Polar Organic Chemical Integrative Sampler Allows CSIA of Substituted Chlorobenzenes at Trace Levels

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*Presenting author

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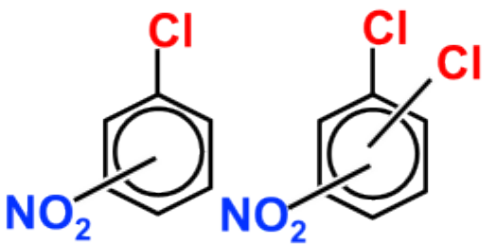
Outline

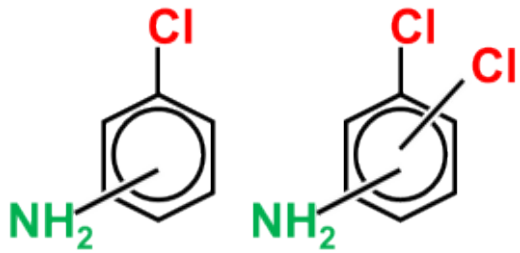
- Background
- Laboratory experiments
- Field application
- Conclusions

Target Semi-Volatile Substituted chlorobenzenes



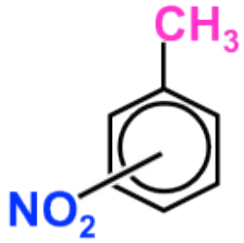
(di)chloronitrobenzenes

CNB & DCNB



(di)chloroanilines

CA & DCA



Nitrotoluenes

NT

Feedstock for

Found in groundwater, surface water, WWTP effluent, and DWTP

Emerging industrial chemicals

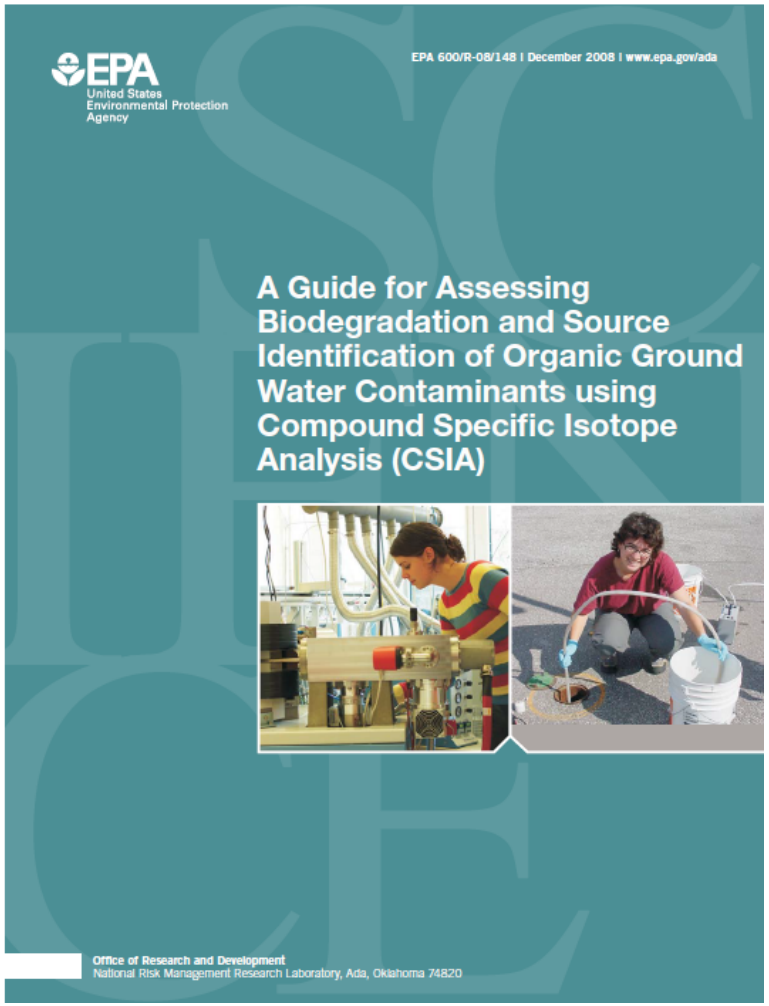
Compound Specific Isotope Analysis (CSIA)

