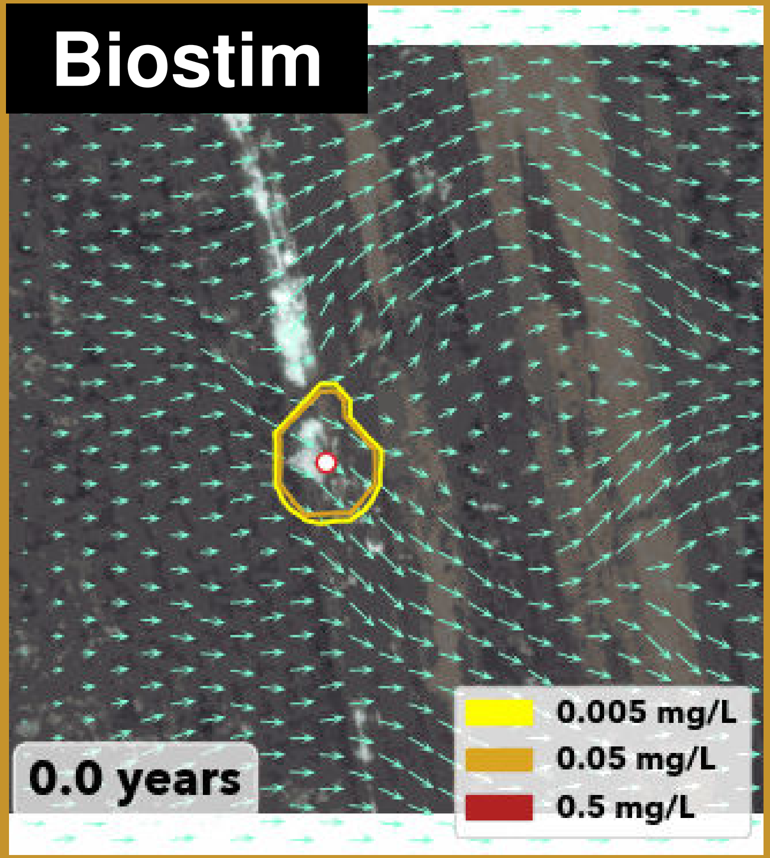


Estimated using indicator gases

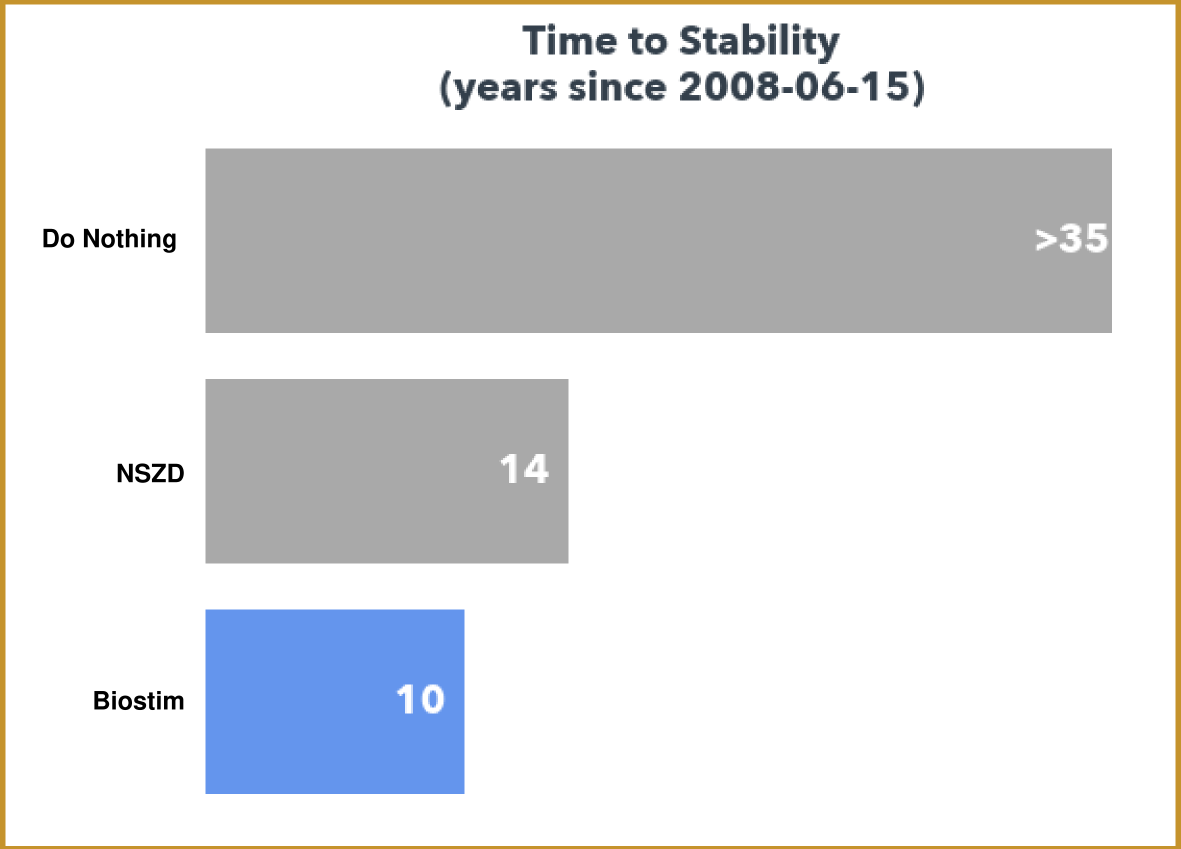
Groundwater Modeling (Benzene)

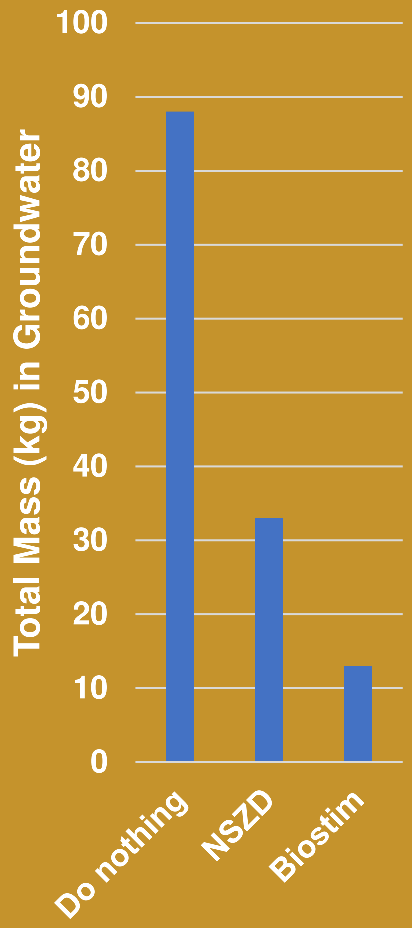






Groundwater Modeling (Benzene)

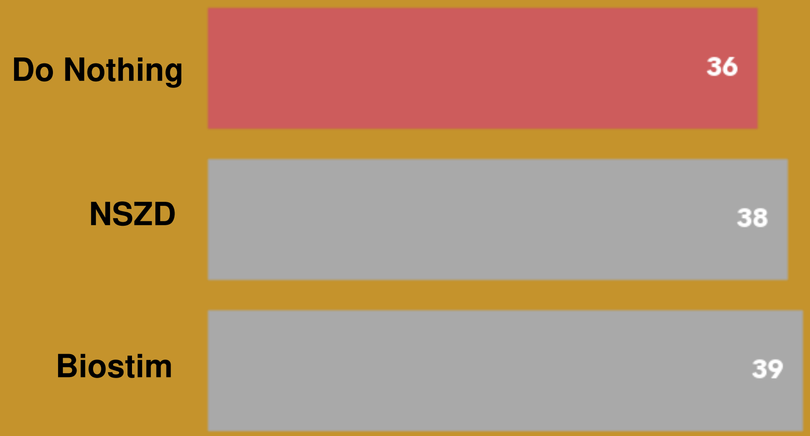




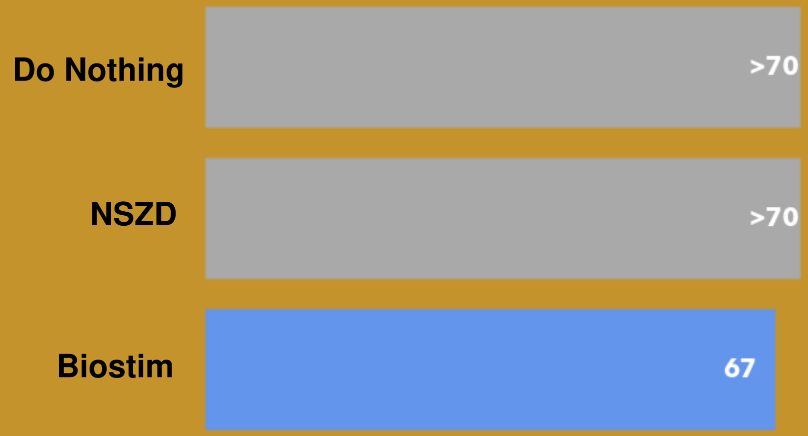
Time to stability based on area and concentration

Groundwater Modeling (Benzene)

Time to fence line
(years since 2023-Jan-01)



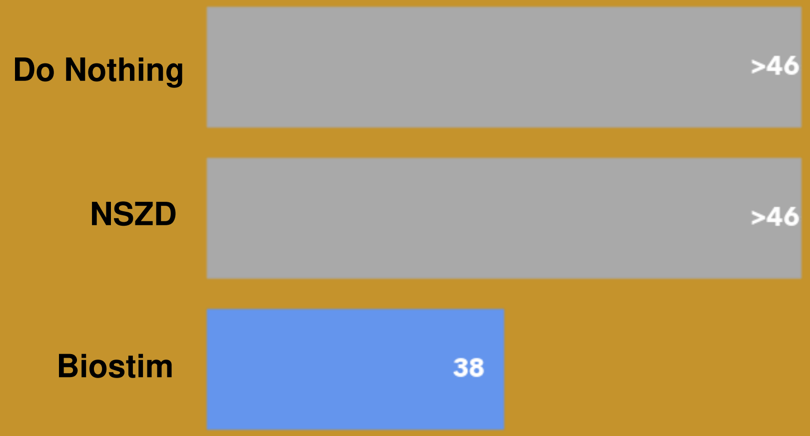
Time to stability
(years since 2023-Jan-01)

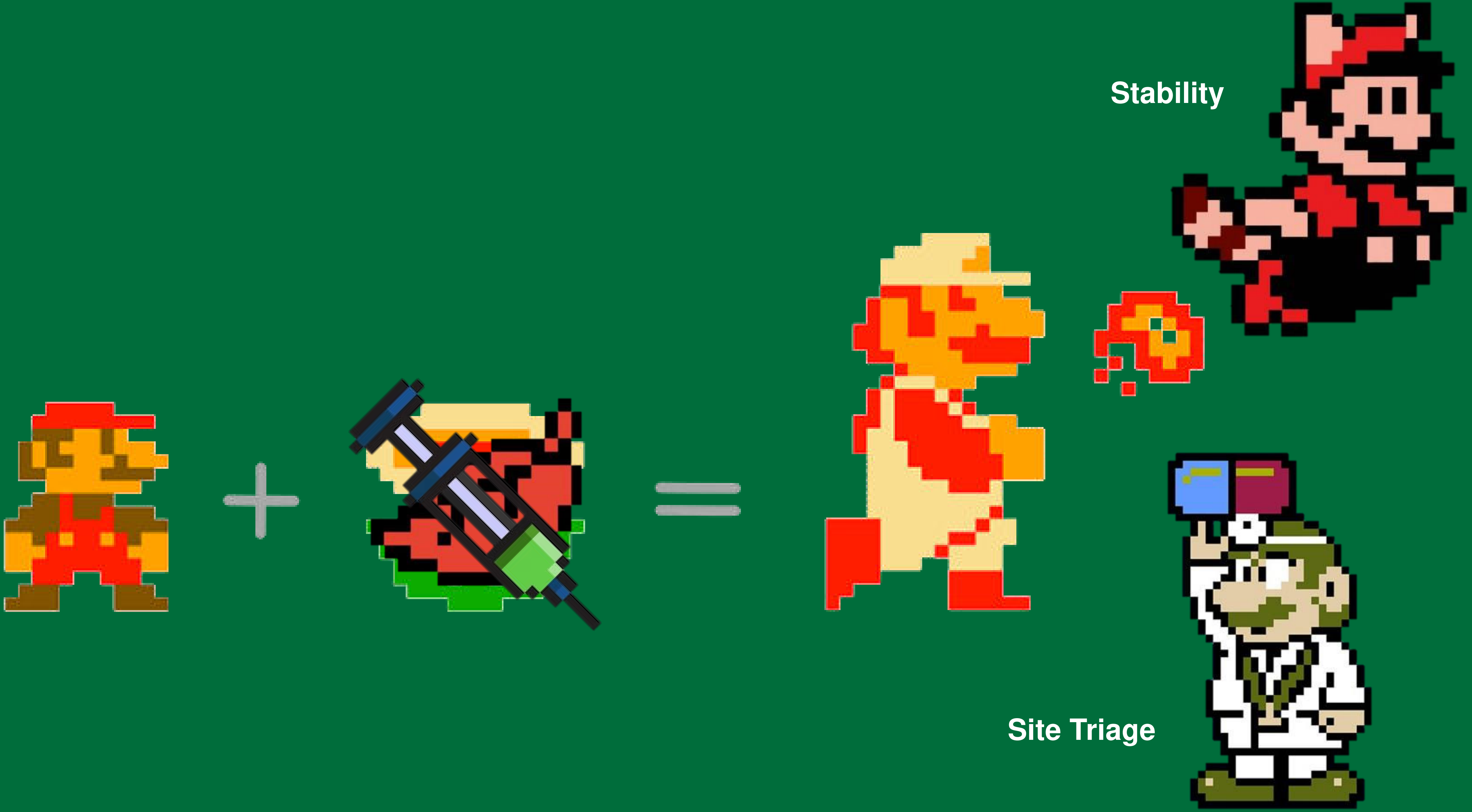


Groundwater Modeling (Benzene)

Time to fence line
(years since 2017-Jan-01)

Time to stability
(years since 2017-Jan-01)




Stability
Site Triage

Highlights: Groundwater Risk and NSZD

- Groundwater modeling is about changing risk vector over time – soil may be PHC source to GW
- Soil modeling is about remediation - ***source*** removal
- Comprehensive groundwater (risk) model should incorporate stimulated and/or natural depletion
- Continuous, real-time data streams empower managers to:
  - Make evidence-based decisions
  - Adapt management strategies to achieve site objectives in a more ***timely*** and ***cost-effective*** fashion.

Can Autonomous, High Data Density Sensors Save Time & Costs in Adaptive Management of Hydrocarbon Impacted Sites?

Thank you!

