Compound Specific Isotope Analysis of 2,3-Dichloroaniline Reveals Aerobic Biotransformation in Constructed Wetlands

Shamsunnahar Suchana[1*], *Sofia P. Araujo*[2], *Line Lomheim*[1], *Elizabeth Edwards*[1], *E. Erin Mack*[3], *Elodie Passeport*[1]

[1] University of Toronto, Canada; [2] Federal University of Pernambuco, Brazil; [3] Corteva Agriscience, USA

*Presenting author

UNIVERSITY OF TORONTO

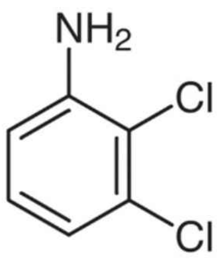
Outline

- Background
- Compound specific isotope analysis
- Laboratory experiments
- Application in constructed wetlands
- Conclusions

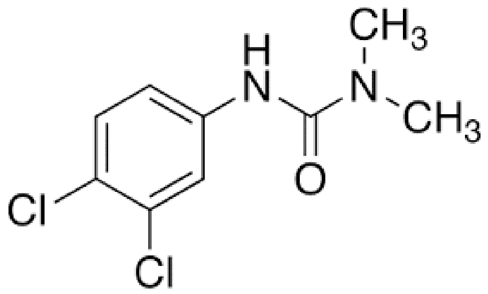
2,3-DCA is a feedstock chemical for herbicide Diuron

Diuron is widely used to control broadleaf and grassy weeds in

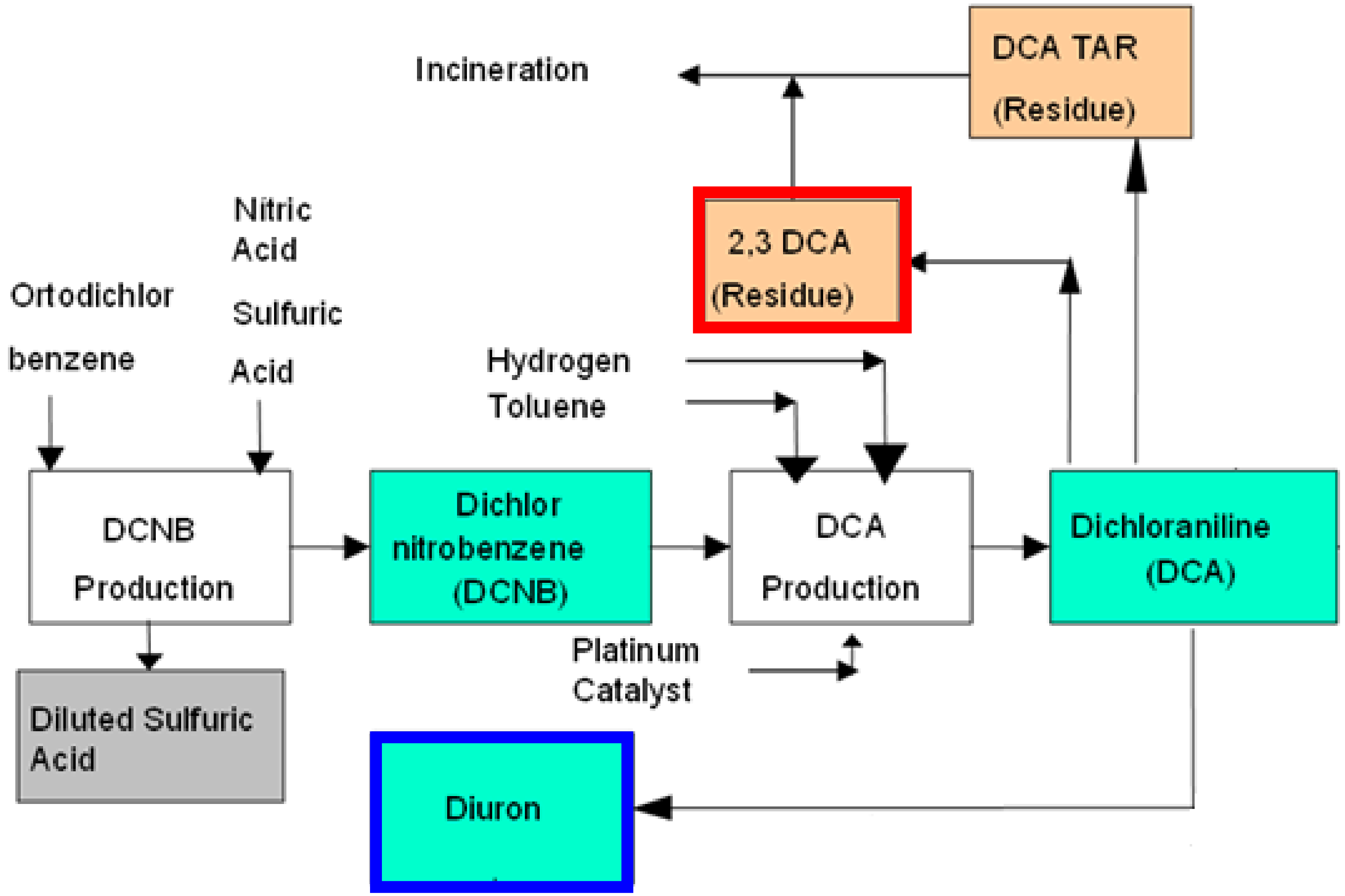
- Agriculture
- Roadside and garden paths



2,3-dichloroaniline (2,3-DCA)



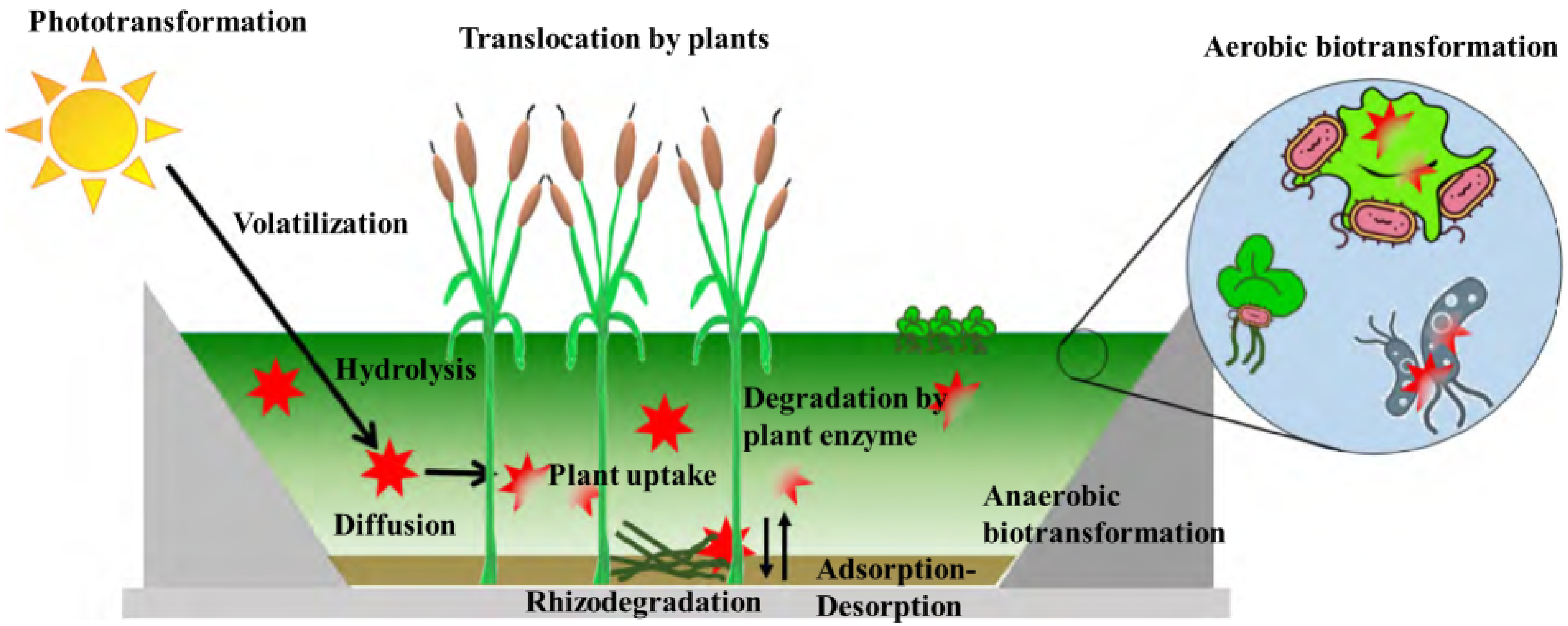
Diuron



Contaminated pesticide production site

- Inactive industrial complex in Brazil
- Pesticides, synthetic fibers, and pharmaceuticals
- Aquifer contaminated by multiple (s)VOCs
- Pre-treated groundwater sent to constructed wetlands

Fate in constructed wetland



Transformation

- Phototransformation
- Biotransformation

Transfer

- Diffusion
- Sorption

- Concentration-based approaches cannot provide direct evidence of transformation
- One promising advanced analytical technique is **compound specific isotope analysis (CSIA)**

Goal

Evaluate the potential of CSIA to track *in situ* transformation of 2,3-dichloroaniline in wetlands