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. $\delta^{13}C$

^{12}C	^{13}C	^{14}C
12.00000 98.89%	13.00335 1.11%	14.0 $t_{1/2}$ = 5715yrs
Stable	Stable	Radioactive

CSIA

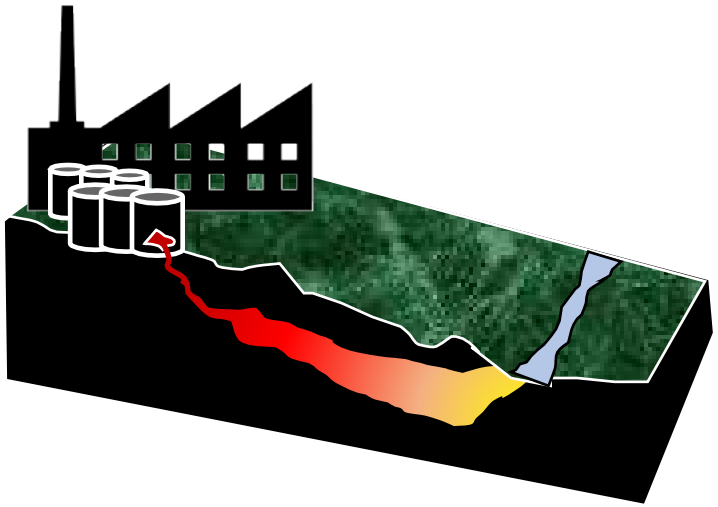


Hunkeler et al. 2008

CSIA for emerging contaminants

Legacy contaminants

Hydrocarbons, chlorinated solvents



High concentration (mg/L)
Mostly volatile compounds
Small volume extraction

Emerging contaminants

Pesticides, pharmaceuticals……

Low concentrations (ng/L – µg/L)
Semi-volatiles and polar
Large volume extraction