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ems

Your roadmap for today

Site-specific NSZD and plumes

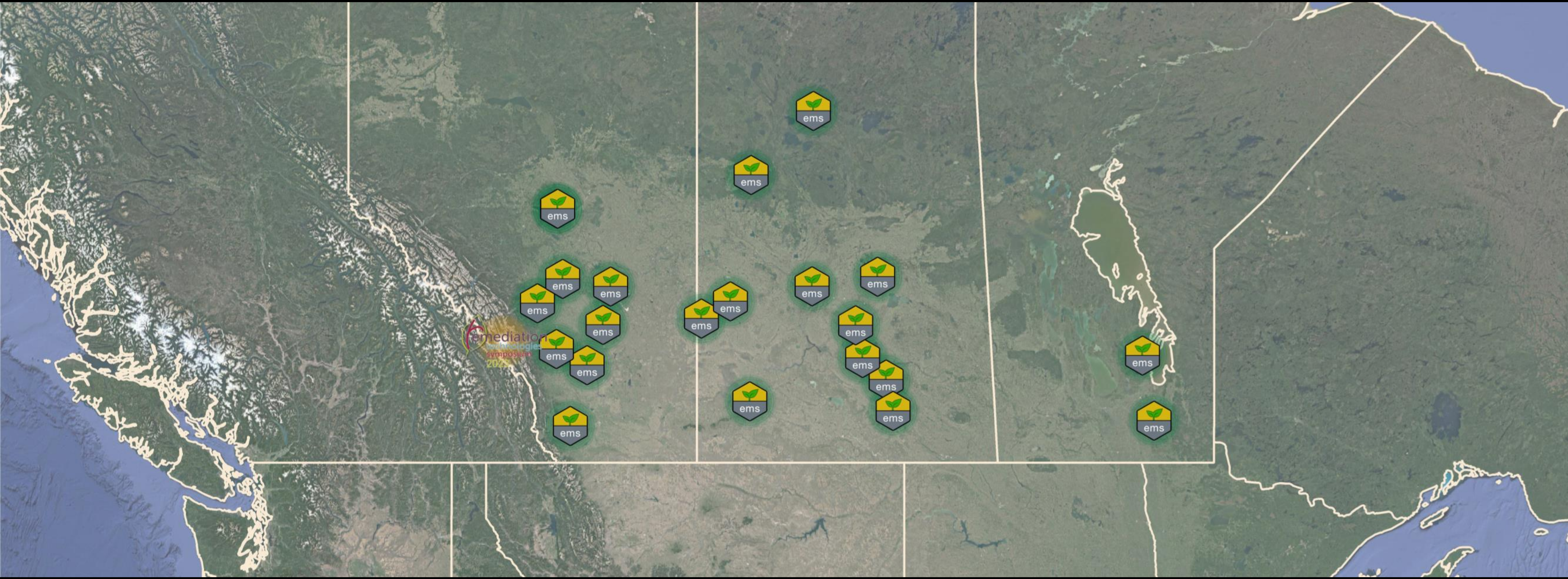
Site-specific stoichiometry

Pedotransfer and soil moisture

Continuous measurements Methane

Soil Sense

NSZD Overview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remediation
technologies
symposium
2023

Natural Source Zone Depletion Explained

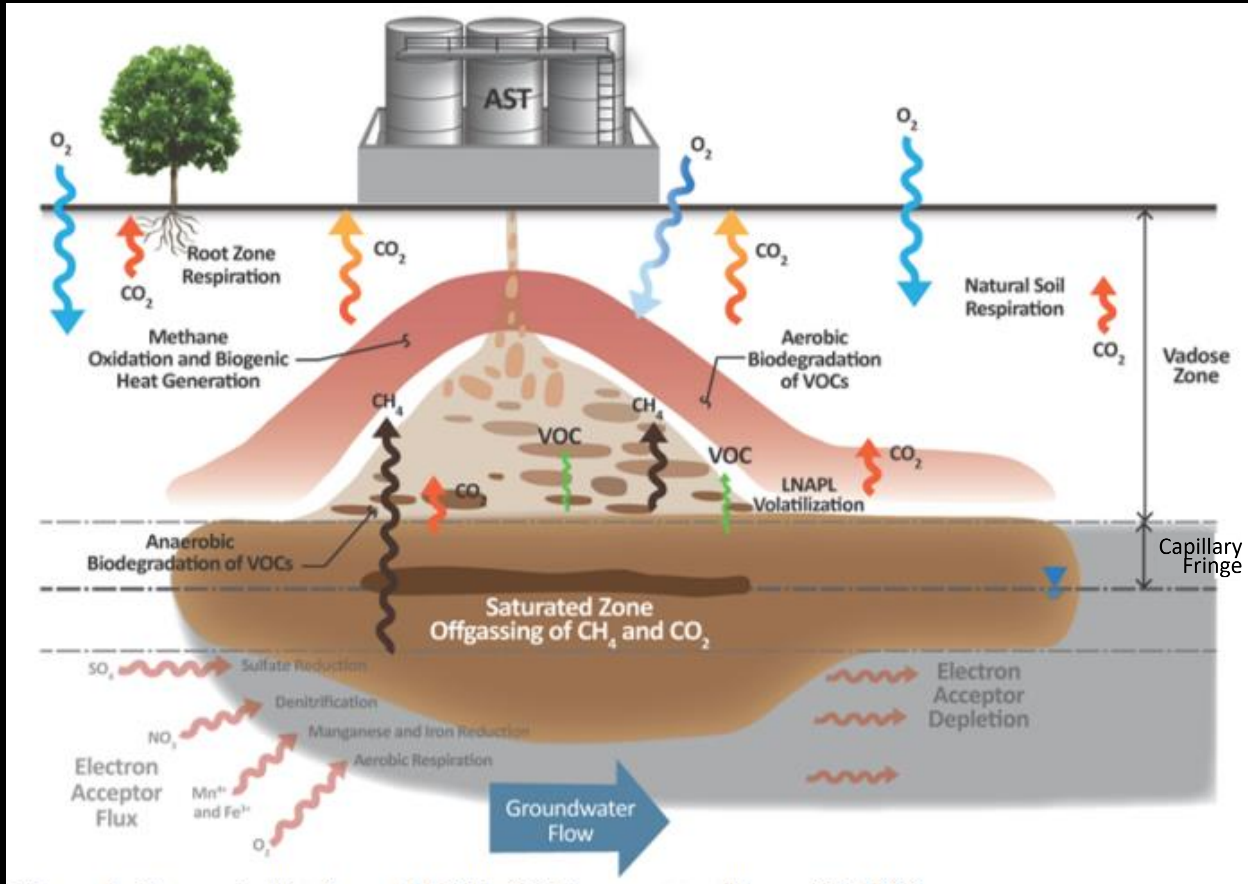


Figure 7: Conceptualisation of LNAPL NSZD processes (from API 2017)

Aerobic Transport

Methane Oxidation

$$CH_4 + 2O_2 \rightarrow CO_{2\,(g)} + 2H_2O$$

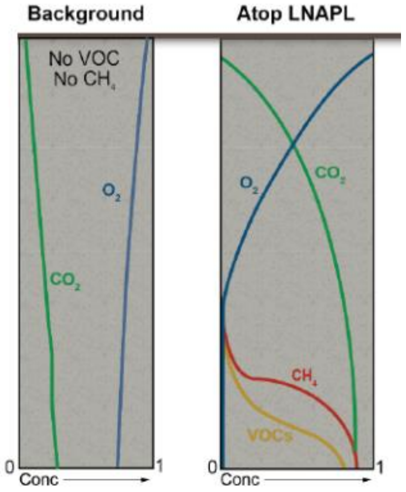
Methane Generation

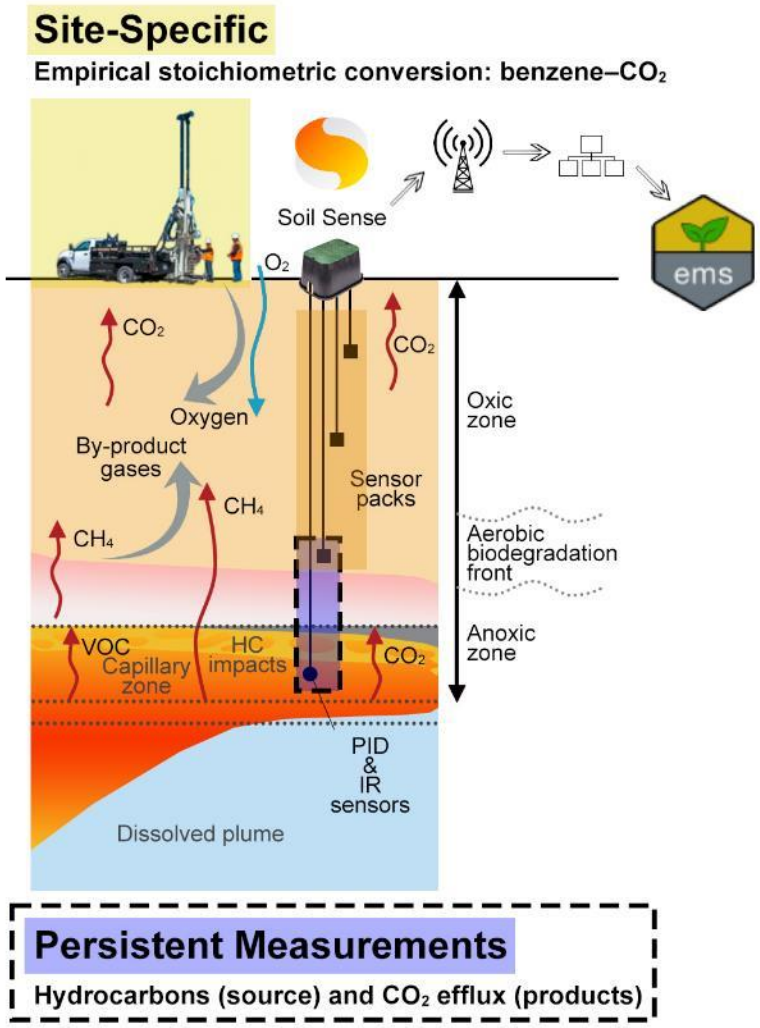
$$C_8H_{18} + 3.5\ H_2O \rightarrow 1.75\ CH_{4\,(g)} + 6.25\ CO_{2\,(g)}$$

CRC CARE Technical Report no. 46

The role of natural source zone depletion in the management of light non-aqueous phase liquid (LNAPL) contaminated sites

Concentration Gradient Method





Fick's First Law of Diffusion - rate of diffusion is proportional to the concentration and surface area

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J = steady state diffusive flux (g/m²-soil/s)

D_v^{eff} = effective vapour diffusion coefficient (m²/s)

$\frac{dC}{dZ}$ = soil gas concentration gradient (g/m³-m)

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Why CH_4 and why high data density?

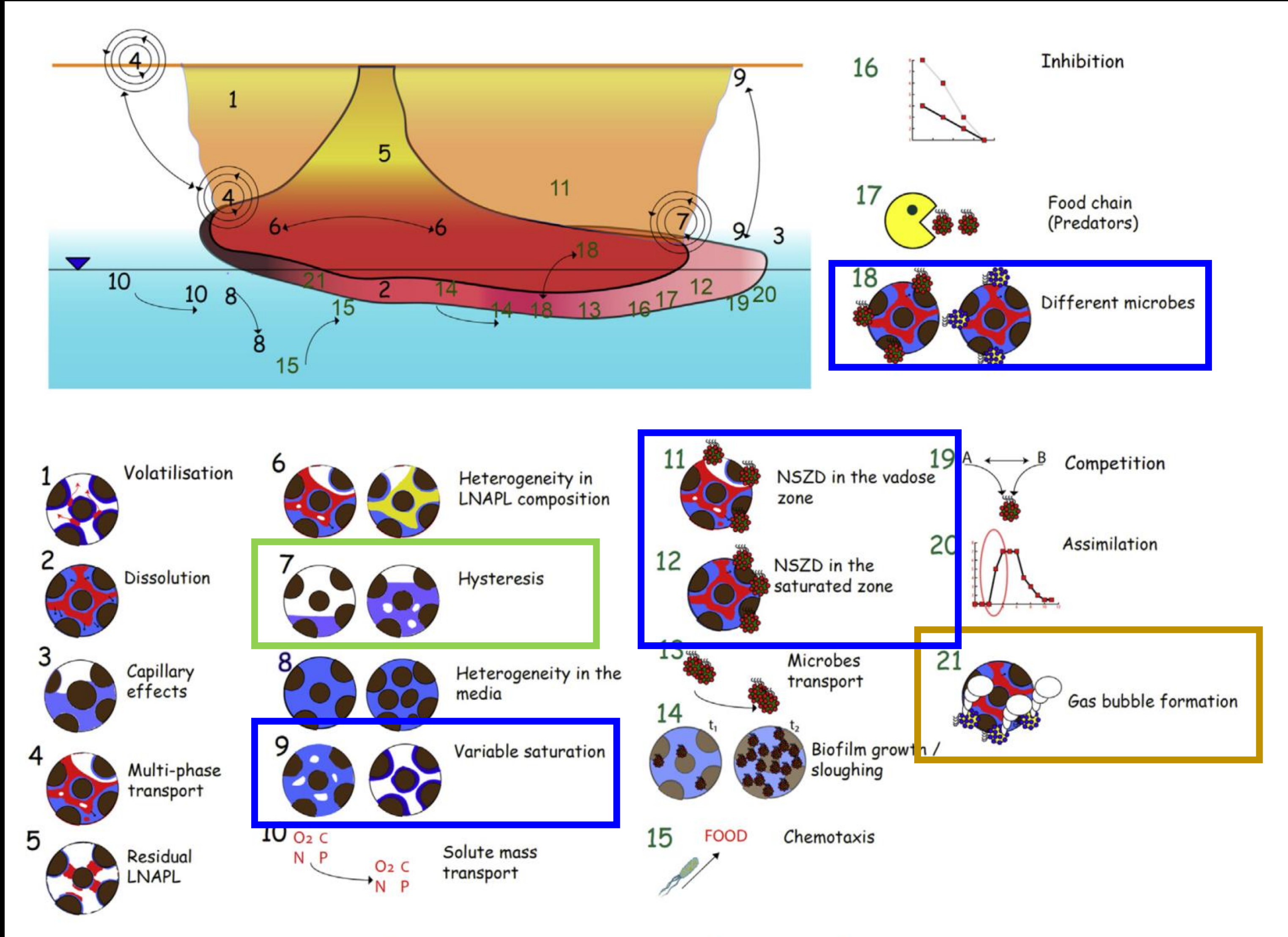
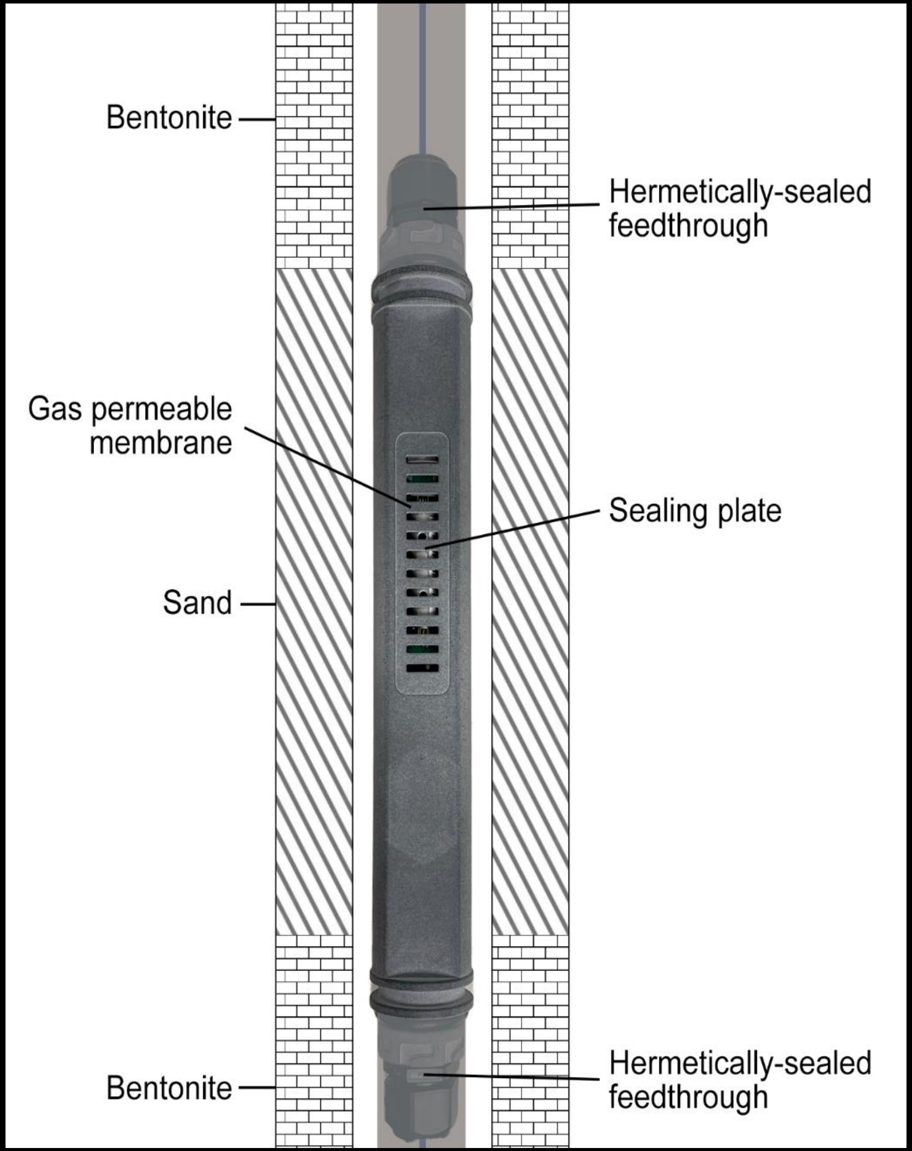


Fig. 1. Some of the major processes and parameters in NSZD.