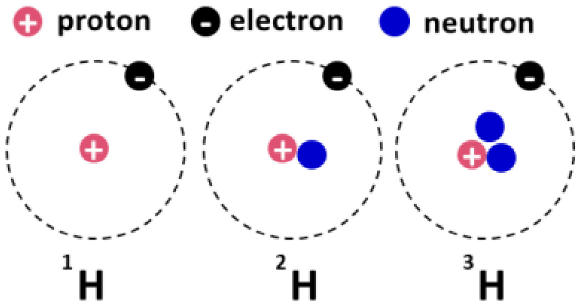
Specific objectives

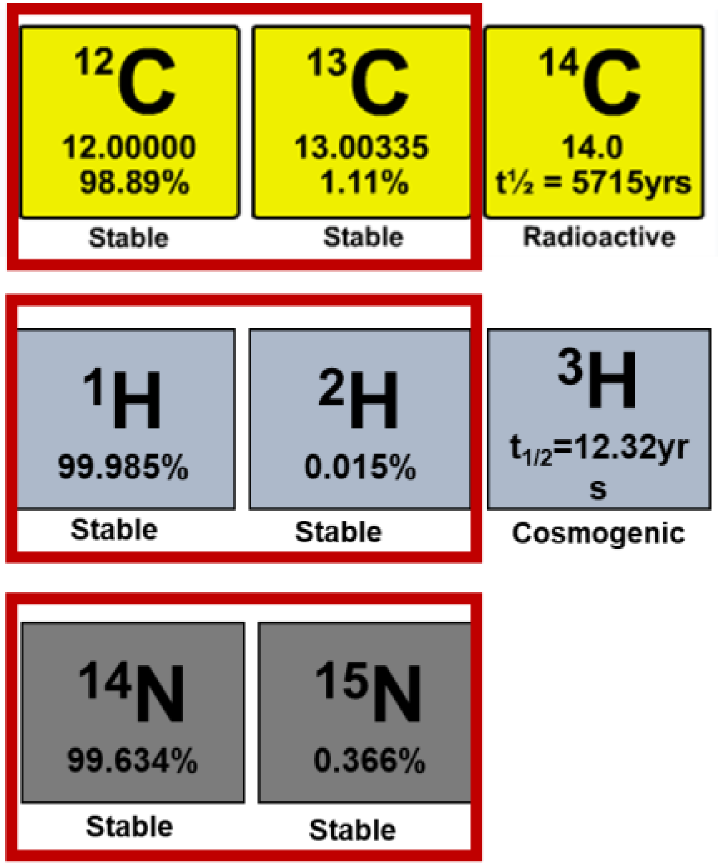
1. Develop a CSIA method for complex aqueous matrix
2. Determine enrichment factor
3. Identify and quantify transformation in wetlands

Compound specific isotope analysis (CSIA)

Isotopes

Same elements but different numbers of neutrons





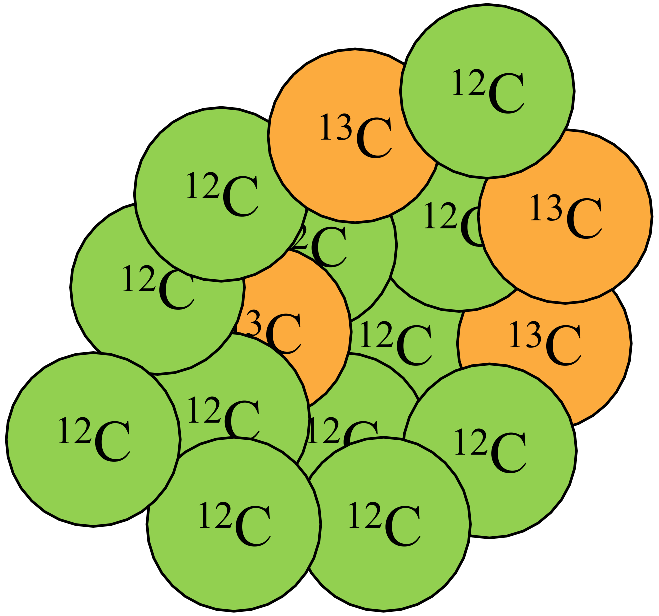
CSIA

CSIA measures the ratio of heavy and light isotopes (e.g., C) in a molecule (e.g., Benzene)

Isotope signature is expressed as delta value, e.g. $\delta^{13}C$ using parts per thousands (‰) unit

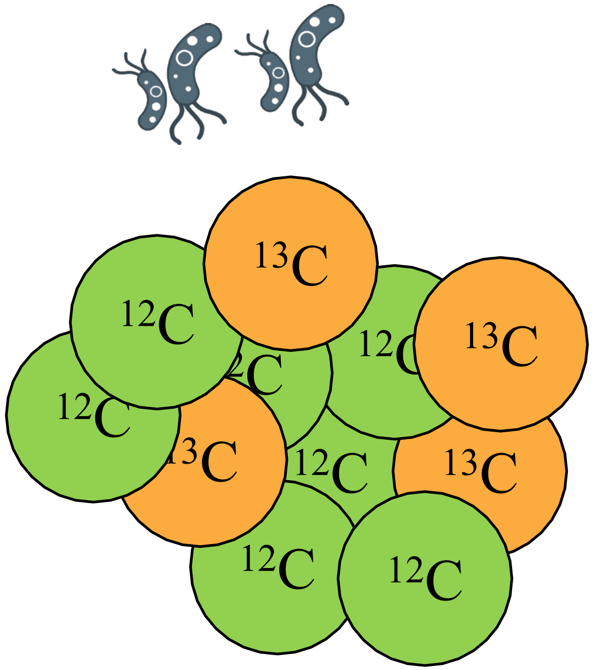
CSIA to investigate *in situ* degradation?

Reaction rate $^{12}C > ^{13}C$



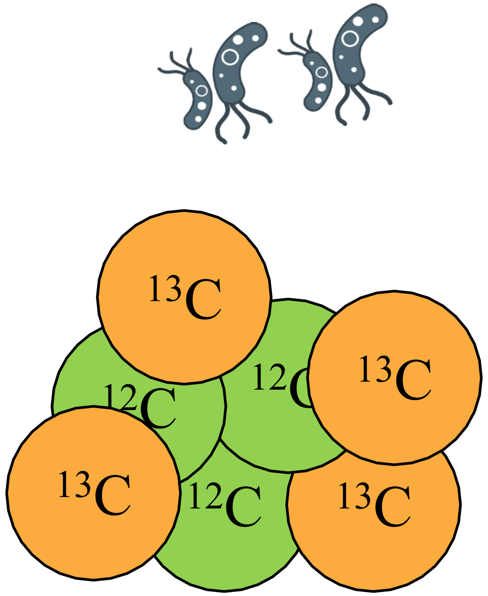
Initial contaminants pool

Ratio of $^{13}C/^{12}C$



After some degradation

Ratio of $^{13}C/^{12}C$ changes



Later stage of degradation

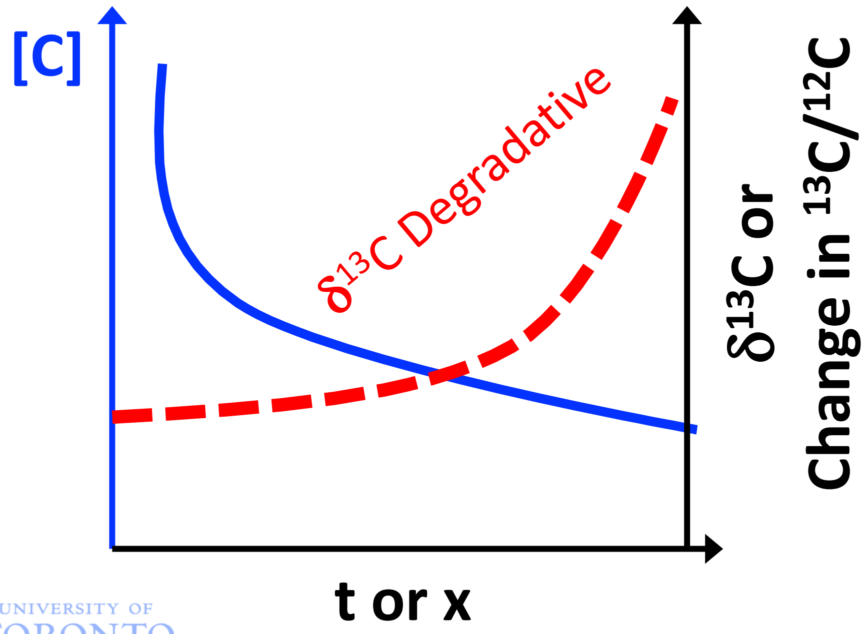
Ratio of $^{13}C/^{12}C$ changes

CSIA to investigate *in situ* degradation?