See recent review Philips et al. 2022 Journal of Hydrology

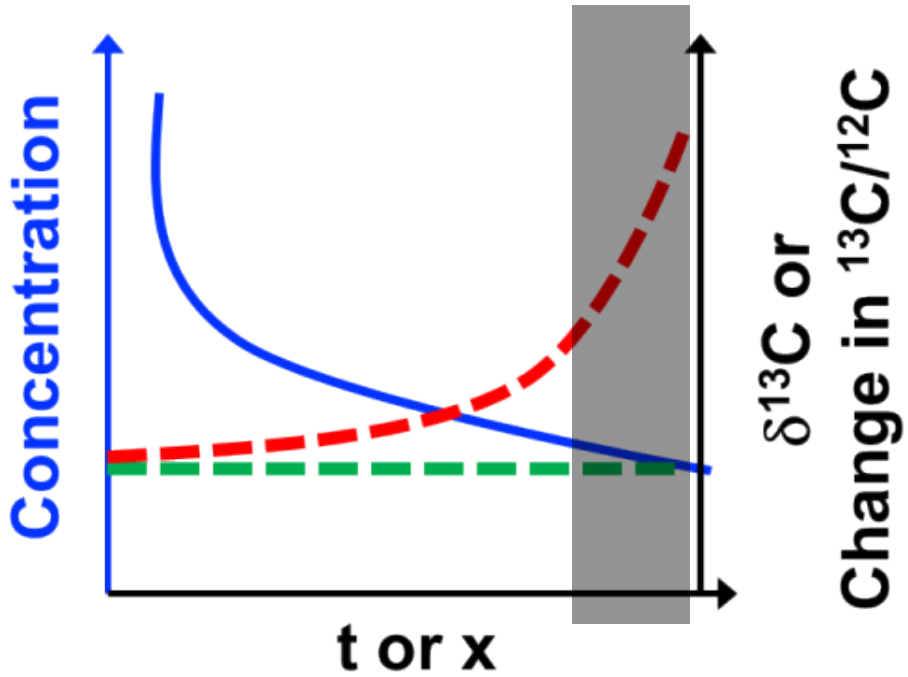
CSIA to investigate *in situ* processes

Bond breaking

Rate of $^{12}C > ^{13}C$

Conc. typically at low µg/L range

Conventional sample extraction techniques often not adequate



Transformation: changes in $\delta^{13}C$

Transfer: no change in $\delta^{13}C$

Rayleigh equation:

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

Limitations of CSIA at low concentrations

- High instrumental detection limit of isotope ratio mass spectrometers
  - Up to 1-10 nmol of carbon on-column

- Solid-phase extraction (SPE) is required for semi-volatiles

- Until recently CSIA mainly limited to
  - Heavily contaminated sites at high mg/L
  - Up to 10 L of water extraction for high µg/L

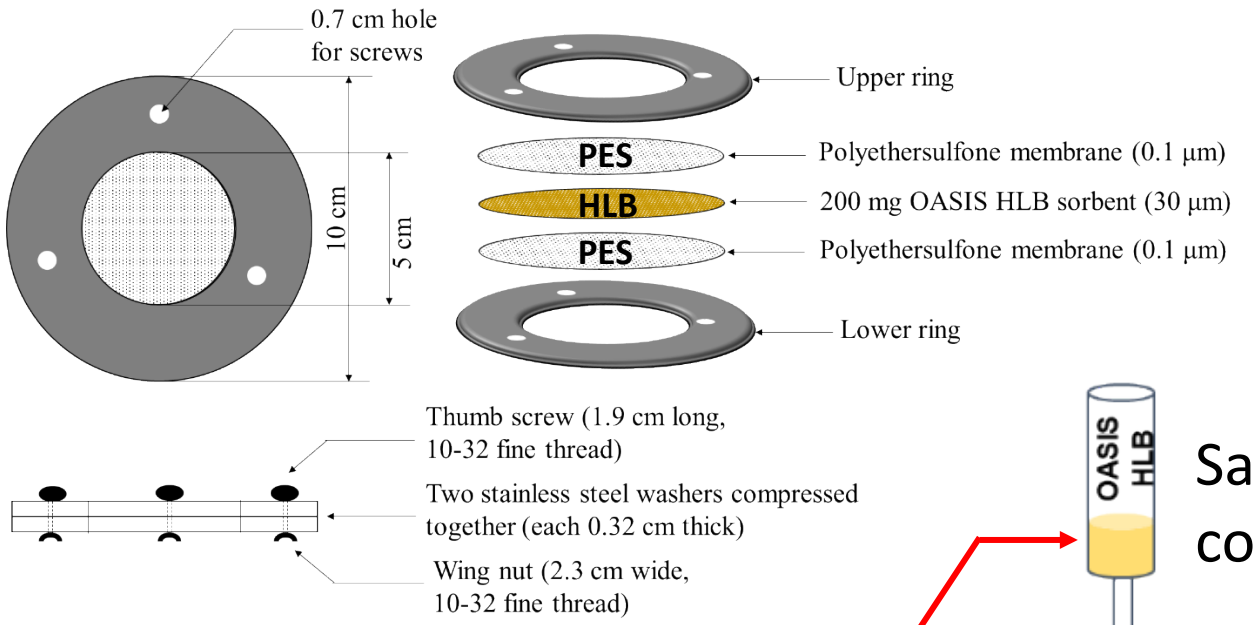
  - Time and labor intensive
  - Method-induced fractionation
  - Matrix interference

One promising approach is *in situ* passive sampler to preconcentrate at sub-µg/L

Polar organic chemical integrative sampler (POCIS)