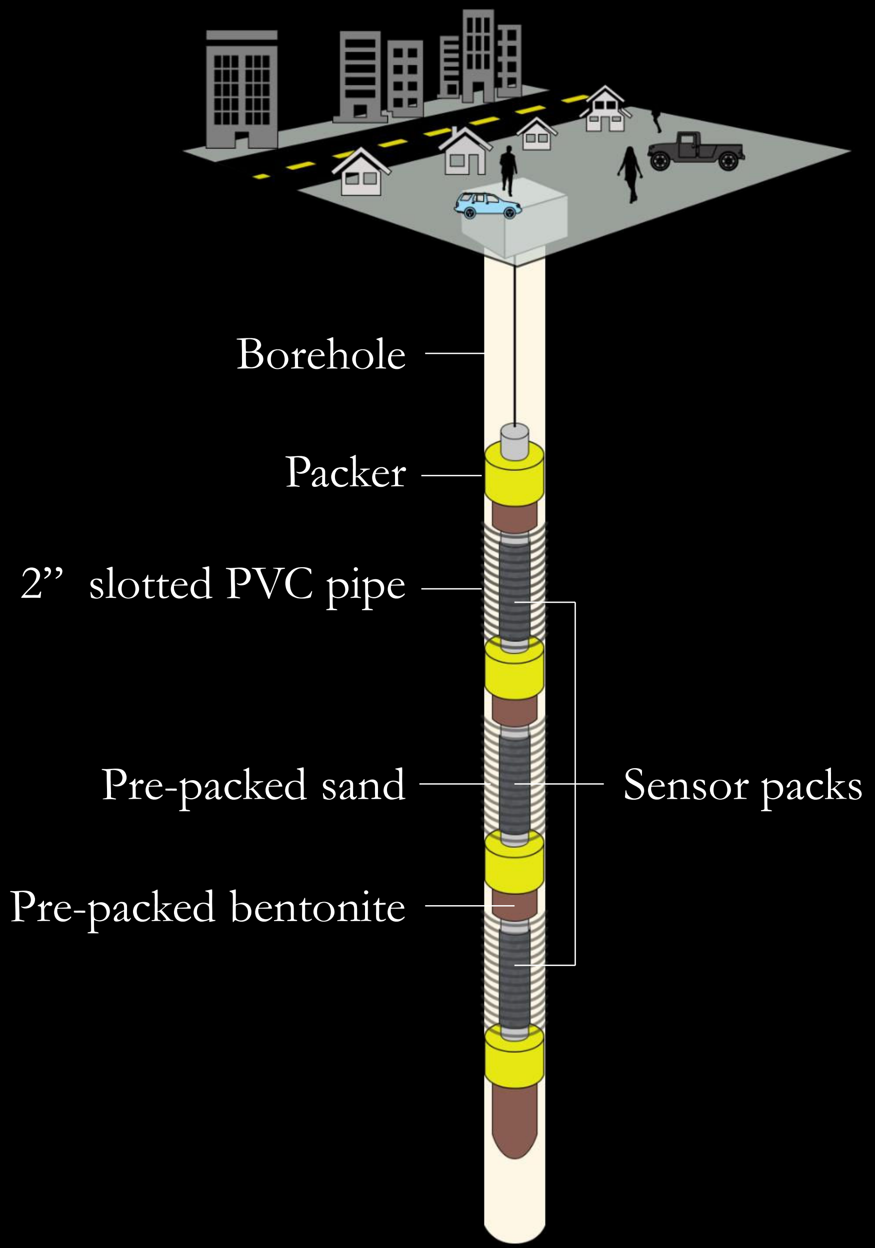
- Early attenuation processes dominated by methanogenic degradation
- "Signal shredding"
- Lag between peak subsurface gas concentrations and peak surface efflux.

Lari et al., 2019. Water Research 157: 630-646.

Soil Sense

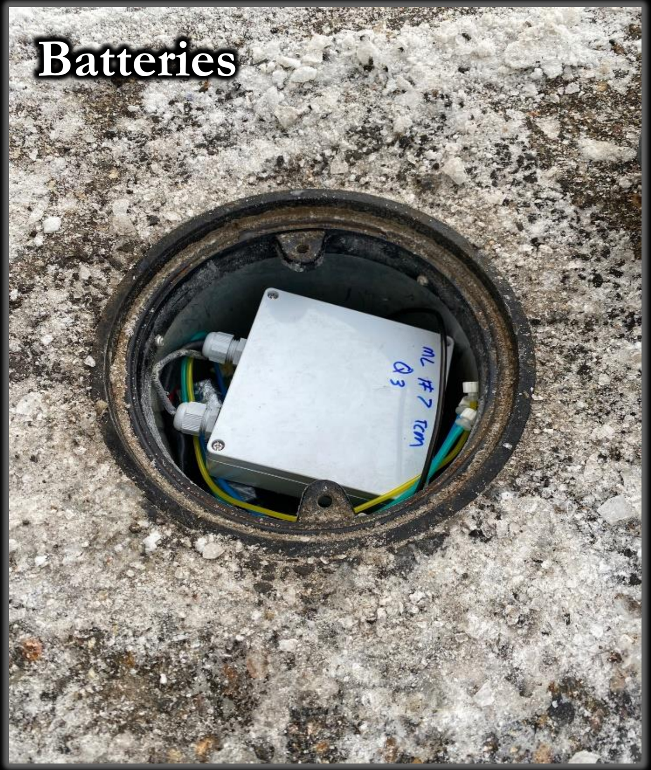


Bentonite
Hermetically-sealed feedthrough
Gas permeable membrane
Sealing plate
Sand
Bentonite
Hermetically-sealed feedthrough

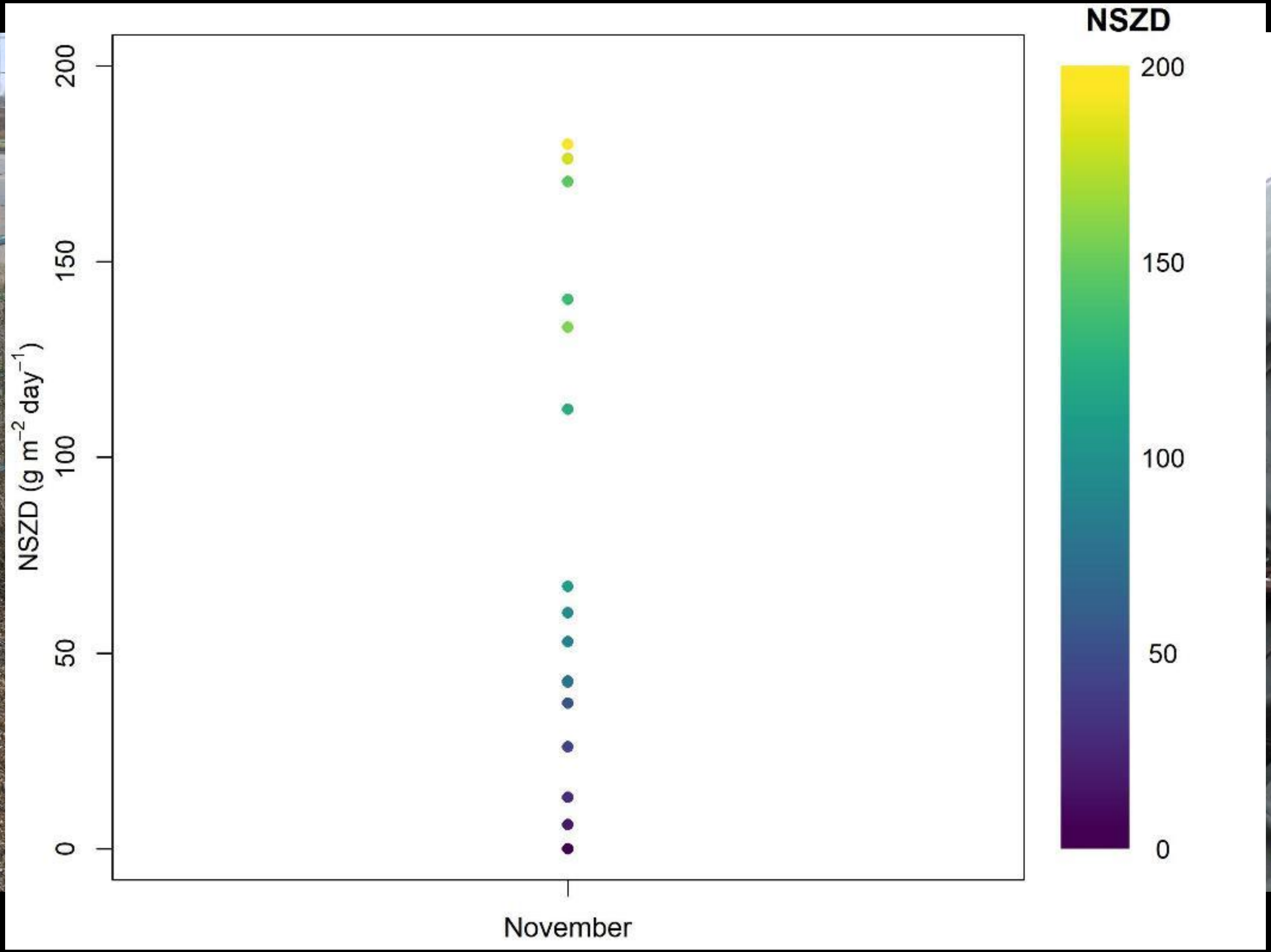


Borehole
Packer
2" slotted PVC pipe
Pre-packed sand
Sensor packs
Pre-packed bentonite

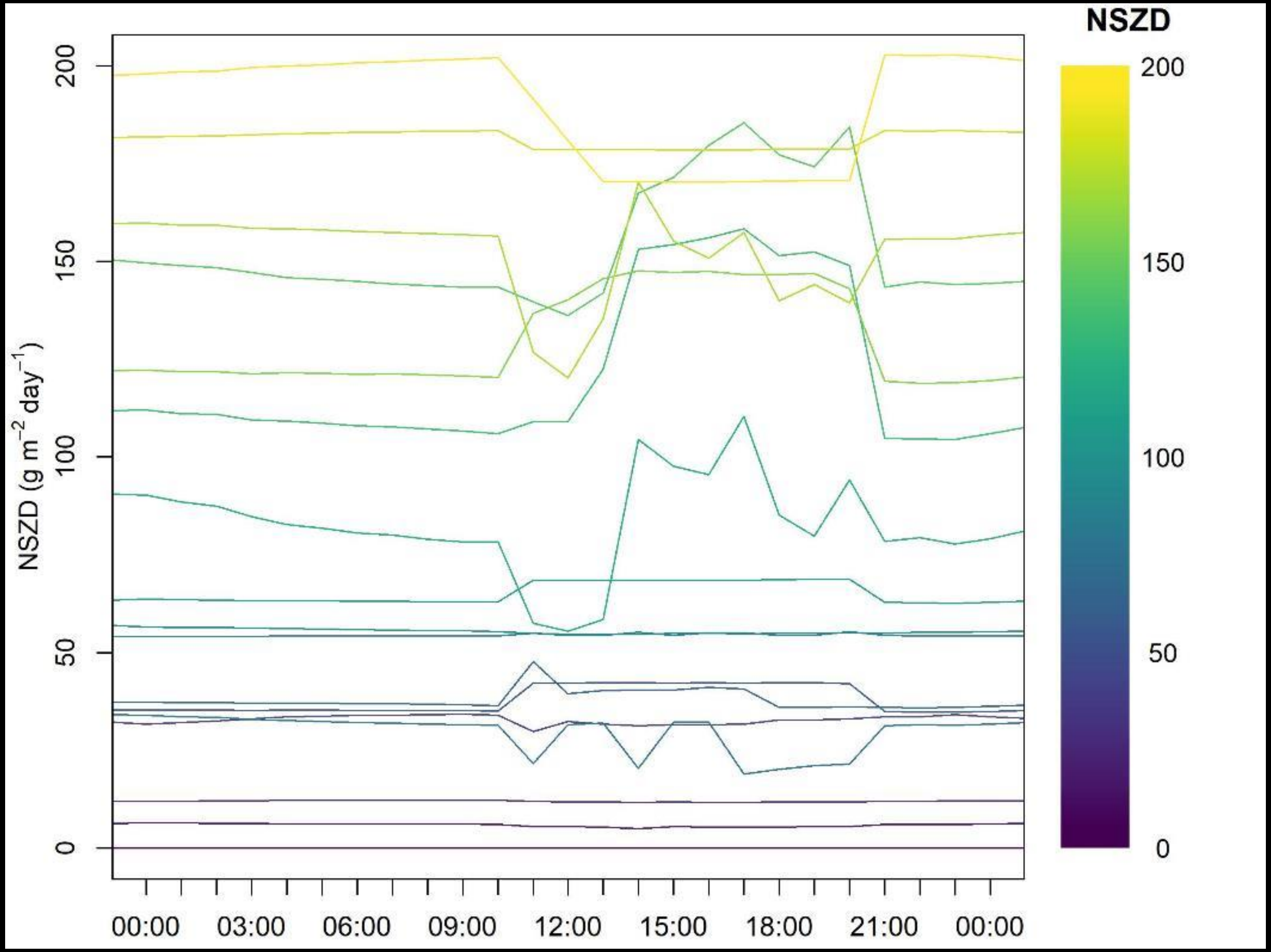
Soil Sense



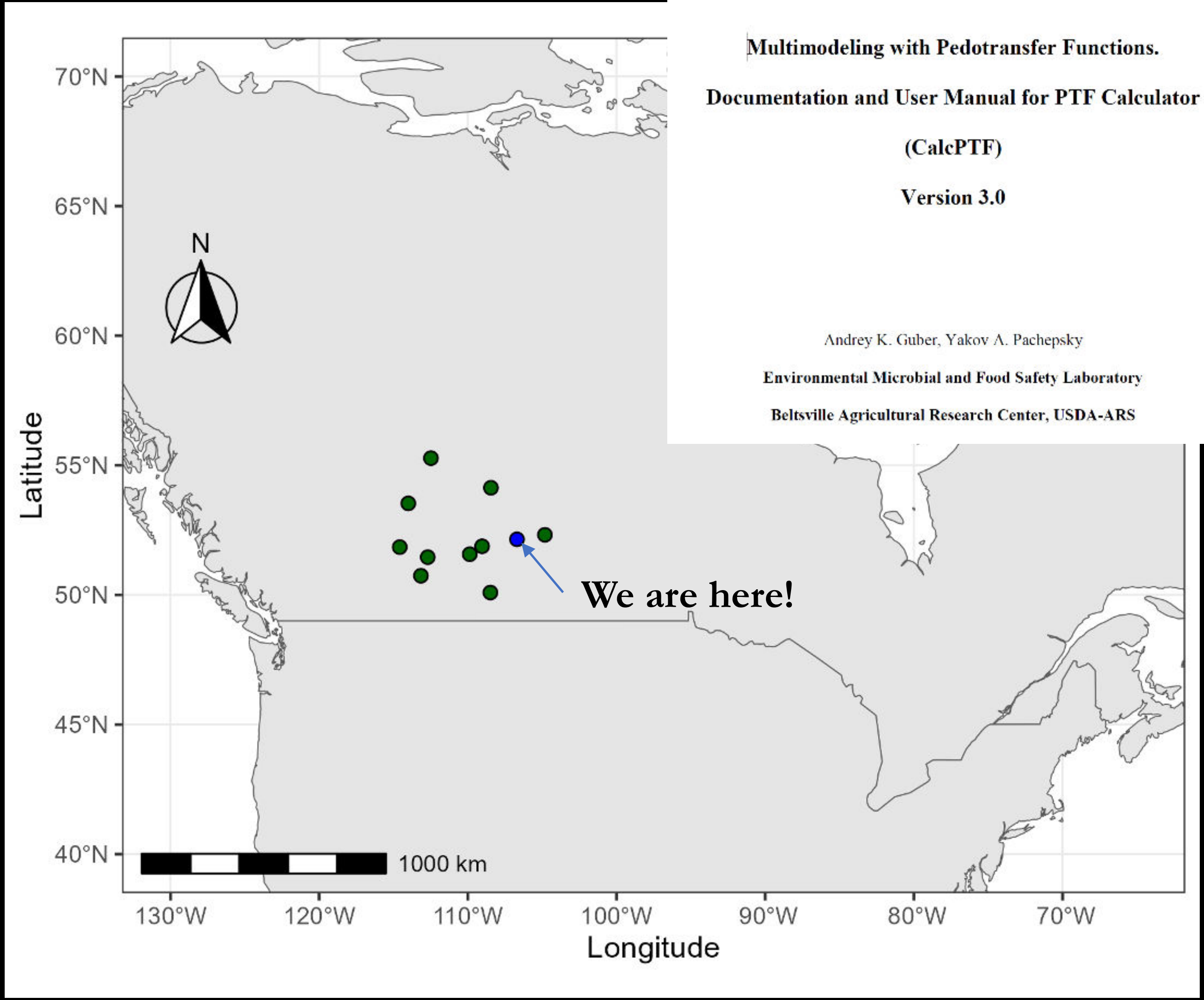
Low sampling frequency (**p**oint-**i**n-**t**ime is the "**pit**s")



Soil Sense collects 48 measurements per day



The Sites



USDA

Multimodeling with Pedotransfer Functions.