Degradative

transformation

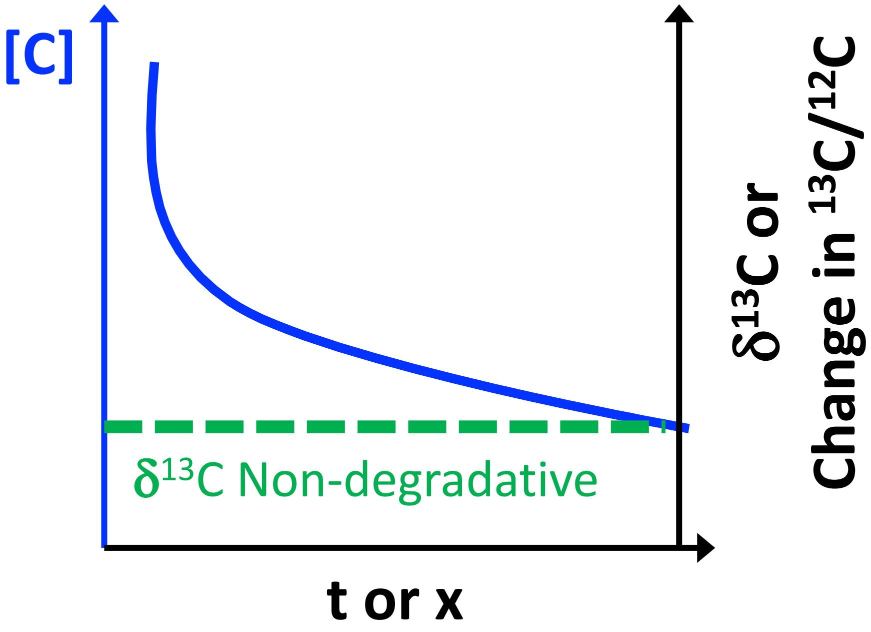
- Bond breaking



Non-degradative

transfer

- Redistribution

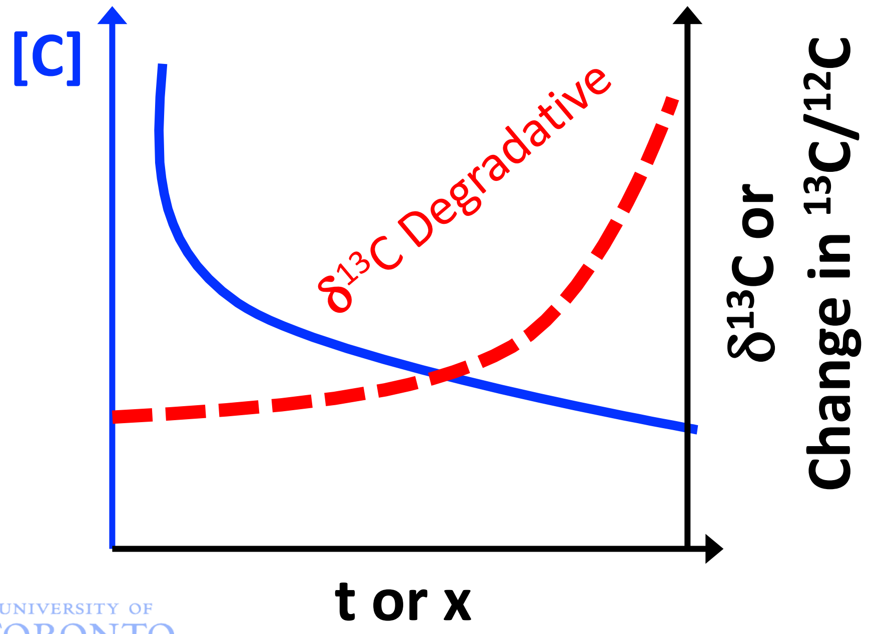


CSIA to investigate *in situ* degradation?

Degradative

transformation

- Bond breaking

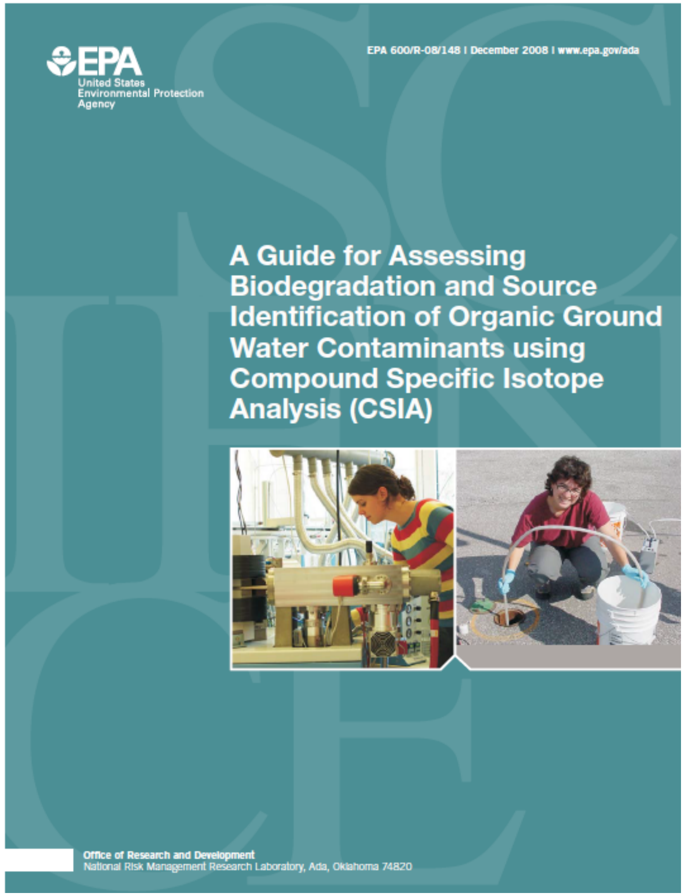


Rayleigh equation:

$$\frac{\delta^{13}C_t + 1}{\delta^{13}C_0 + 1} = f^{\varepsilon}$$

ε = Lab-derived factor

f = extent of degradation



Hunkeler et al. 2008

Goal

Evaluate the potential of CSIA to track *in situ* transformation of 2,3-dichloroaniline in wetlands

Specific objectives

1. Develop a CSIA method for complex aqueous matrix ✓ (Trust me!!)

analytical chemistry

pubs.acs.org/ac Article

Compound-Specific Carbon, Hydrogen, and Nitrogen Isotope Analysis of Nitro- and Amino-Substituted Chlorobenzenes in Complex Aqueous Matrices

Shamsunnahar Suchana, Langping Wu, and Elodie Passeport*

Cite This: https://doi.org/10.1021/acs.analchem.2c05099 Read Online

S. Suchana et al. (2023), ACS Analytical Chemistry

Goal

Evaluate the potential of CSIA to track *in situ* transformation of 2,3-dichloroaniline in wetlands

Specific objectives

1. Develop a CSIA method for complex aqueous matrix ✓ (Trust me!!)
2. Determine enrichment factor
3. Identify and quantify transformation in wetlands

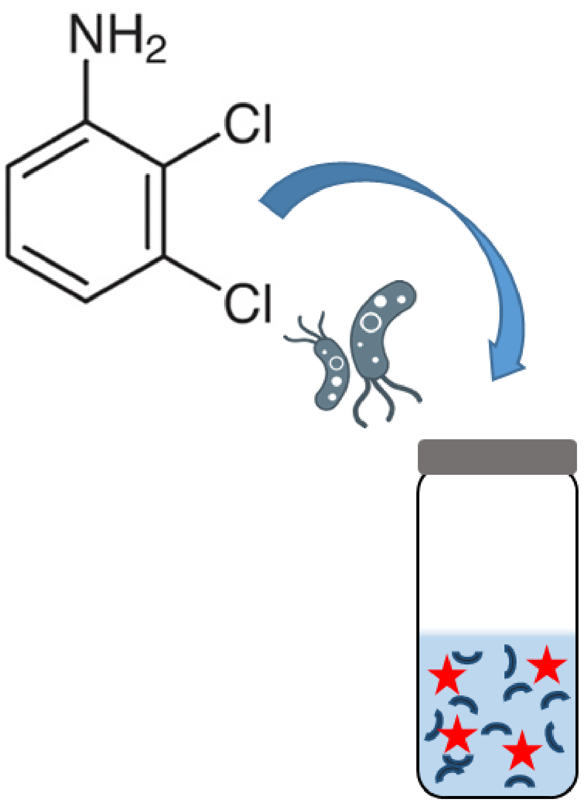
Dichloroanilines isotope fractionation

	AEROBIC	ANAEROBIC	ABIOTIC
(di)chloroanilines	**2,3-DCA?**		ε_C = -0.5 to -2.7 (DP), -0.2, -1.0 (IP) ε_N = -2.7 to -9.1 (DP), -1.7, -3.5 (IP) ε_N = -1.9 (MnO_2)

UNIVERSITY OF TORONTO

Pati et al. 2014, 2016, Skarpeli-Liati et al. 2011, Ratti et al. 2015

Aerobic biotransformation of 2,3-DCA



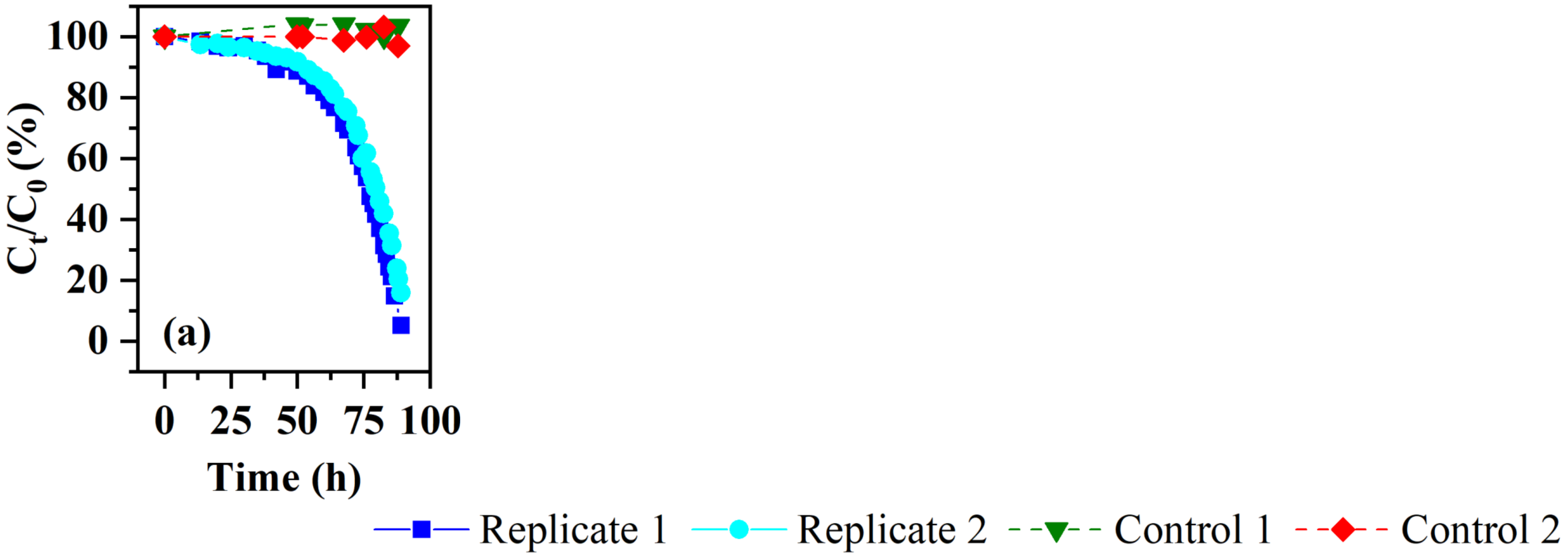
- Laboratory controlled experiment
- Media spiked with 2,3-DCA (substrate)
- Inoculated with site enrichment culture
- Conc. and isotope signature measured over time
- Results were fitted with Rayleigh model