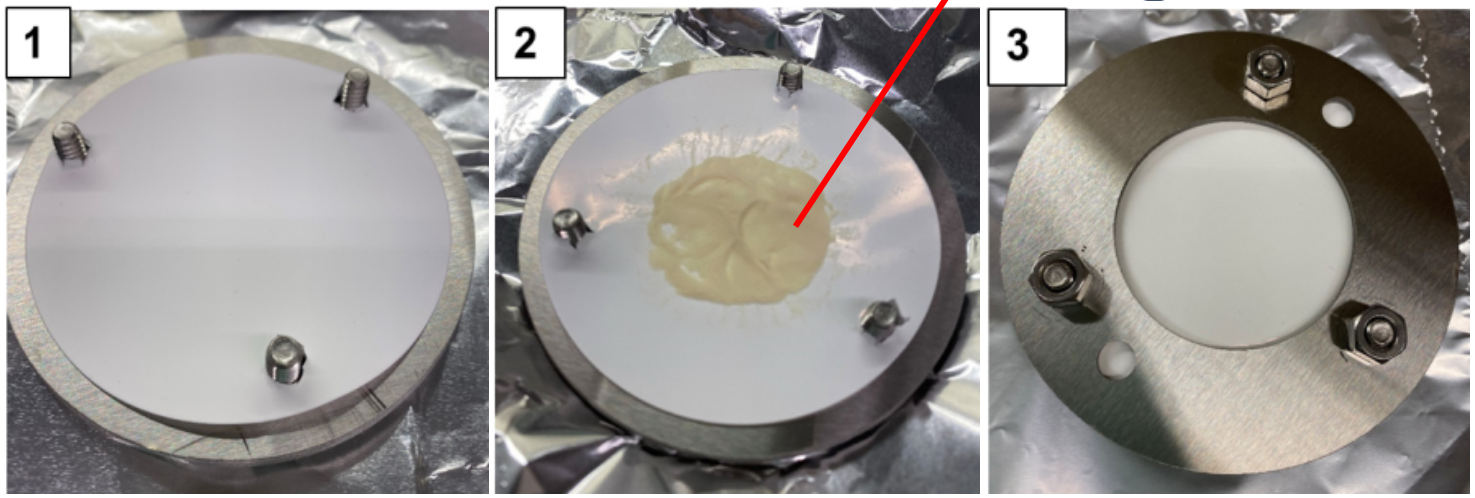
Hunkeler et al. 2008; Torrentó et al. 2019

Polar organic chemical integrative sampler (POCIS)