Documentation and User Manual for PTF Calculator

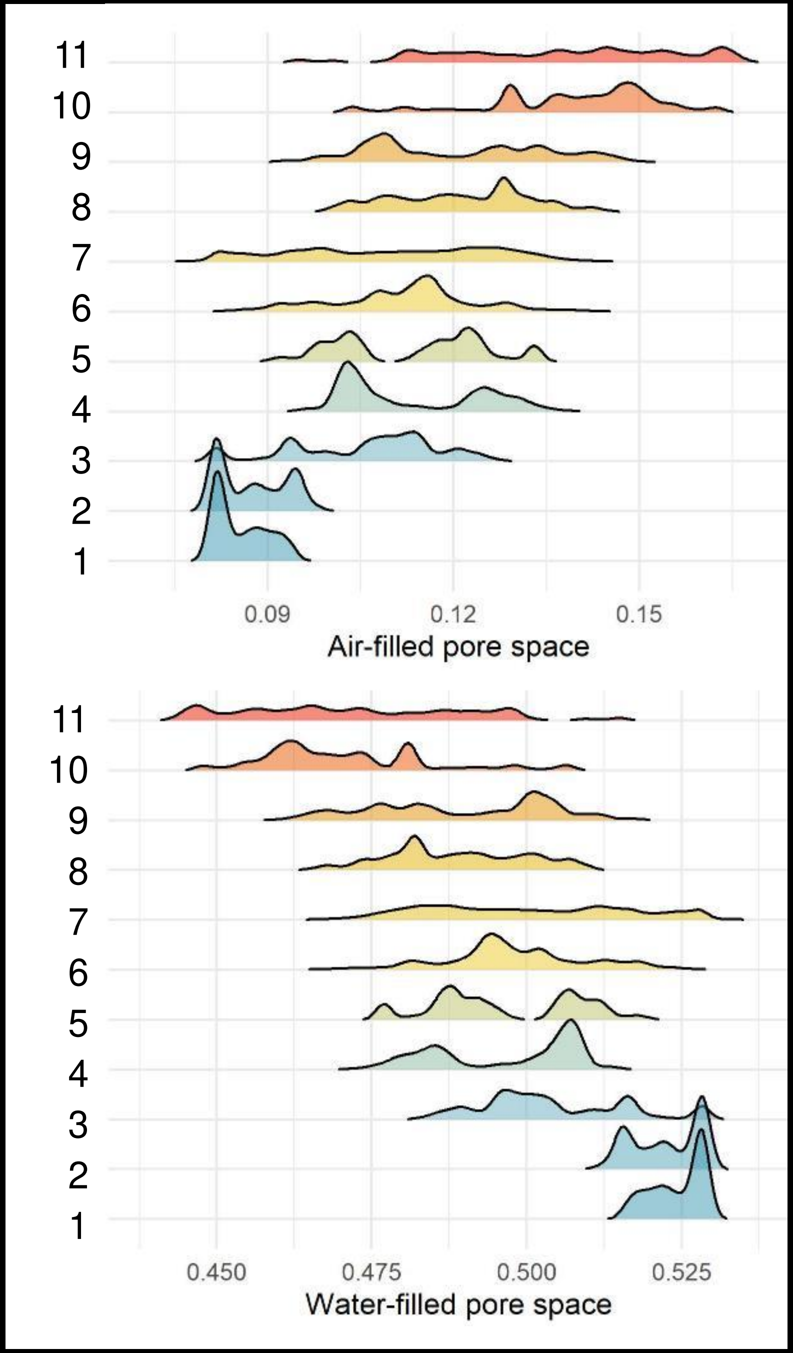
(CalcPTF)

Version 3.0

Andrey K. Guber, Yakov A. Pachepsky

Environmental Microbial and Food Safety Laboratory

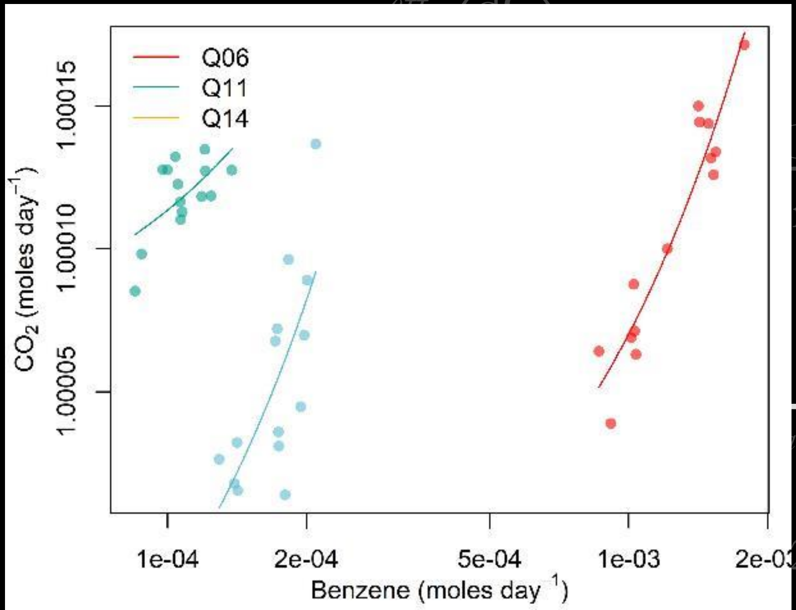
Beltsville Agricultural Research Center, USDA-ARS

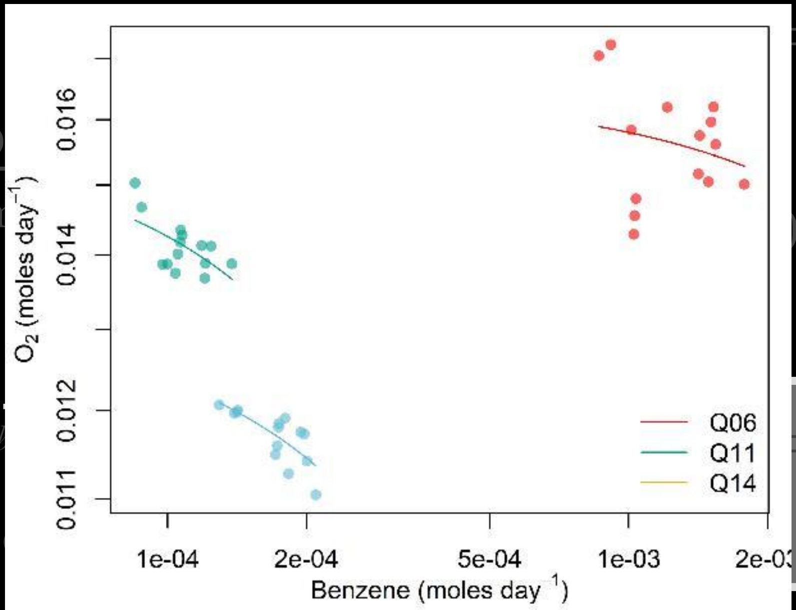


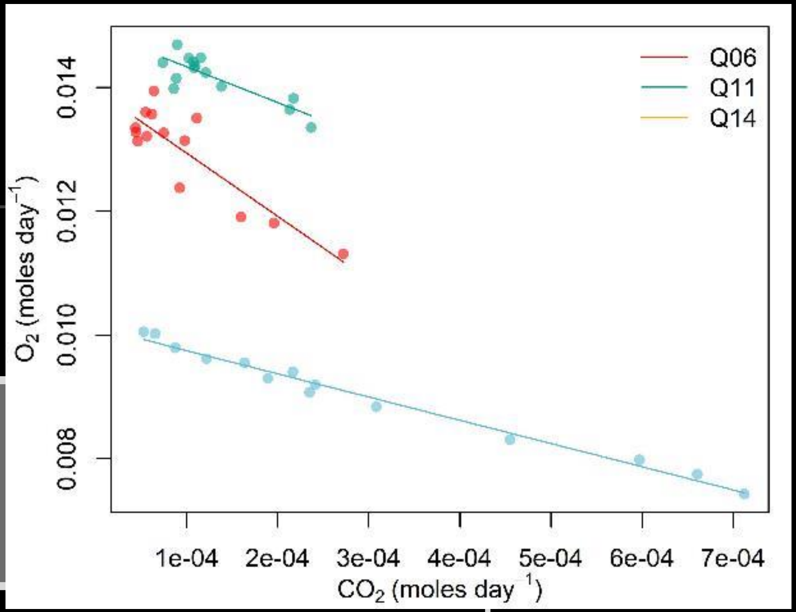
Guidance values

Convert Flux to Hydrocarbon Depletion (GUIDANCE)

CONVERT FLUX TO HYDROCARBON DEPLETION (SITE-SPECIFIC)







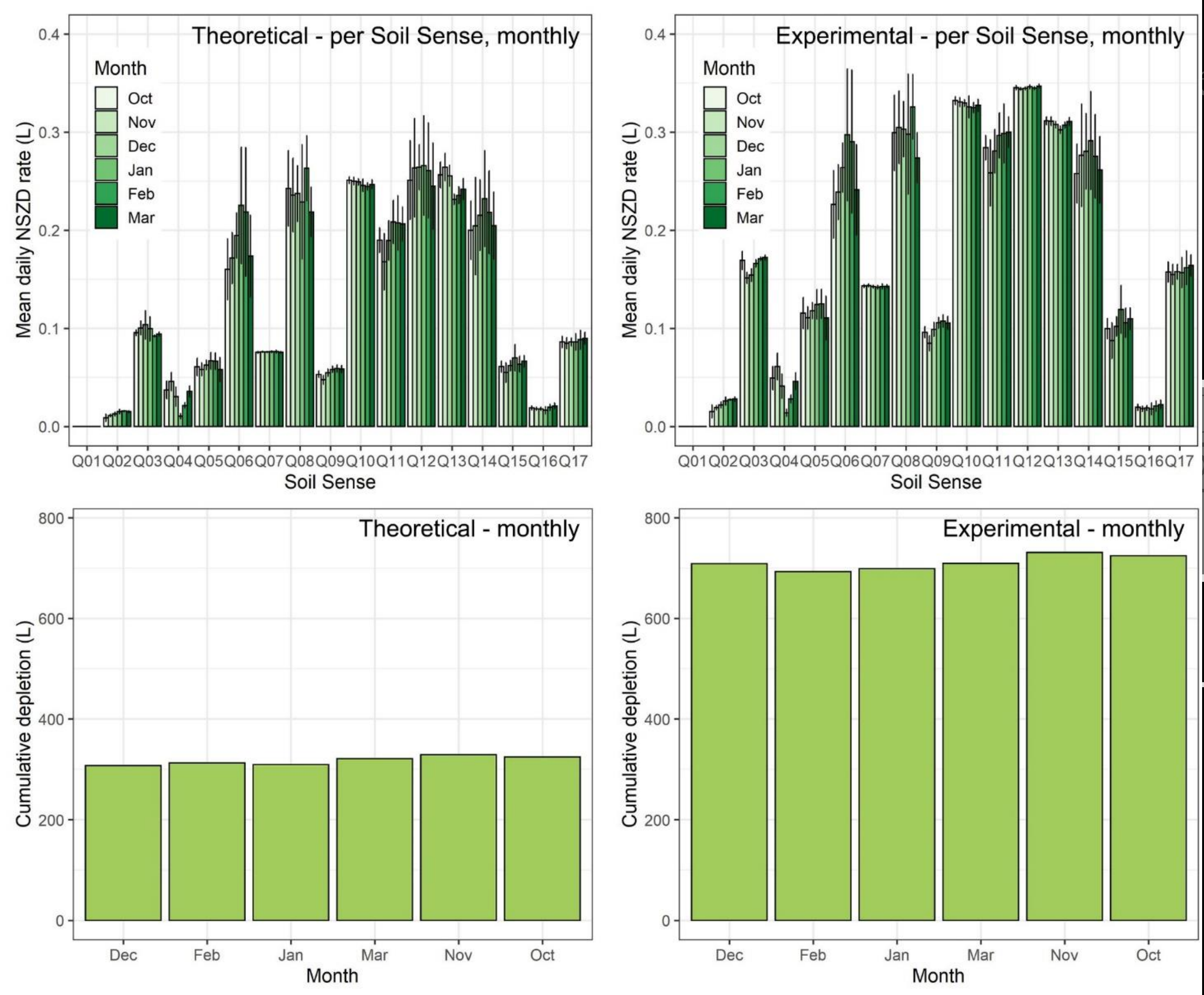
$$\text{Molar Ratio} = \frac{78.11\,\frac{gC_6H_6}{mol}}{44.11\,\frac{gCO_2}{mol}} \quad 2\ mol_{C_6H_6}$$

Ratio	Guidance (mass)	Site-specific (mass)
$C_6H_6:CO_2$	0.296	0.329
$C_6H_6:O_2$	0.325	0.179
$C_6H_6:CH_4$	1.038	1.038

Adapted from CRC CARE 2018

Convert Flux to Hydrocarbon Depletion (GUIDANCE)

CONVERT FLUX TO HYDROCARBON DEPLETION (SITE-SPECIFIC)