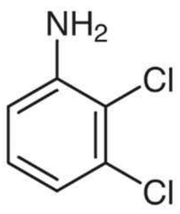
Rayleigh equation:

$$\frac{\delta^{13}C_t + 1}{\delta^{13}C_0 + 1} = \left[\frac{Conc._t}{Conc._0}\right]^{\varepsilon}$$

ε: Enrichment factors (‰)

Aerobic biotransformation of 2,3-DCA

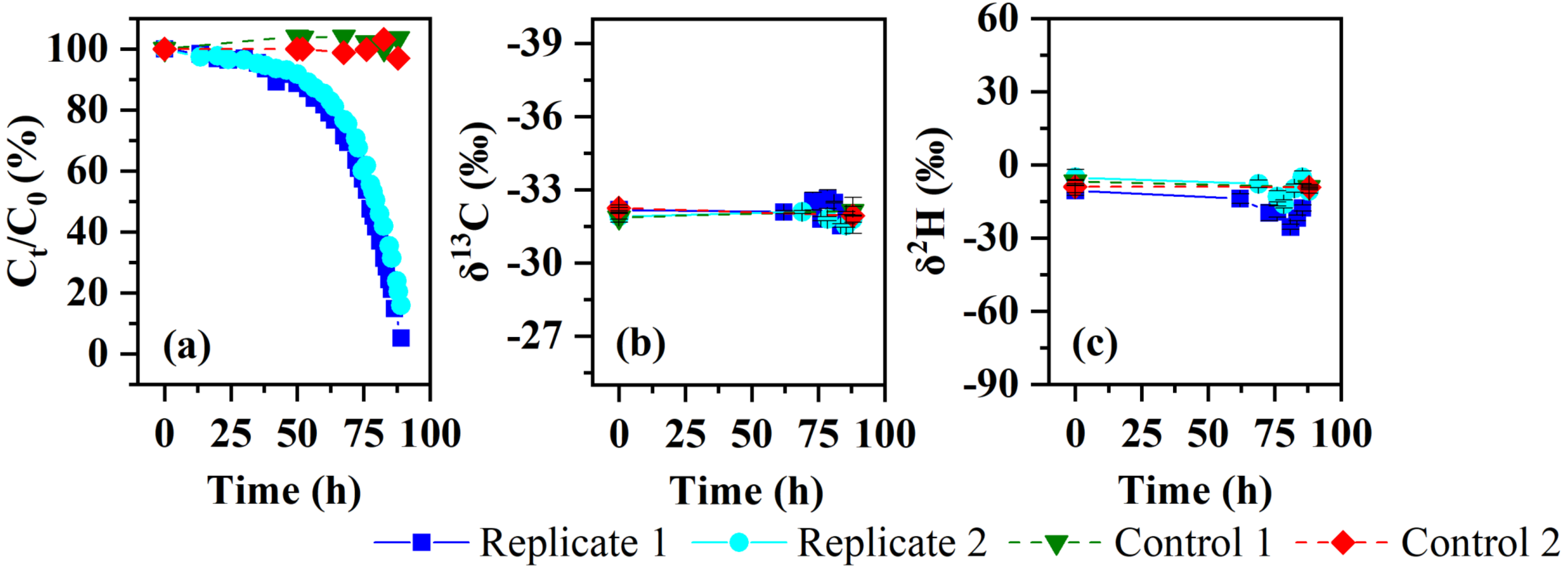


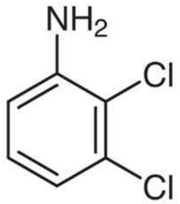


- No change in controls

Suchana et al. available on ChemRxiv

Aerobic biotransformation of 2,3-DCA





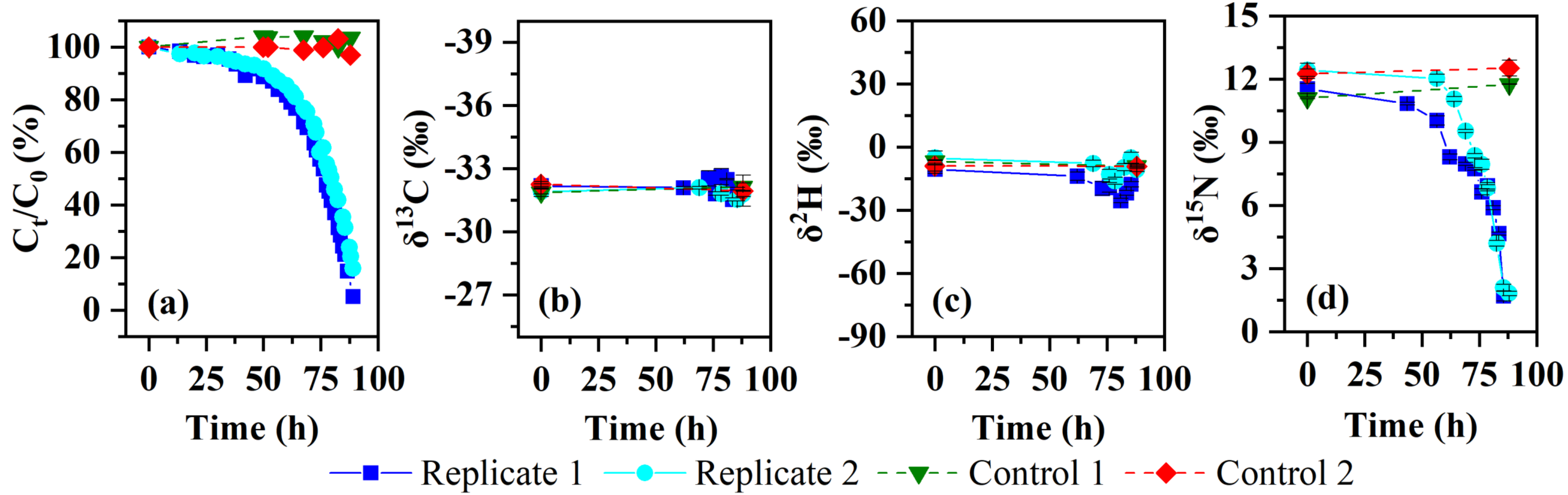
- No change in controls

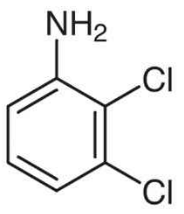
$\varepsilon_C \sim 0$

$\varepsilon_H \sim 0$

Suchana et al. available on ChemRxiv

Aerobic biotransformation of 2,3-DCA





- No change in controls

$\varepsilon_C \sim 0$

$\varepsilon_H \sim 0$

$\varepsilon_{N,1} = 6.2 \pm 0.3$ ‰

$\varepsilon_{N,2} = 7.9 \pm 0.4$ ‰

UNIVERSITY OF TORONTO

Suchana et al. available on ChemRxiv

Dichloroanilines isotope fractionation

	AEROBIC	ANAEROBIC	ABIOTIC
(di)chloroanilines	ε_C = 0 ε_H = 0 ε_N = +6.2 to +7.9		ε_C = -0.5 to -2.7(DP), -0.2, -1.0(IP) ε_N = -2.7 to -9.1(DP), -1.7, -3.5(IP) ε_N = -1.9(MnO_2)

UNIVERSITY OF TORONTO

Pati et al. 2014, 2016, Skarpeli-Liati et al. 2011, Ratti et al. 2015

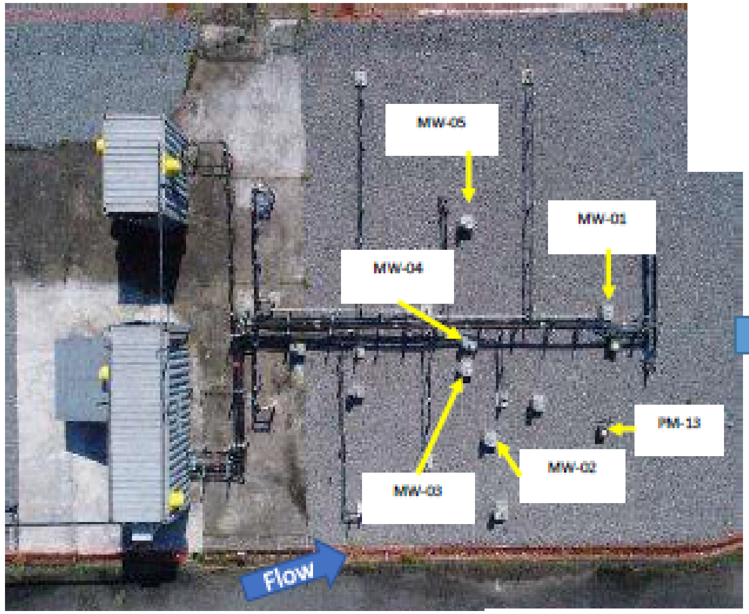
Goal

Evaluate the potential of CSIA to track *in situ* transformation of 2,3-dichloroaniline in wetlands

Specific objectives

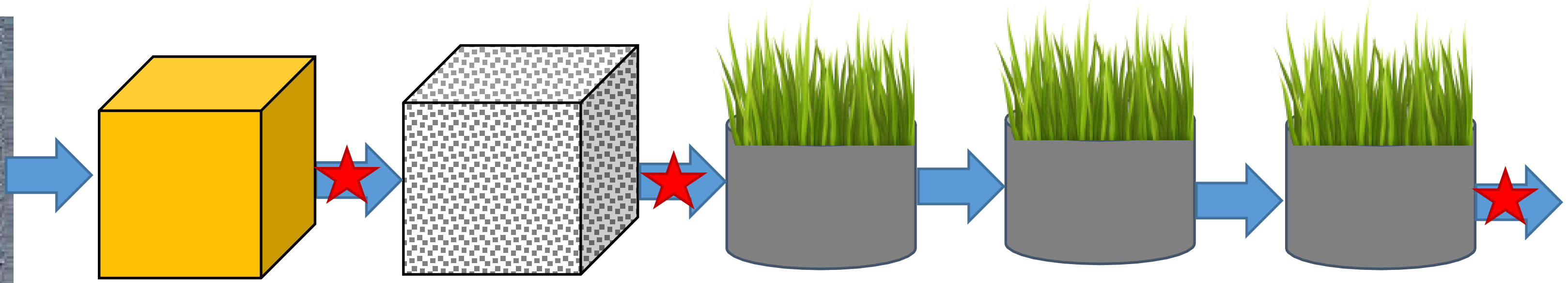
1. Develop a CSIA method for complex aqueous matrix ✓ (Trust me!!)
2. Determine enrichment factor
3. Identify and quantify transformation in wetlands