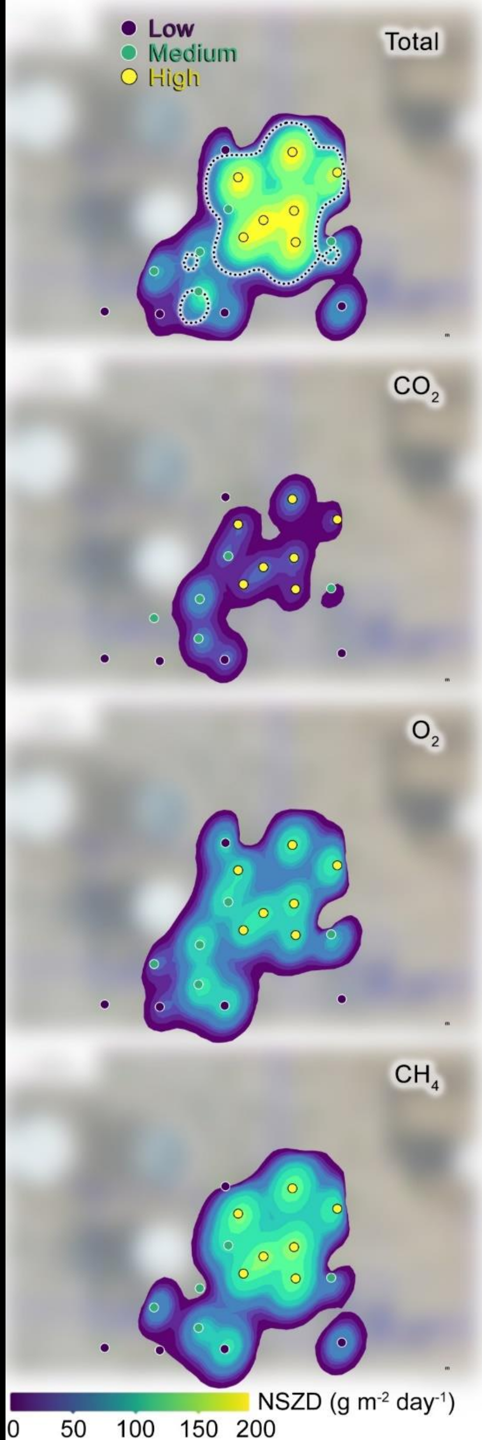
ed * Molar Ratio

* 0.3 * 86400

Convert to g – Repres

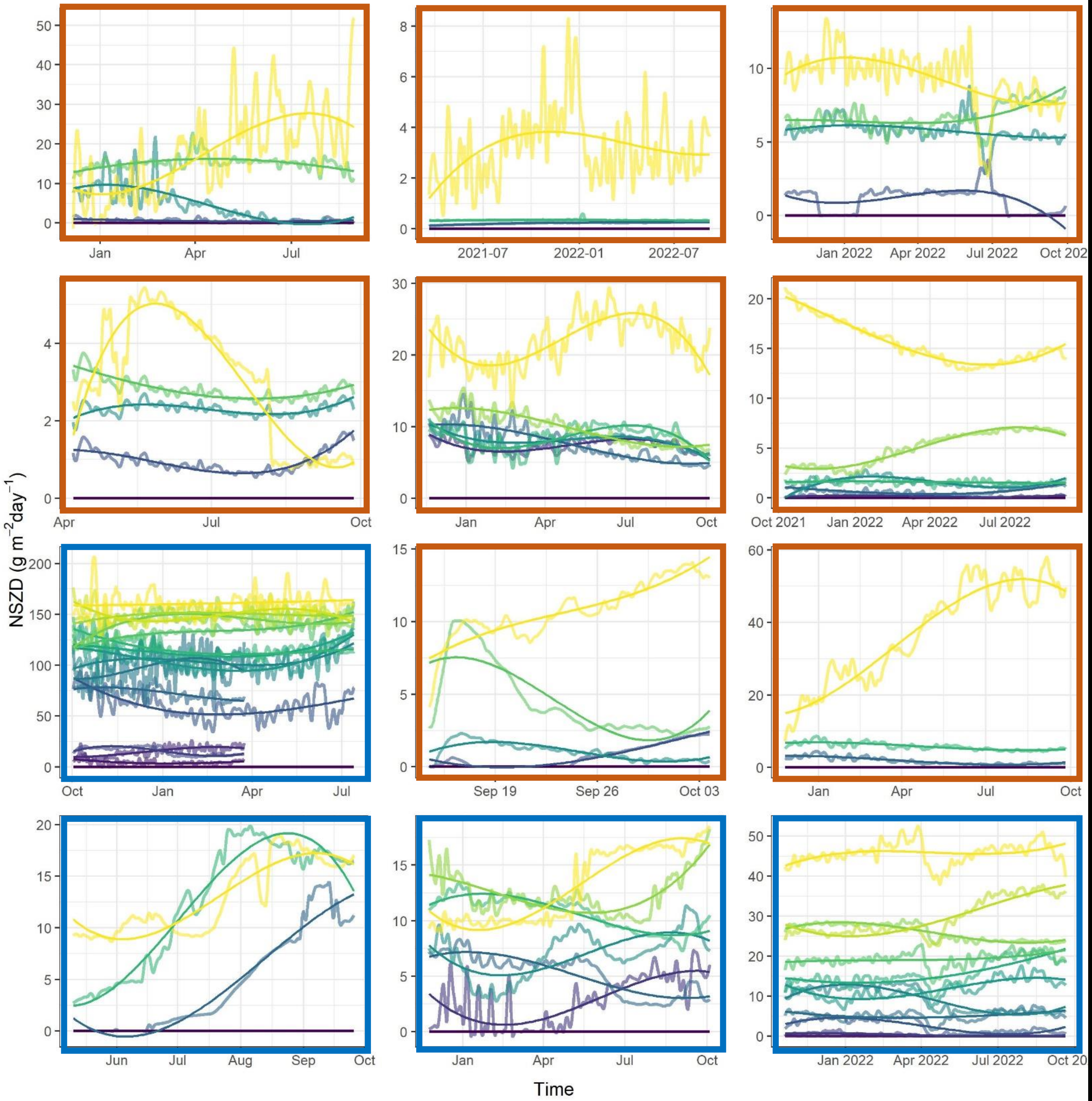
$$\text{Molar Ratio} = \frac{78.11\ \frac{gC_6H_6}{mol}}{44.11\ \frac{gCO_2}{mol}}$$

Adapted from CRC CARE 2018



NSZD through space

- NSZD estimates incorporate methane and paired CO_2 production/O_2 consumption
- More representative estimates of biological activity.



NSZD Site Variability

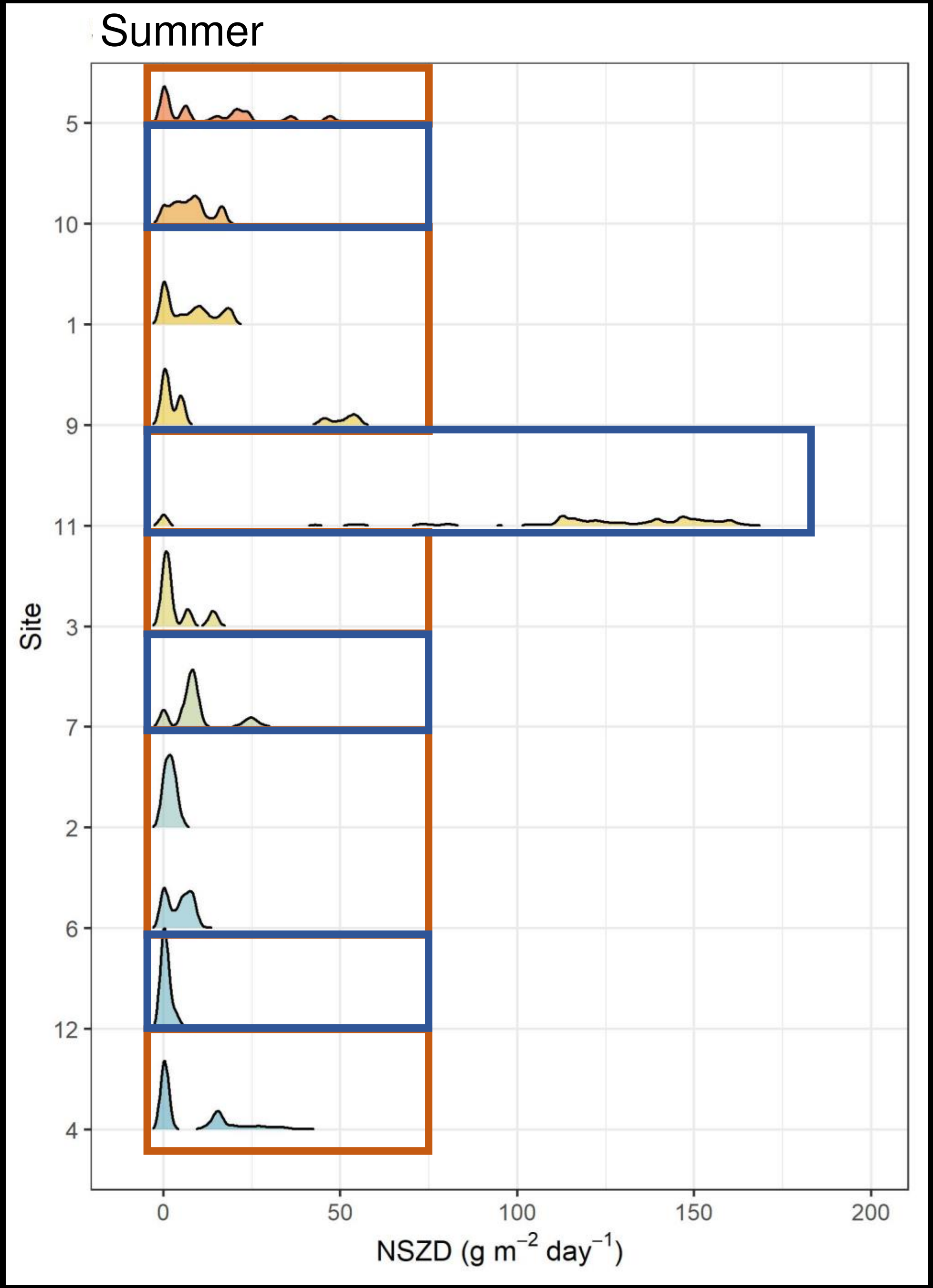
Localized Activity

12 sites
76 Soil Senses
228 Sensor packs
>100,000,000 data points!

Site Wide Activity

NSZD
Site Variability

Localized Activity



12 sites
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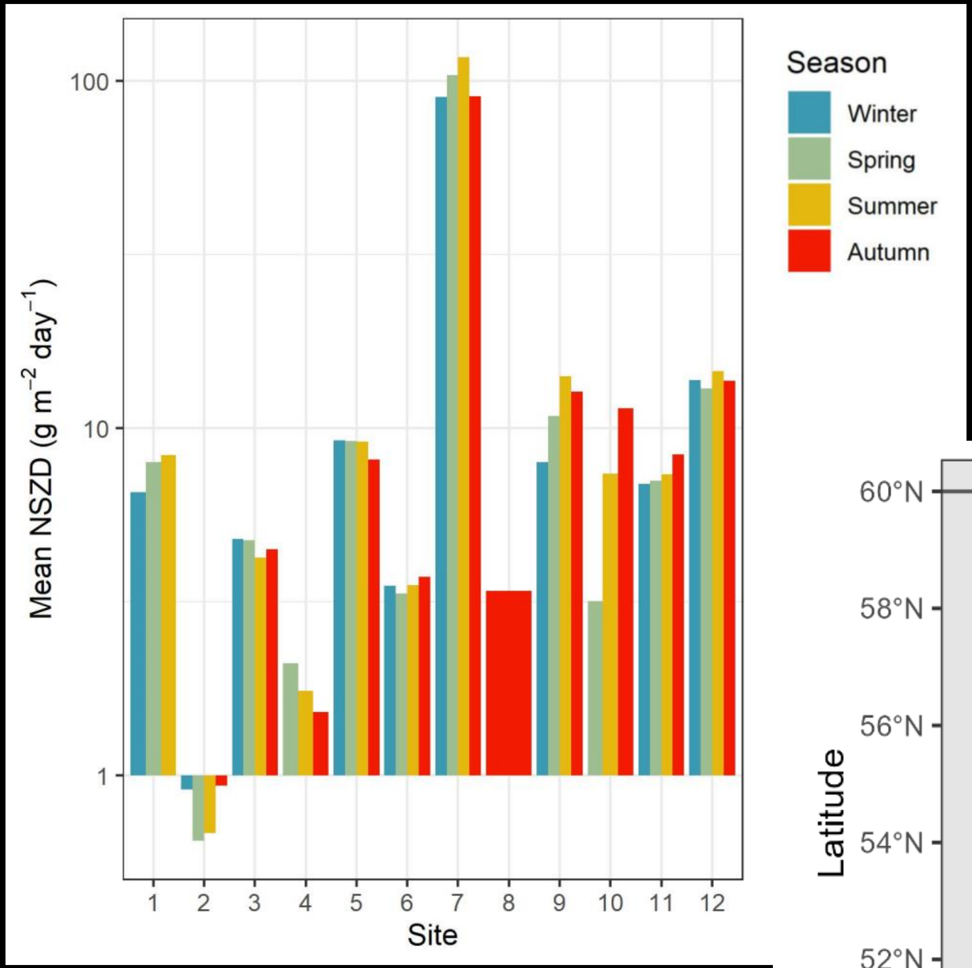
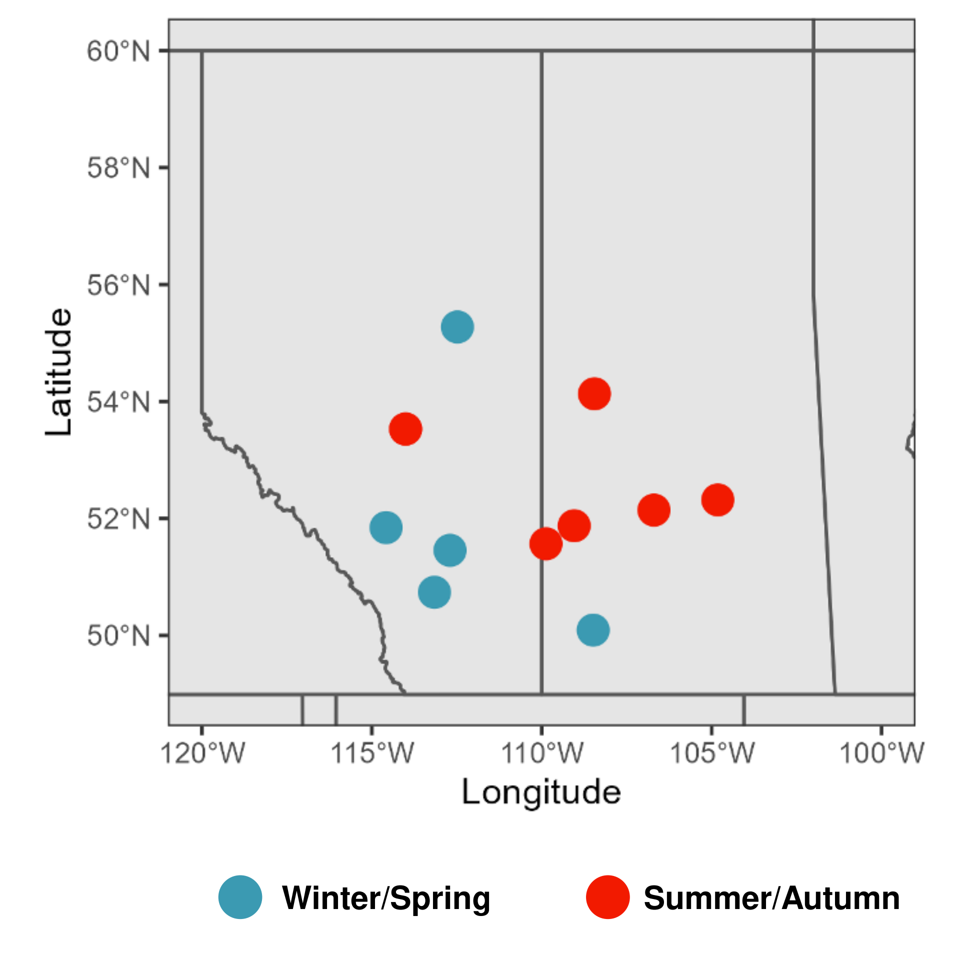
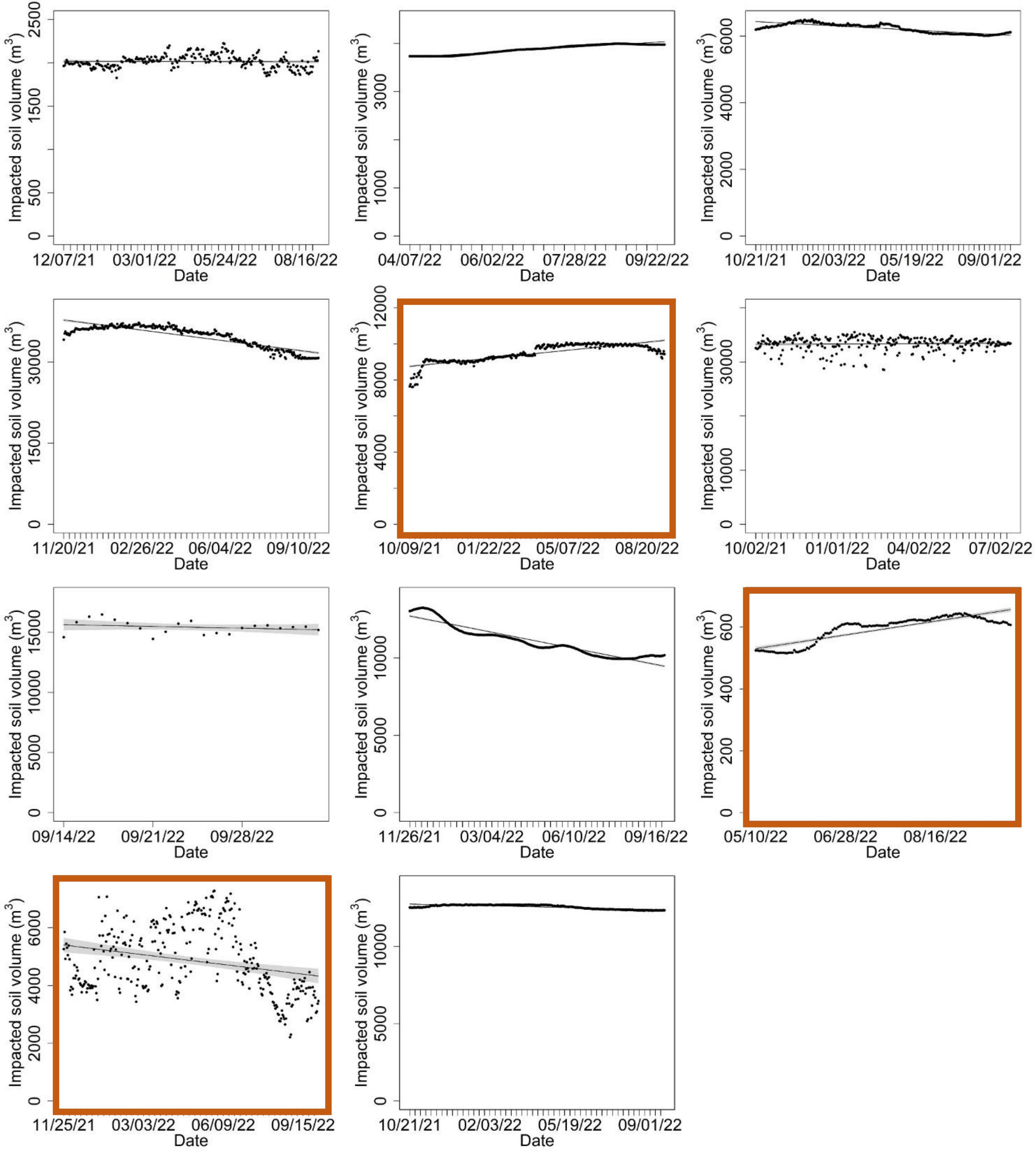
Site Wide Activity

NSZD Seasonality





NSZD peaks in either winter/spring or summer/fall

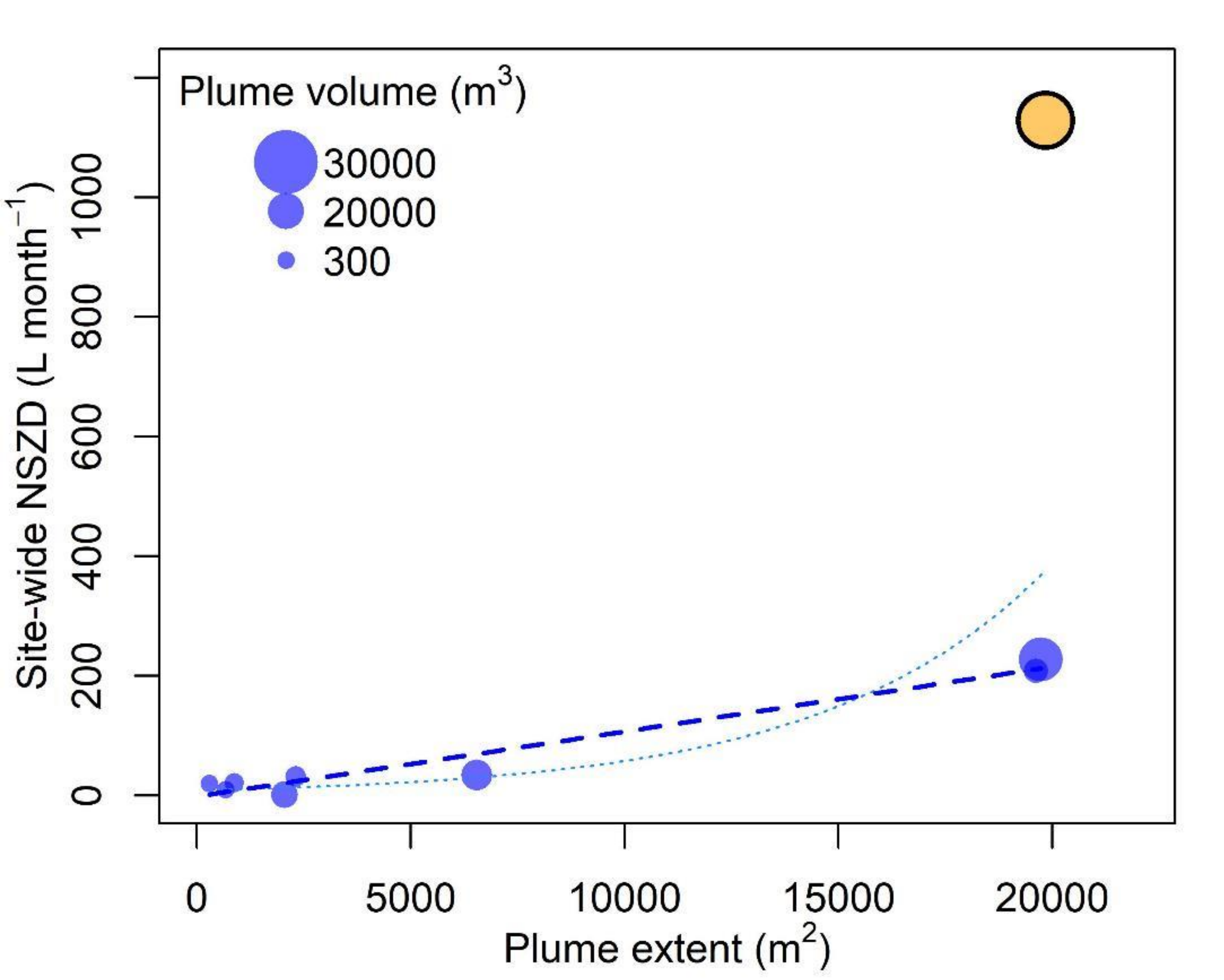


Plume volume

Typically stable over seasons

- Active site
- Additional sensor install and equilibration
- Site with high-water table and fall ice-up.

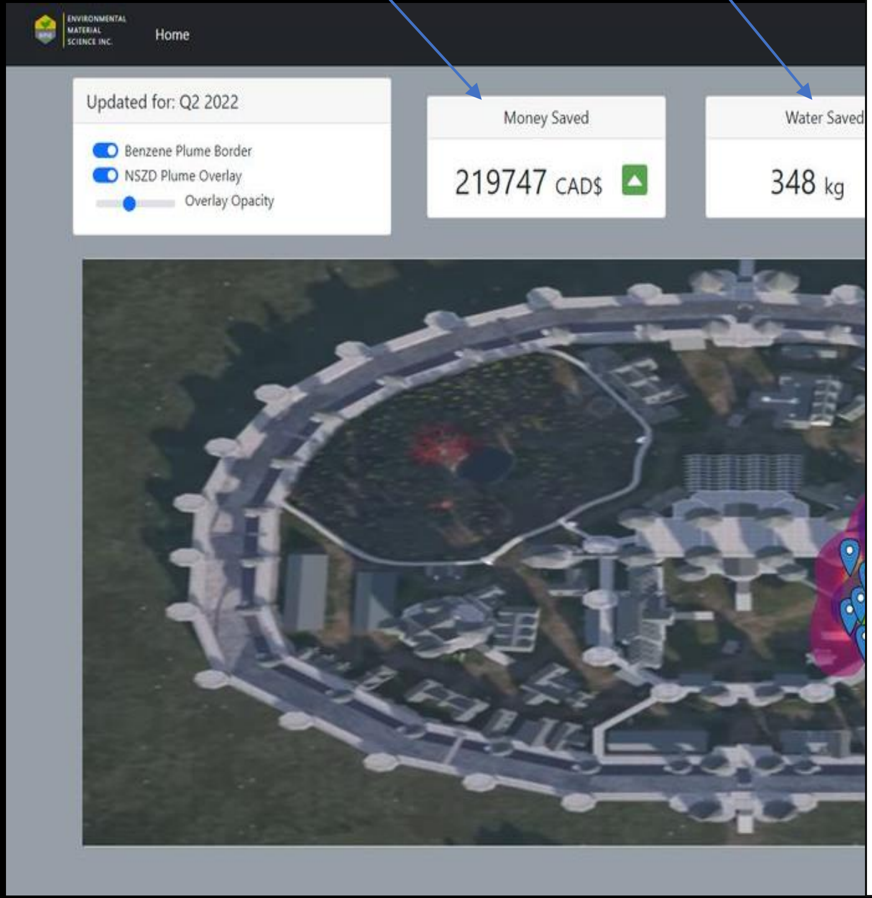
How do sites compare?

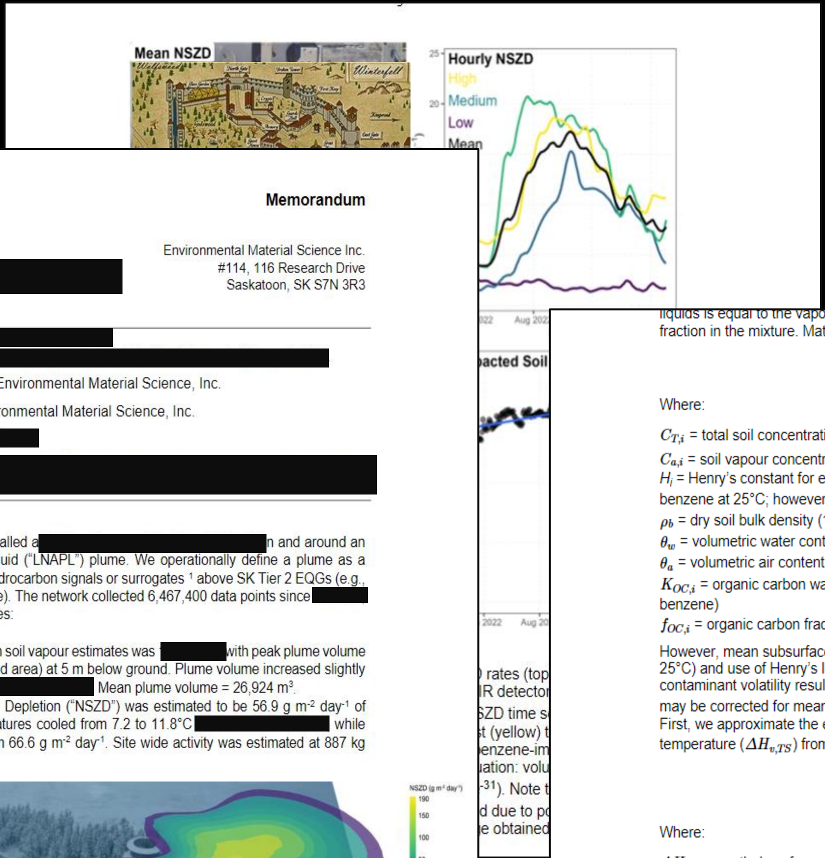


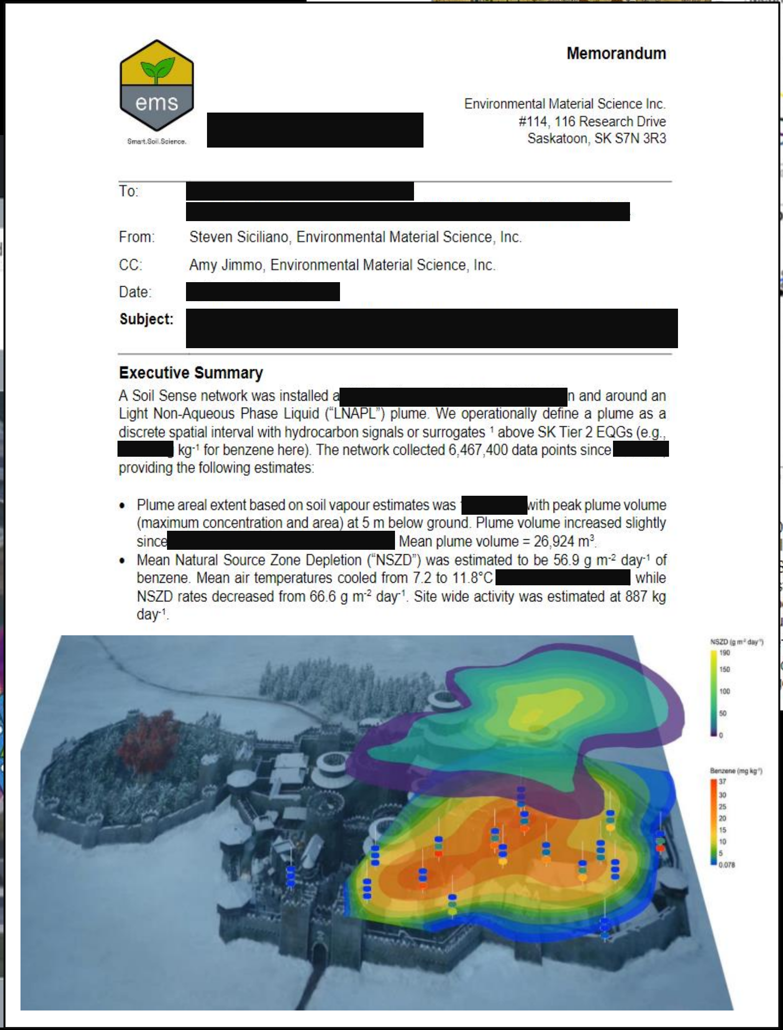
Continuous Site Monitoring

Money saved

Water saved







ems

Smart.Soil.Science.

[redacted]

Memorandum

Environmental Material Science Inc.
#114, 116 Research Drive
Saskatoon, SK S7N 3R3

To: [redacted]

From: Steven Siciliano, Environmental Material Science, Inc.

CC: Amy Jimmo, Environmental Material Science, Inc.