CSIA in constructed wetlands



Groundwater well in contaminated site

Contaminated groundwater pumped to a supply tank



Tank

UG

PM-1

PM-2

PM-3

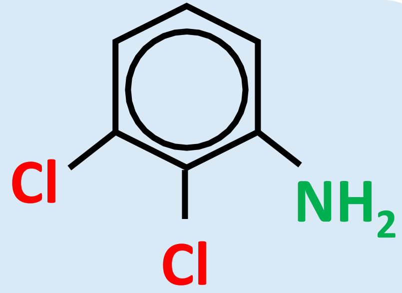
Unplanted gravel bed (UG)

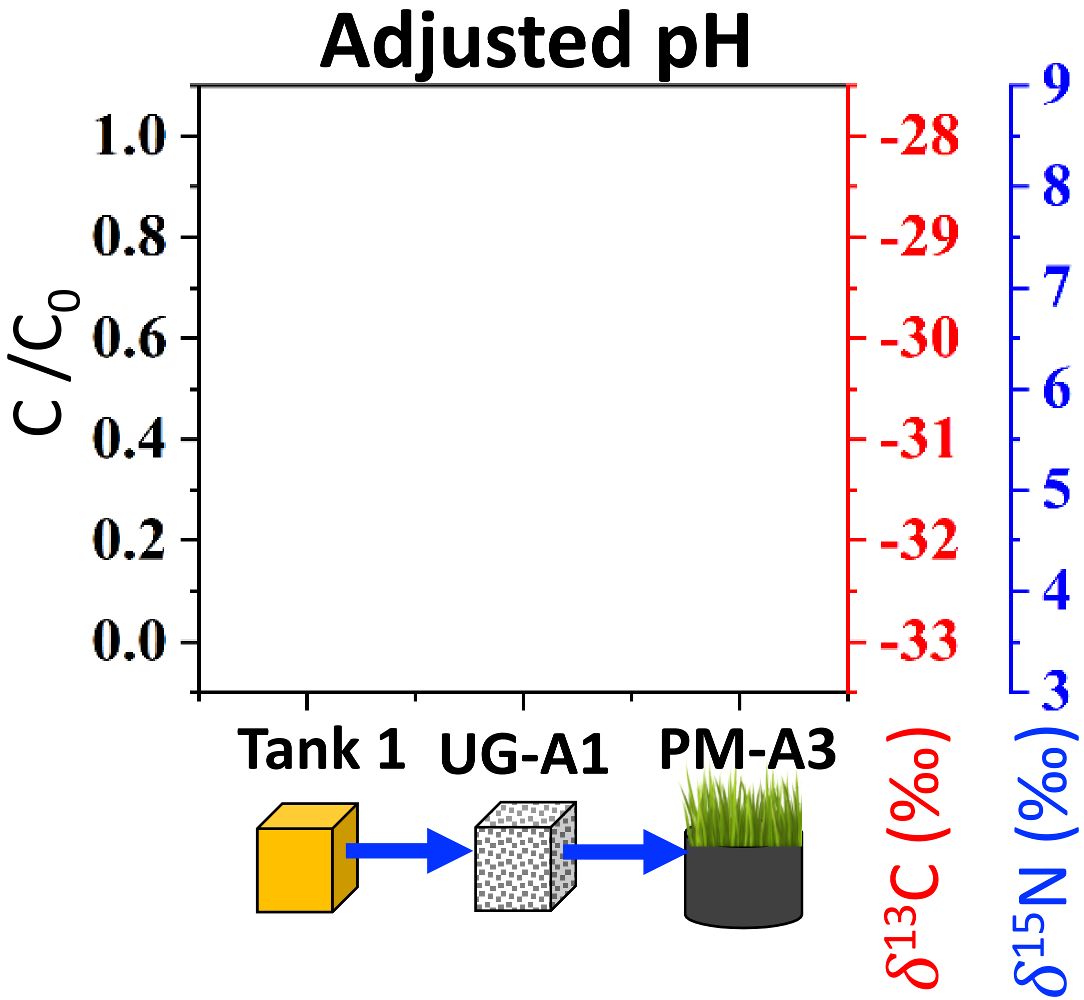
Three planted marsh (PM) in series

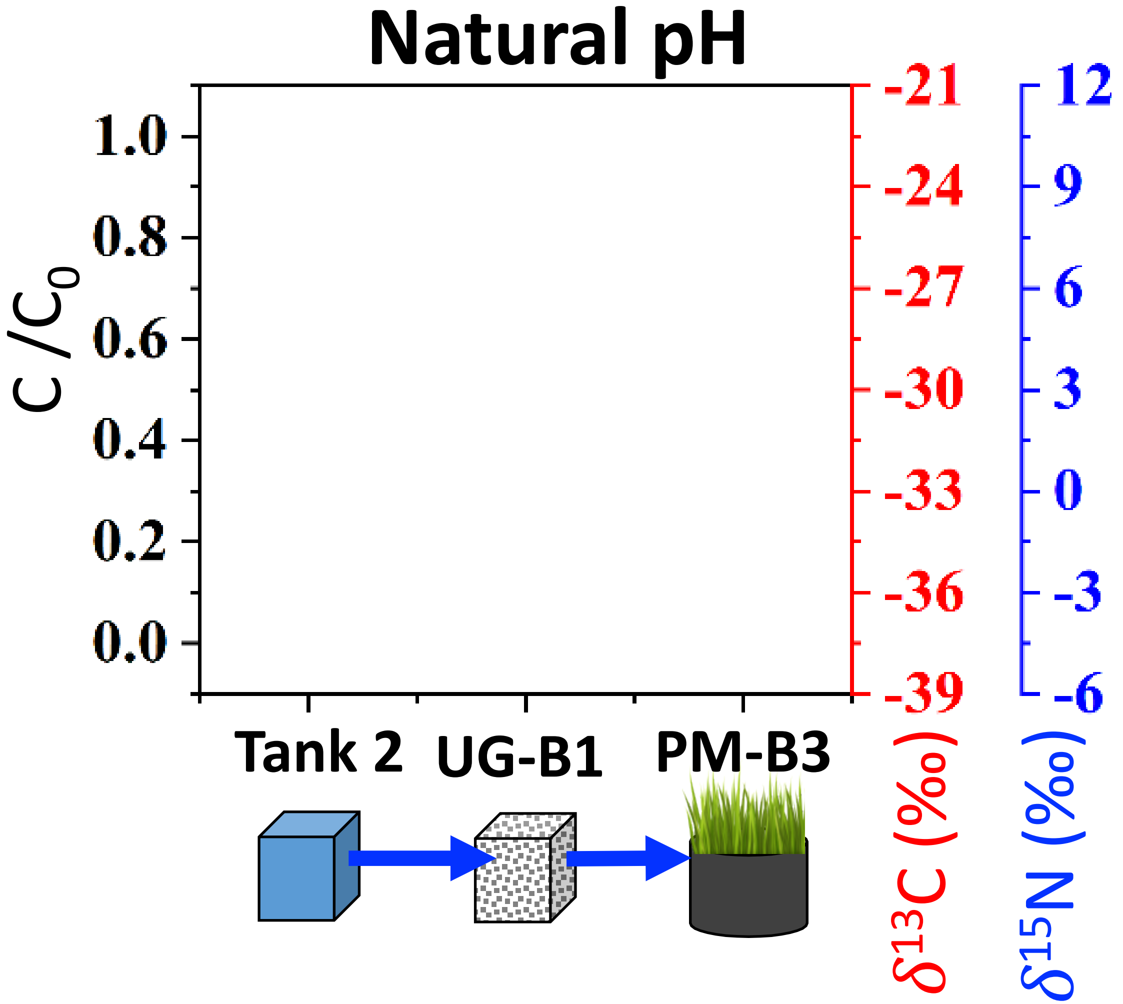
★ Sampling locations

C- & N-CSIA in constructed wetlands

2,3-DCA



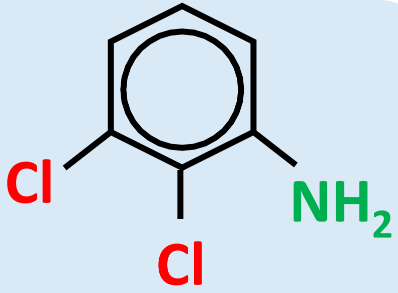


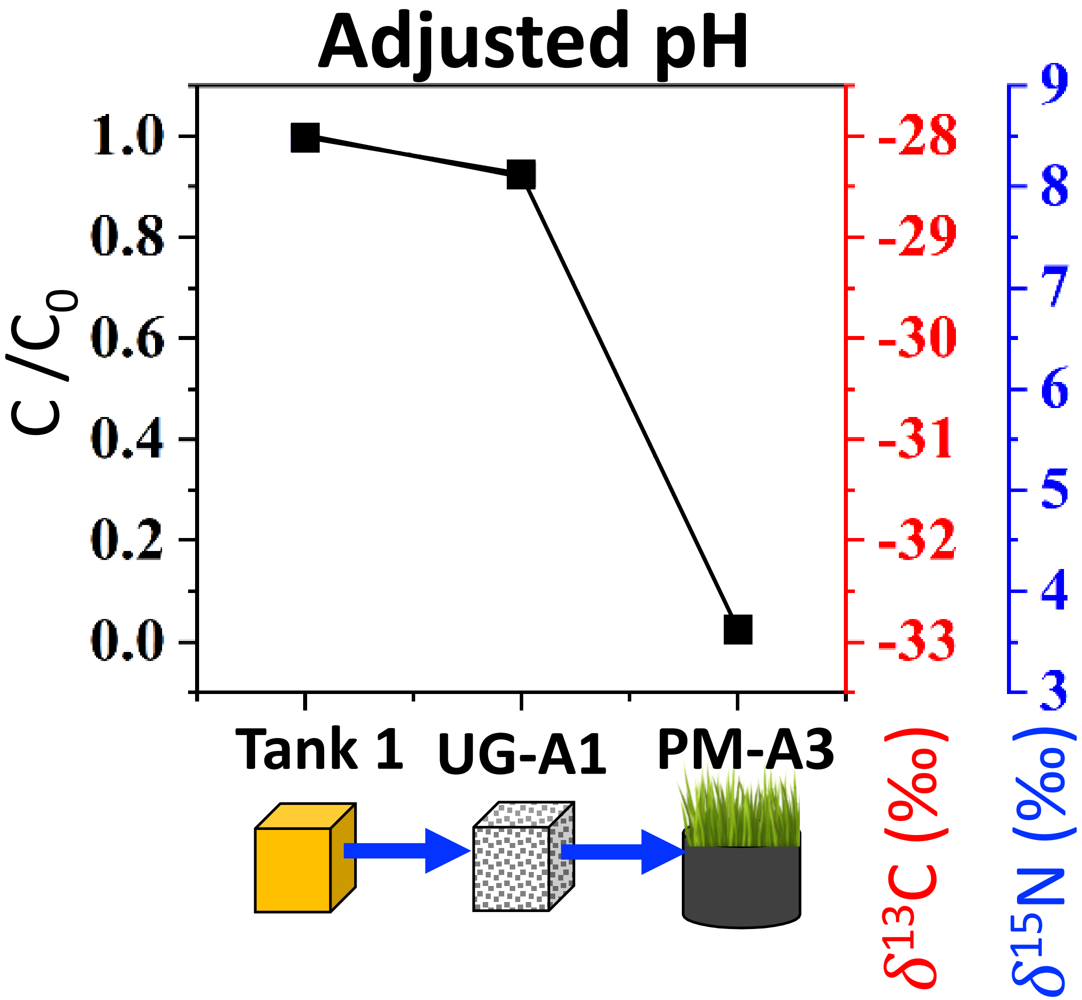