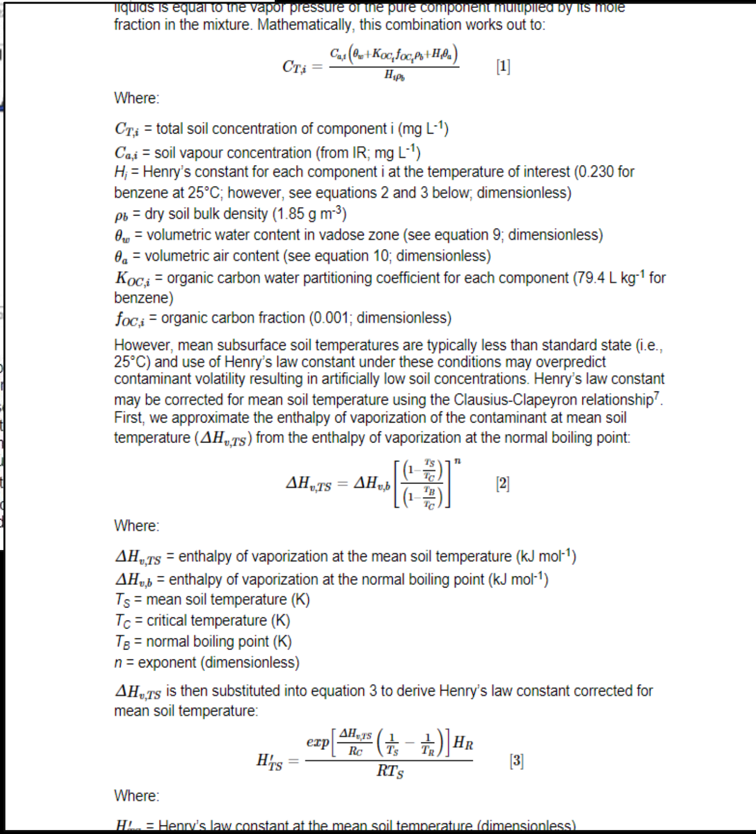
Date: [redacted]

Subject: [redacted]

Executive Summary

A Soil Sense network was installed a [redacted] n and around an Light Non-Aqueous Phase Liquid ("LNAPL") plume. We operationally define a plume as a discrete spatial interval with hydrocarbon signals or surrogates [1] above SK Tier 2 EQGs (e.g., [redacted] kg^{-1} for benzene here). The network collected 6,467,400 data points since [redacted] providing the following estimates:

- Plume areal extent based on soil vapour estimates was [redacted] with peak plume volume (maximum concentration and area) at 5 m below ground. Plume volume increased slightly since [redacted] Mean plume volume = 26,924 m^3.
- Mean Natural Source Zone Depletion ("NSZD") was estimated to be 56.9 g m^{-2} day^{-1} of benzene. Mean air temperatures cooled from 7.2 to 11.8°C [redacted] while NSZD rates decreased from 66.6 g m^{-2} day^{-1}. Site wide activity was estimated at 887 kg day^{-1}.



liquids is equal to the vapor pressure of the pure component multiplied by its mole fraction in the mixture. Mathematically, this combination works out to:

$$C_{T,i} = \frac{C_{a,i}\left(\theta_w + K_{OC_i} f_{OC_i} \rho_b + H_i \theta_a\right)}{H_i \rho_b} \quad [1]$$

Where:

$C_{T,i}$ = total soil concentration of component i (mg L^{-1})
$C_{a,i}$ = soil vapour concentration (from IR; mg L^{-1})
H_i = Henry's constant for each component i at the temperature of interest (0.230 for benzene at 25°C; however, see equations 2 and 3 below; dimensionless)
ρ_b = dry soil bulk density (1.85 g m^{-3})
θ_w = volumetric water content in vadose zone (see equation 9; dimensionless)
θ_a = volumetric air content (see equation 10; dimensionless)
$K_{OC,i}$ = organic carbon water partitioning coefficient for each component (79.4 L kg^{-1} for benzene)
$f_{OC,i}$ = organic carbon fraction (0.001; dimensionless)

However, mean subsurface soil temperatures are typically less than standard state (i.e., 25°C) and use of Henry's law constant under these conditions may overpredict contaminant volatility resulting in artificially low soil concentrations. Henry's law constant may be corrected for mean soil temperature using the Clausius-Clapeyron relationship[7]. First, we approximate the enthalpy of vaporization of the contaminant at mean soil temperature ($\Delta H_{v,TS}$) from the enthalpy of vaporization at the normal boiling point:

$$\Delta H_{v,TS} = \Delta H_{v,b}\left[\frac{\left(1-\frac{T_S}{T_C}\right)}{\left(1-\frac{T_B}{T_C}\right)}\right]^n \quad [2]$$

Where:

$\Delta H_{v,TS}$ = enthalpy of vaporization at the mean soil temperature (kJ mol^{-1})
$\Delta H_{v,b}$ = enthalpy of vaporization at the normal boiling point (kJ mol^{-1})
T_S = mean soil temperature (K)
T_C = critical temperature (K)
T_B = normal boiling point (K)
n = exponent (dimensionless)

$\Delta H_{v,TS}$ is then substituted into equation 3 to derive Henry's law constant corrected for mean soil temperature:

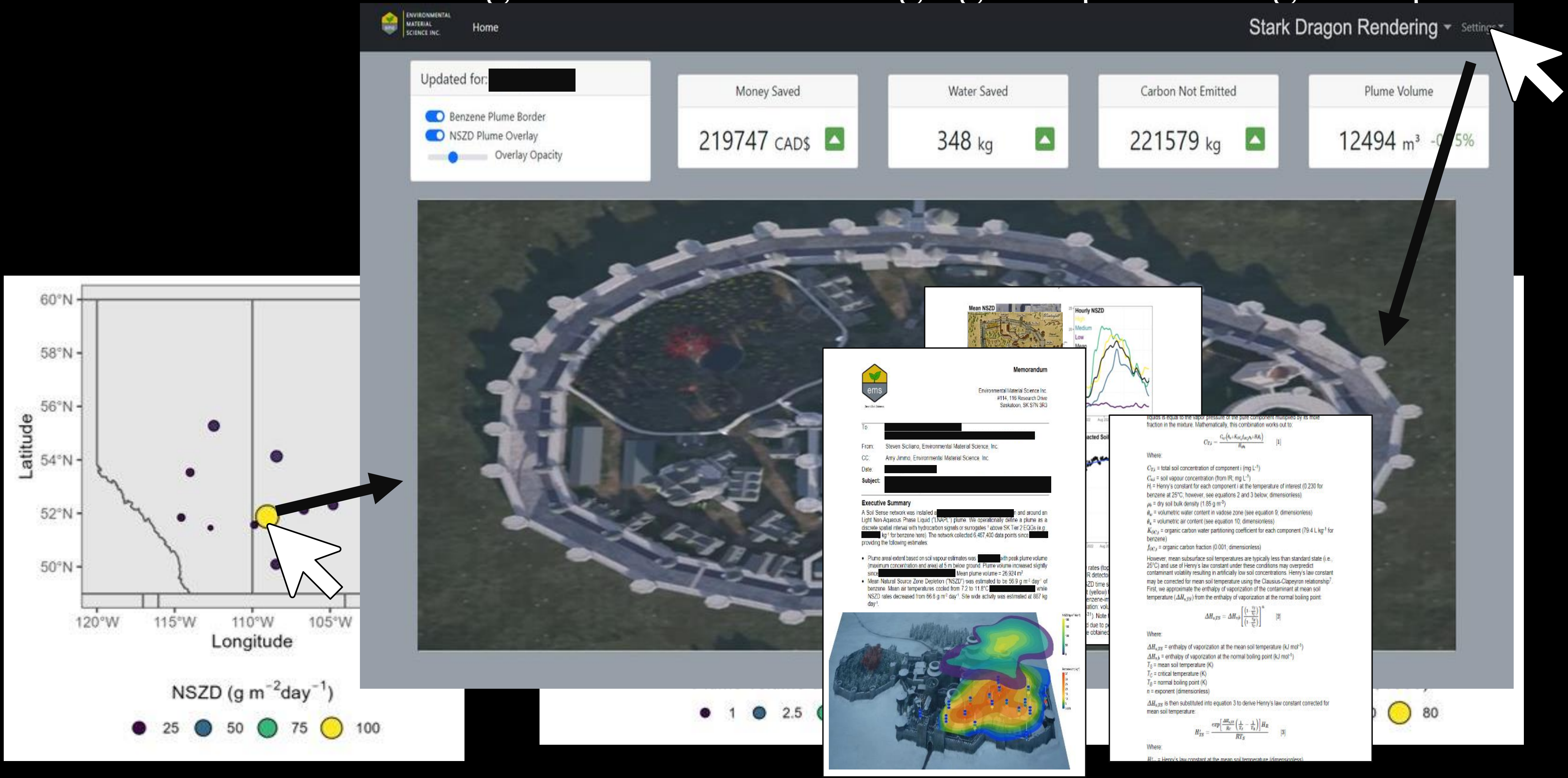
$$H'_{TS} = \frac{exp\left[\frac{\Delta H_{v,TS}}{R_C}\left(\frac{1}{T_S} - \frac{1}{T_R}\right)\right] H_R}{RT_S} \quad [3]$$

Where:

H'_{TS} = Henry's law constant at the mean soil temperature (dimensionless)

Managing Multiple Sites

- The goal is to make managing and prioritizing multiple



Where are we now?

- High density continuous measurements
  - Diurnal and seasonal nuances, site-driven variation
  - CH_4 may make up the bulk of NSZD in some sites
- Soil moisture
  - Implications for fluid transfer and PHC distributions
- Site-specific estimates
  - Theoretical stoichiometry may not represent site processes
- Stay-tuned for next year!
  - modflow
  - Data assimilation
  - AgTech.

Thank you!

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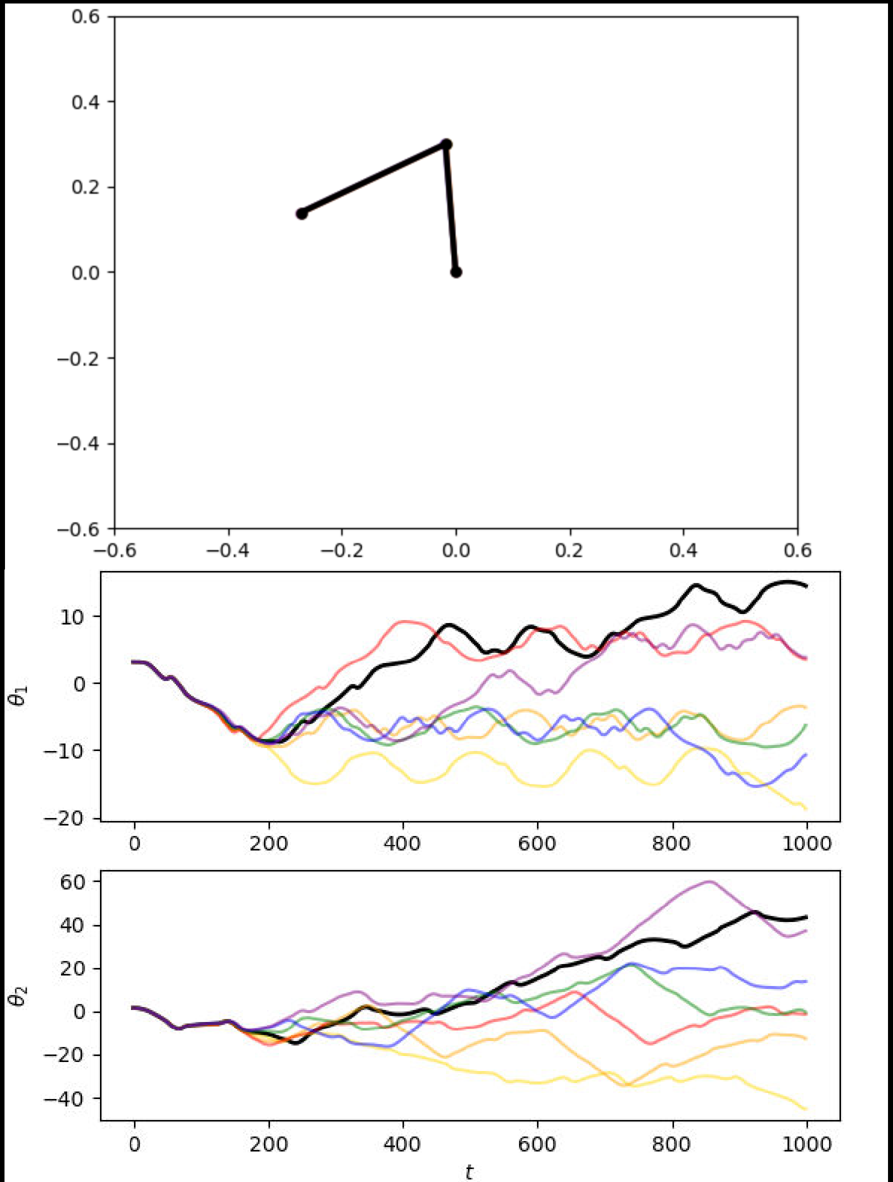
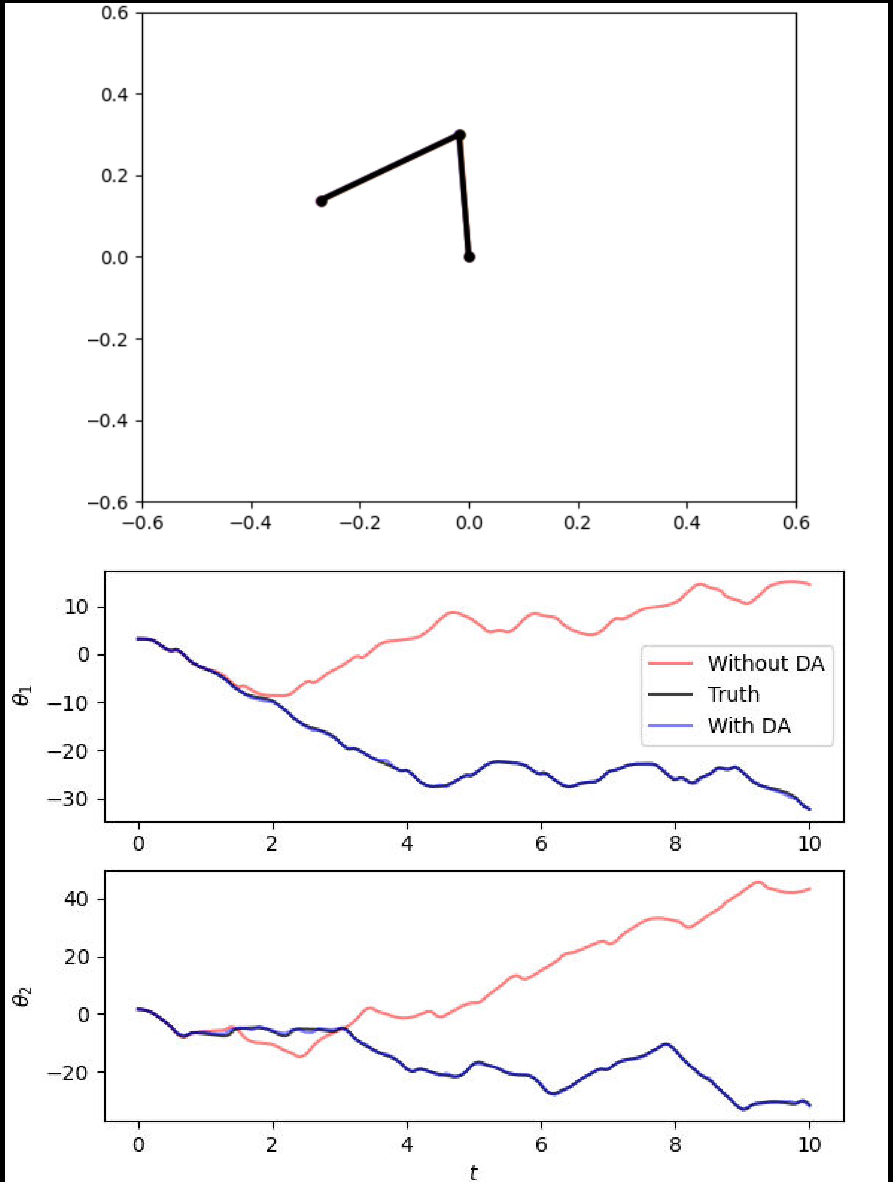
Data Assimilation – Double Pendulum Example



- Small differences in parameters or initial conditions propagate into large intractable errors in model output

- Data Assimilation uses observations/measurements to update models to prevent them from diverging.