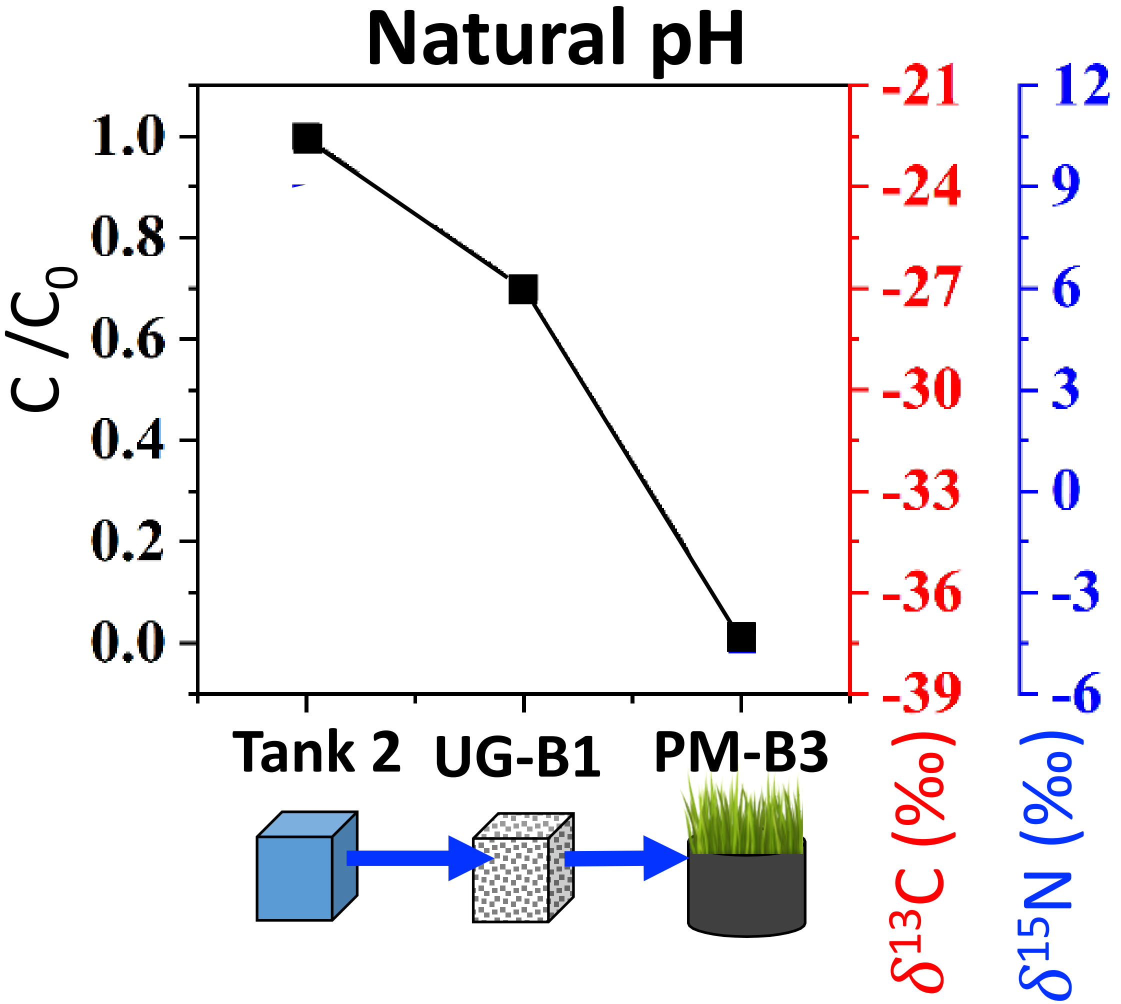
UNIVERSITY OF TORONTO

C- & N-CSIA in constructed wetlands

2,3-DCA

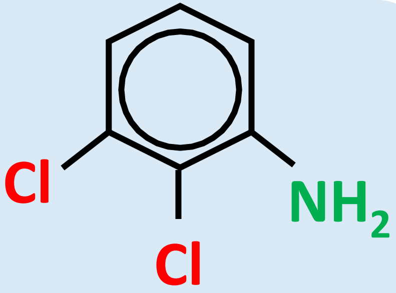




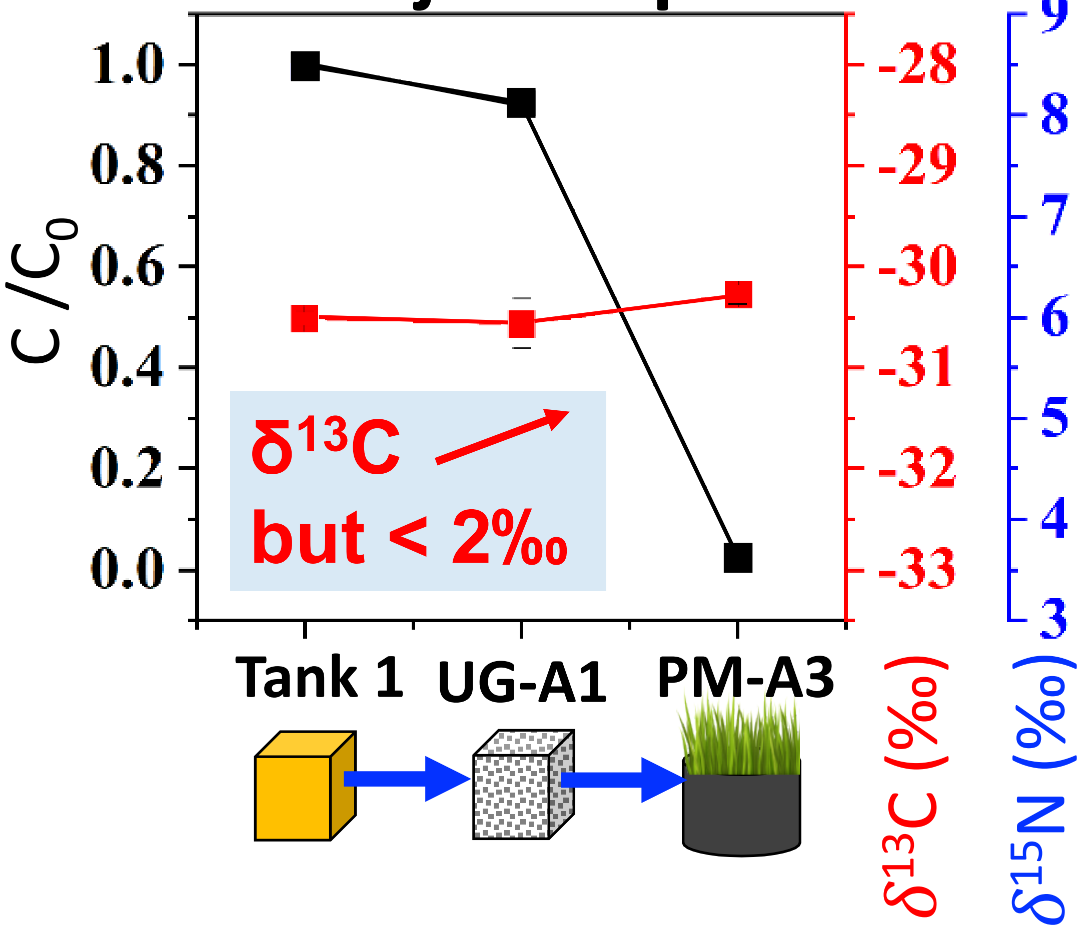


C- & N-CSIA in constructed wetlands

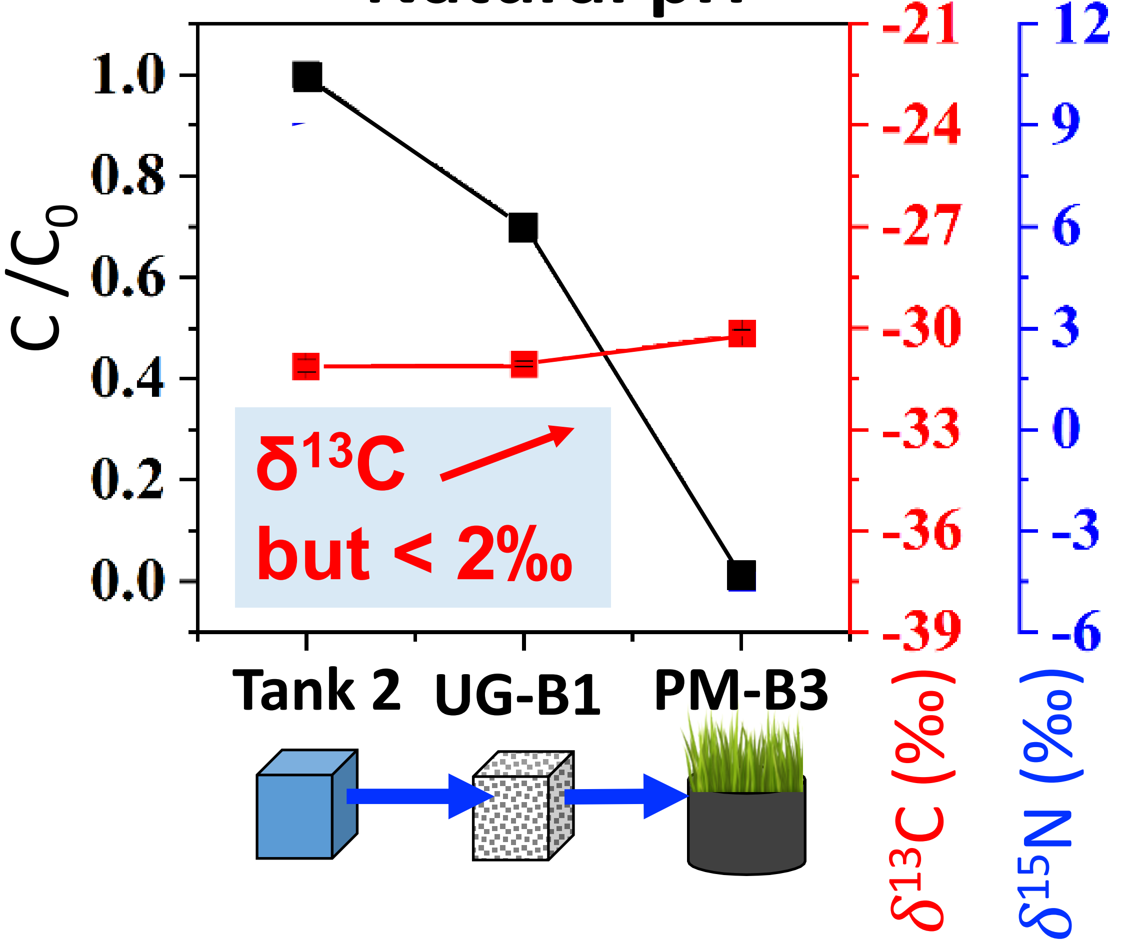
2,3-DCA



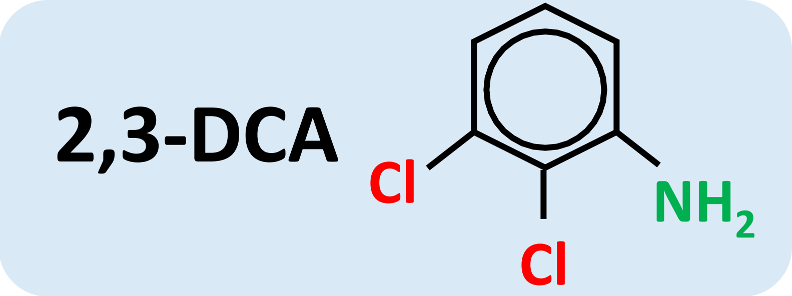
Adjusted pH

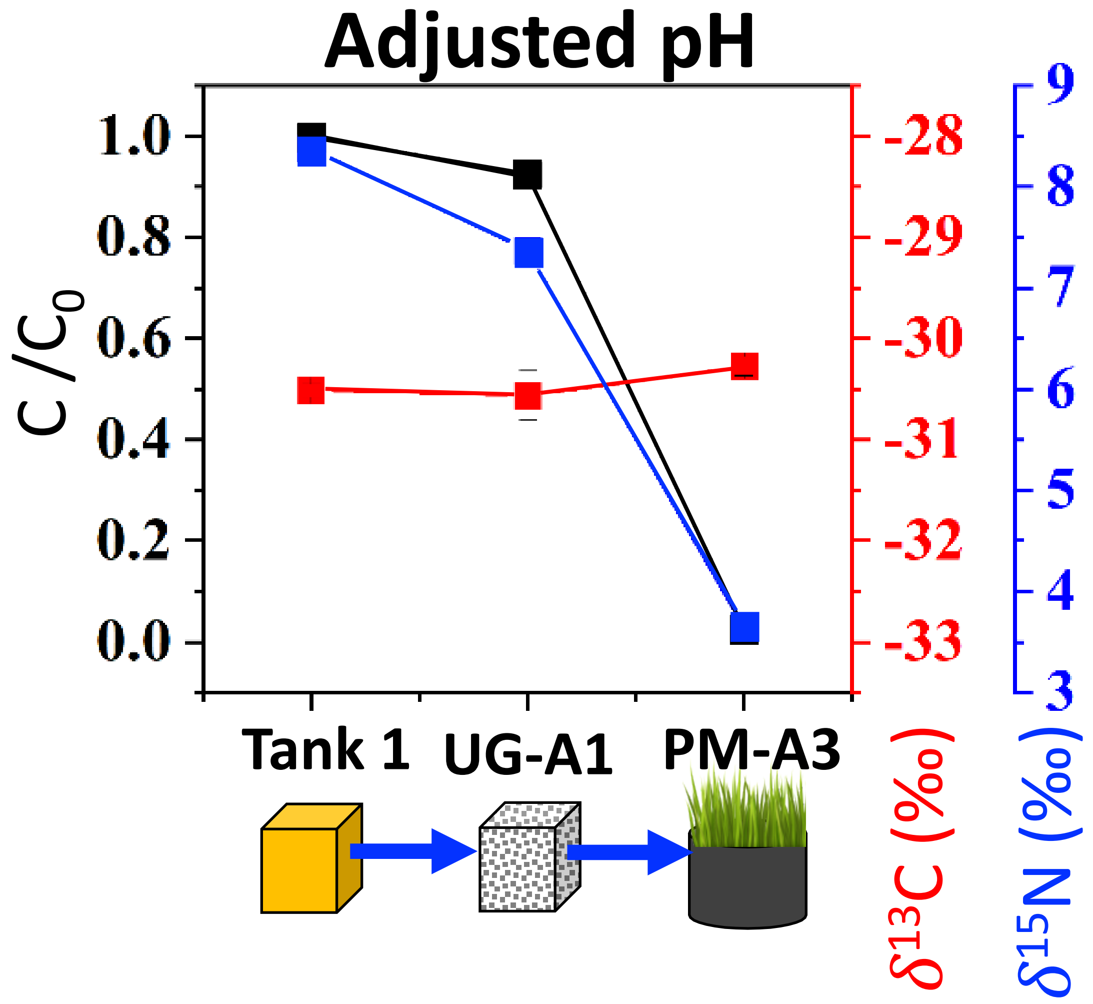


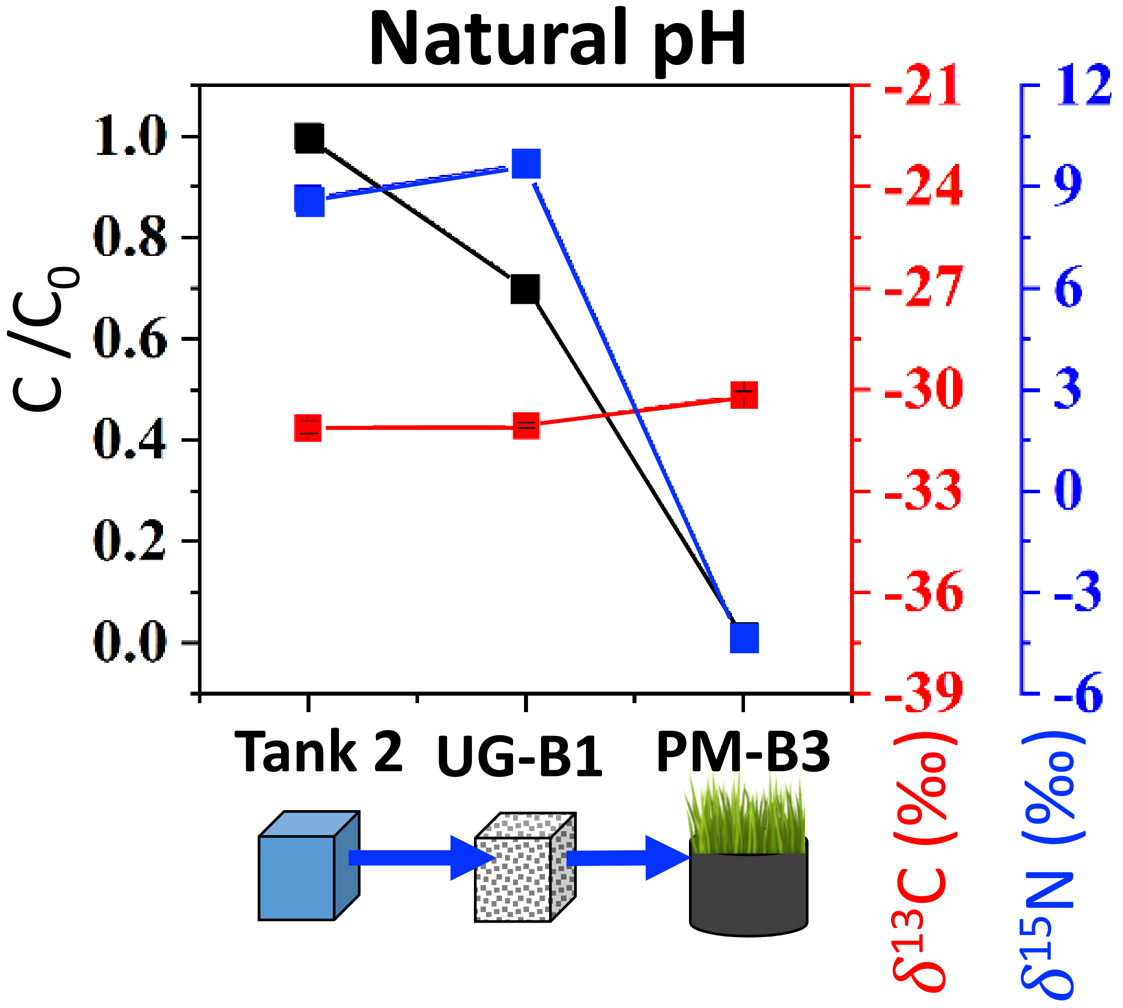
Natural pH



C- & N-CSIA in constructed wetlands