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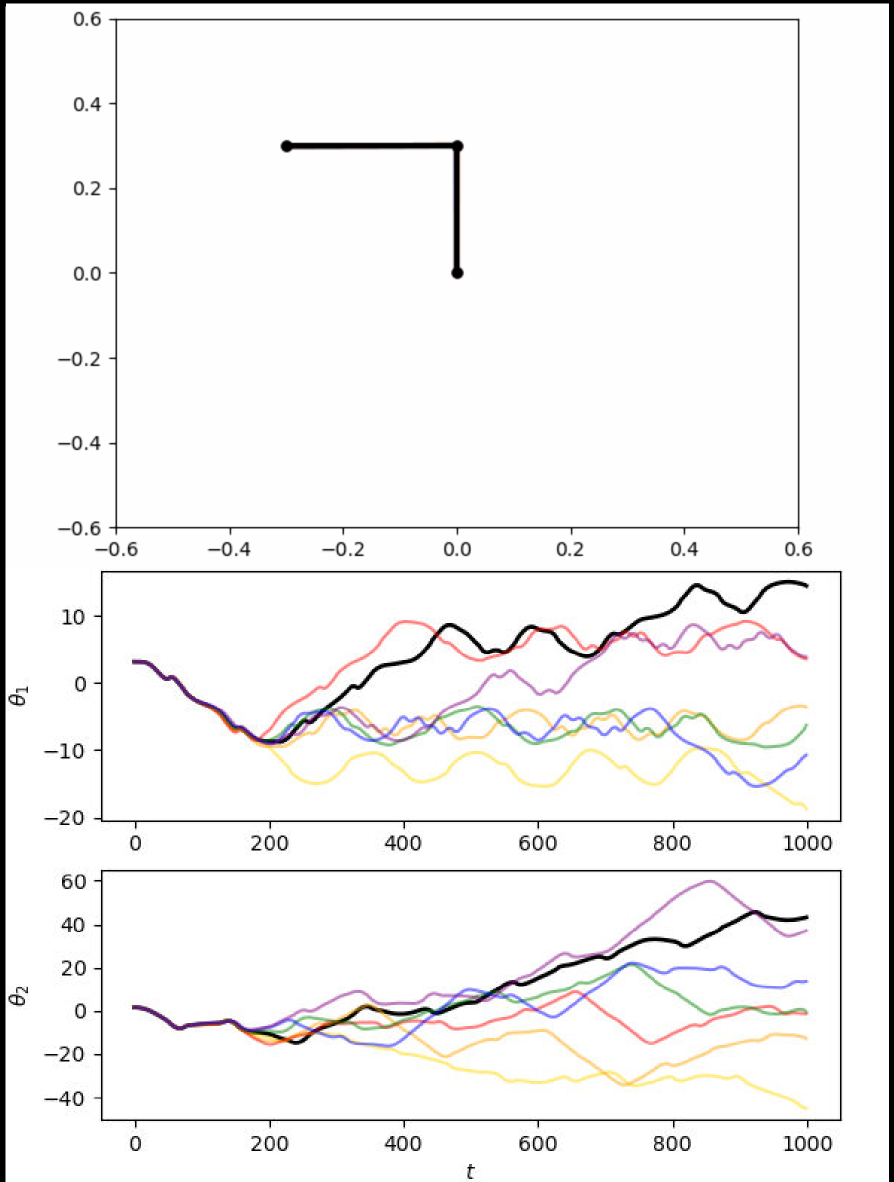

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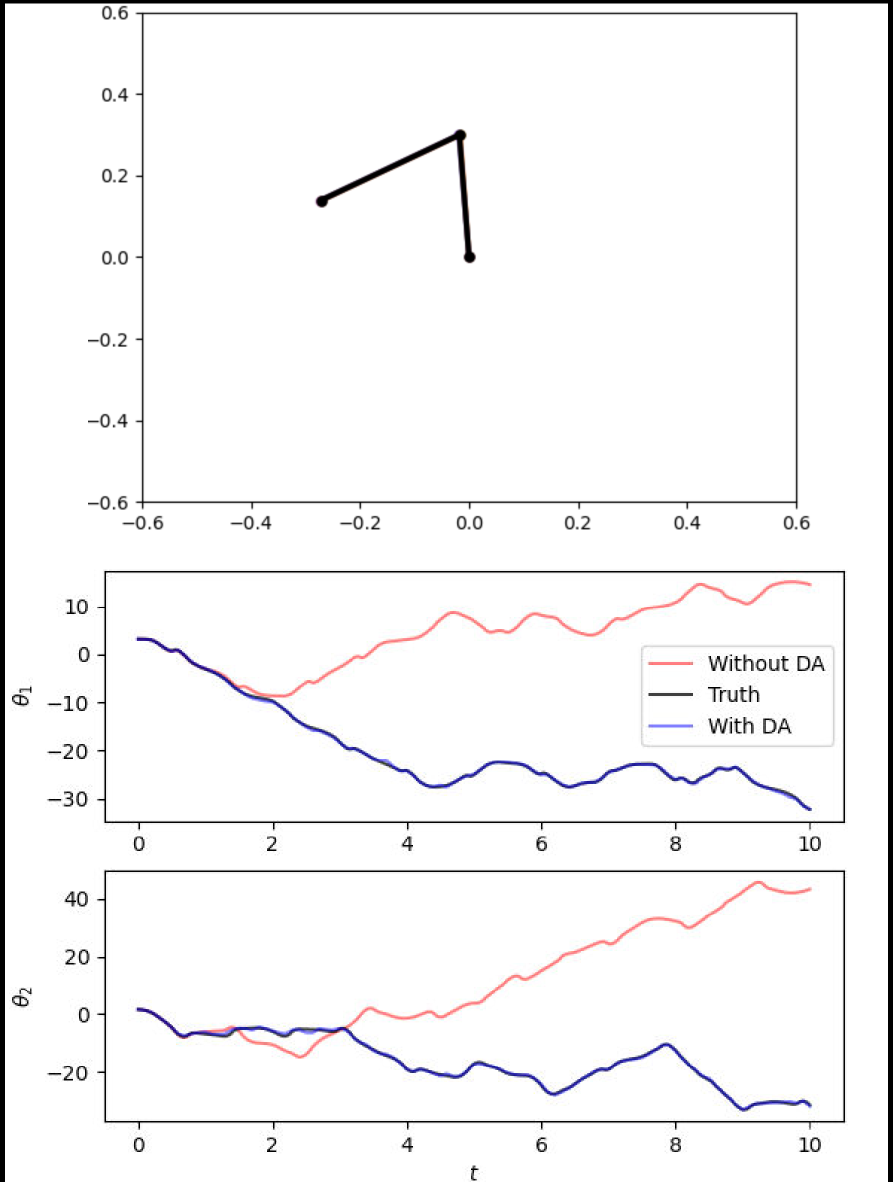

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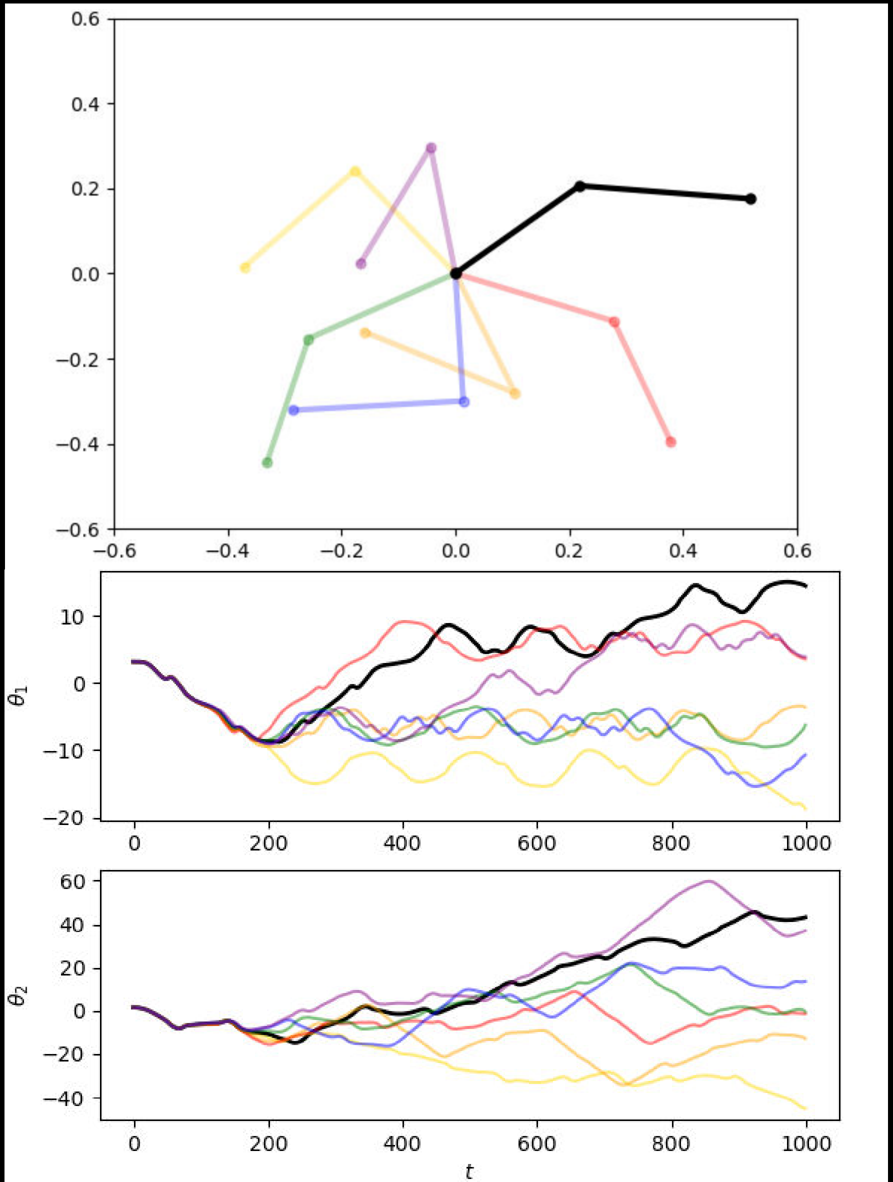

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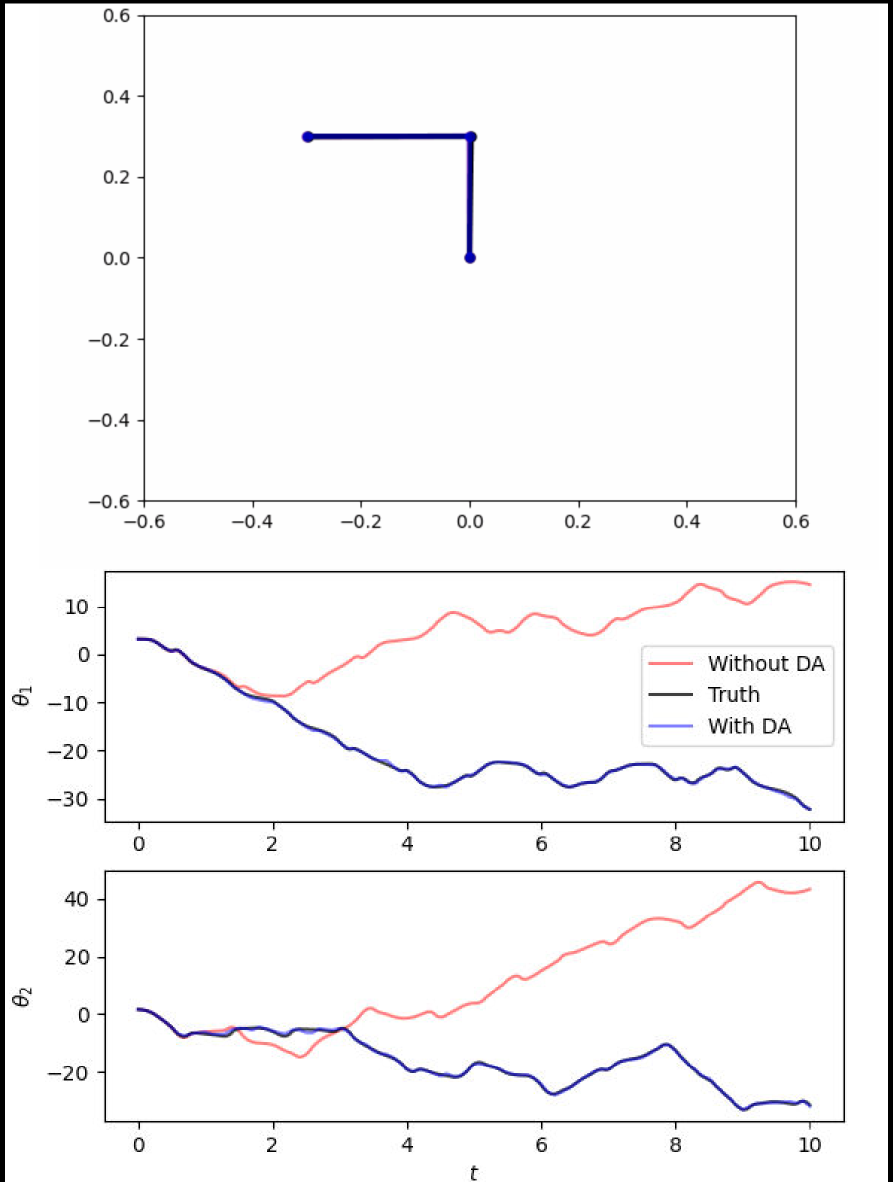
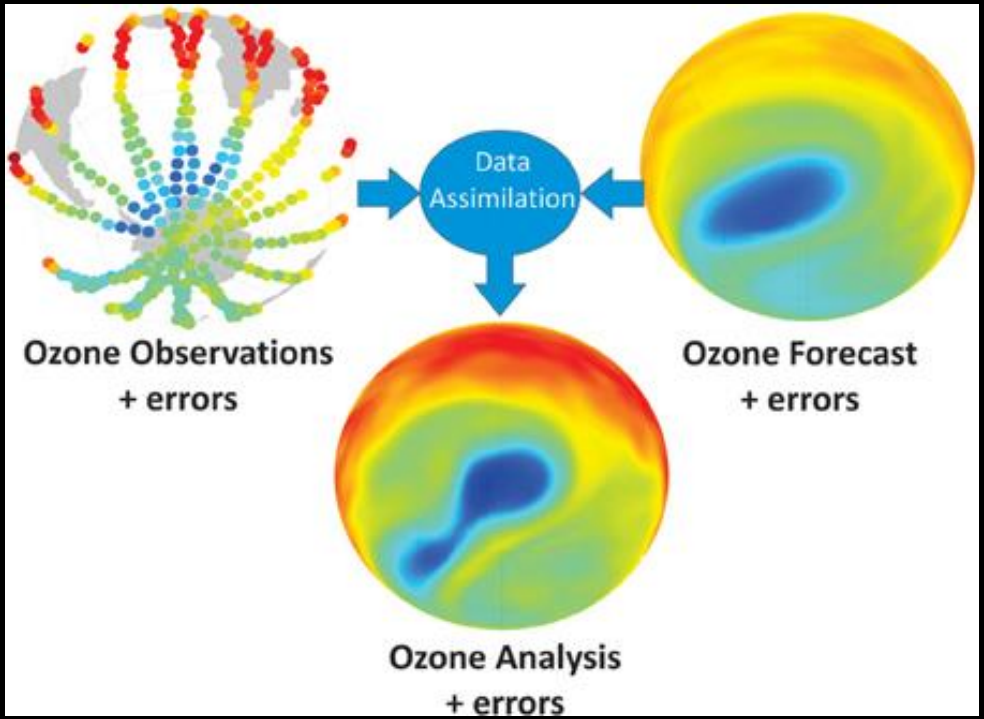


Data Assimilation

- Data Assimilation is utilized in a large number of fields including weather prediction, self-driving cars, missile tracking, nuclear power, and GPS



Lahoz and Schneider, 2014. Frontiers in Env. Sci.

- EMS' sensor data leverages Data Assimilation to improve estimates of plume-maps, biodegradation, and soil gas profiles.