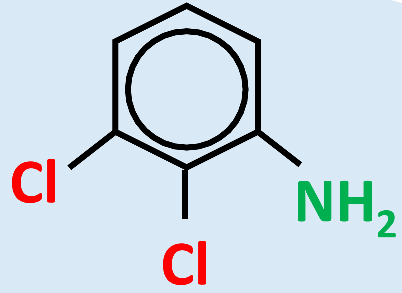




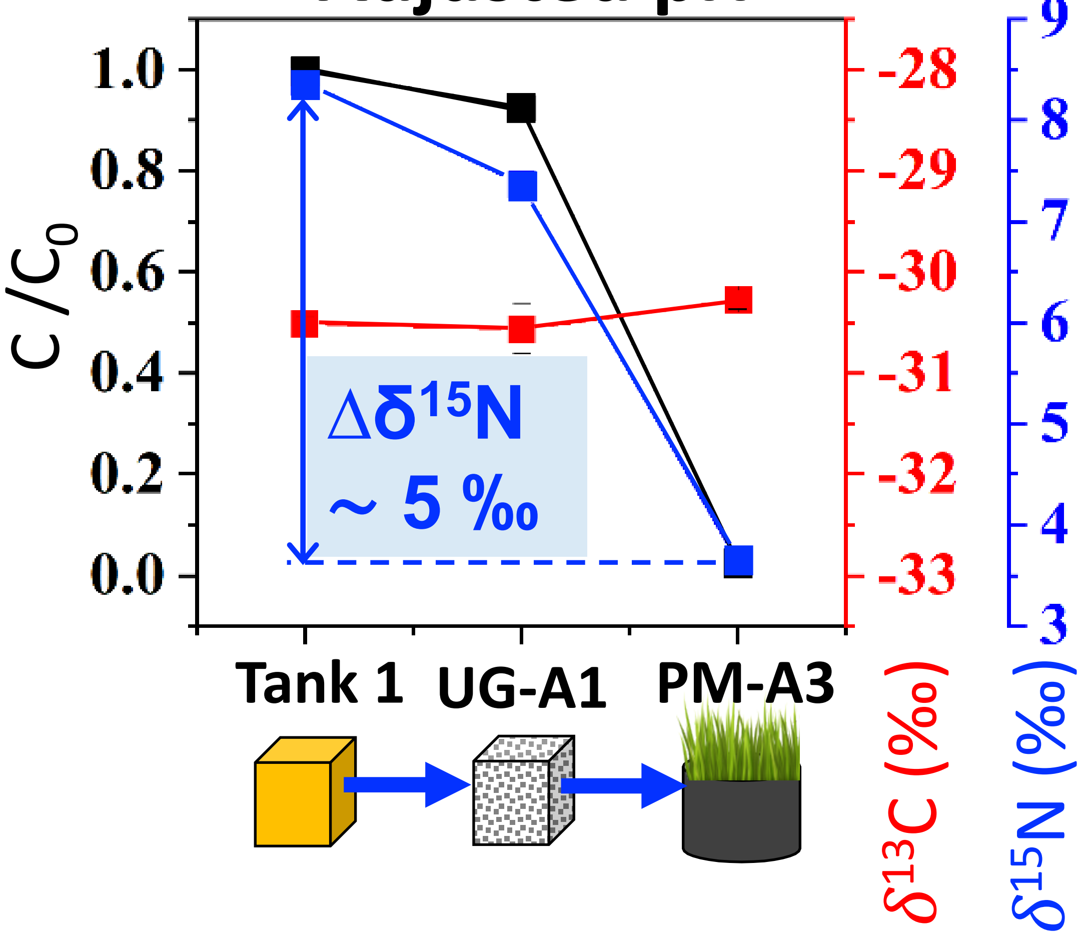
UNIVERSITY OF TORONTO

C- & N-CSIA in constructed wetlands

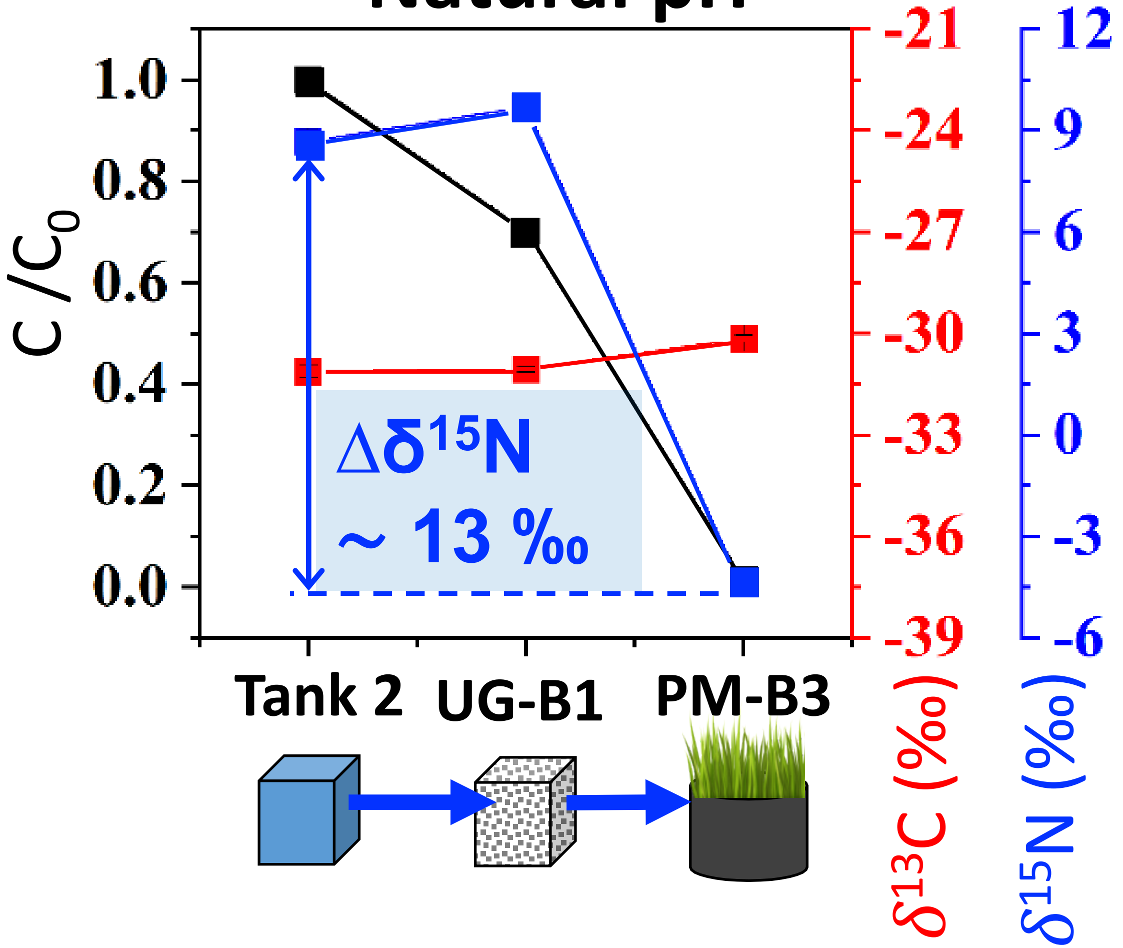
2,3-DCA



Adjusted pH

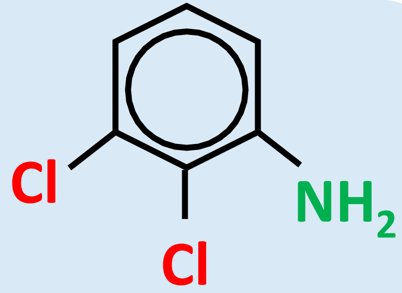


Natural pH



C- & N-CSIA in constructed wetlands

2,3-DCA



Key points:

- Sorption in unplanted gravel (UG)
- Natural attenuation in planted marsh (PM):
  - 40-50% (Adjusted pH)
  - 80-90% (Natural pH)
- pH adjustment not needed

Take home messages

- Surface flow wetlands are effective for 2,3-DCA natural attenuation
- CSIA is an effective tool to assess remediation of 2,3-DCA
  - N: identify & quantify transformation
  - C, H: identify sources

Thank you!

Questions?

shamsunnahar.suchana@mail.utoronto.ca

CORTEVA agriscience

Geosyntec consultants

engineers | scientists | innovators

Advisian Worley Group

Jacobs

NSERC CRSNG

UNIVERSITY OF TORONTO Connaught International Awards