Widely used as alternative of grab sampling for low concentrations

Same as commercial SPE



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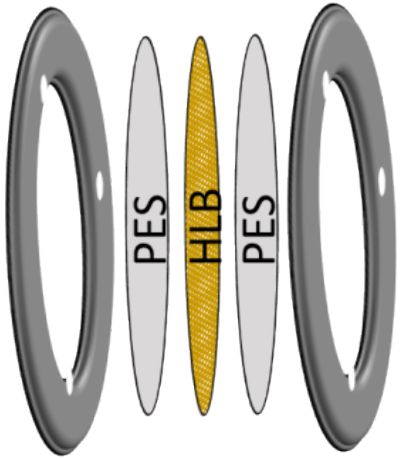
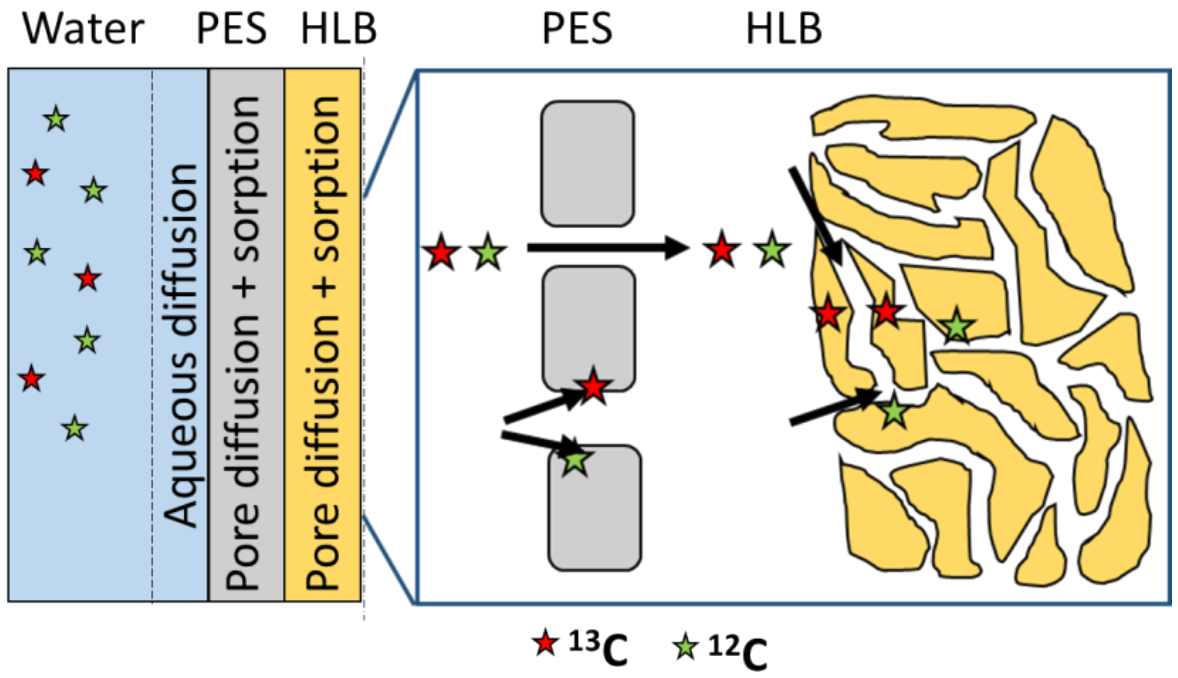
Alvarez et al. 2004, 2010

POCIS preconcentration

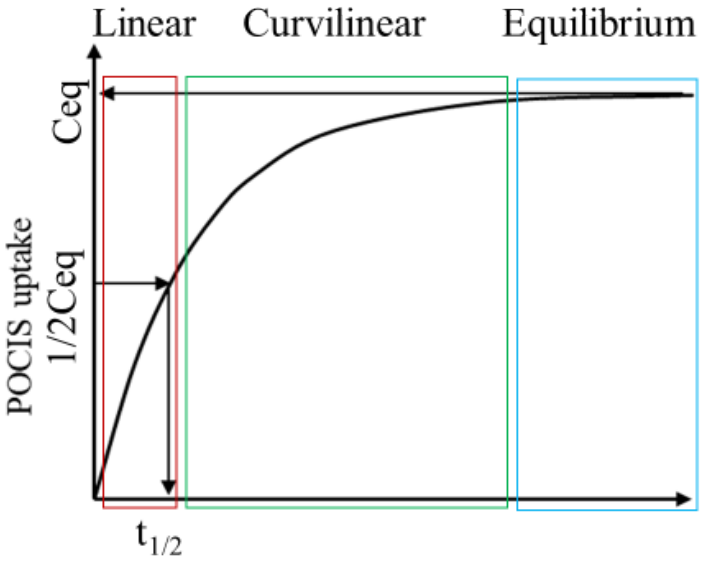
Configuration



Mechanism



In situ preconcentration



Typically 7-60 days

Process 1: Aqueous phase diffusion

Process 2: Pore diffusion in PES membrane and HLB sorbent

Process 3: (chemi)sorption in PES membrane and HLB sorbent

Goal

Evaluate the potential of POCIS to enable CSIA at trace level environmental concentrations

Specific objectives

1. Evaluate sorption- and diffusion-induced isotope fractionation
2. Performance evaluation under field conditions

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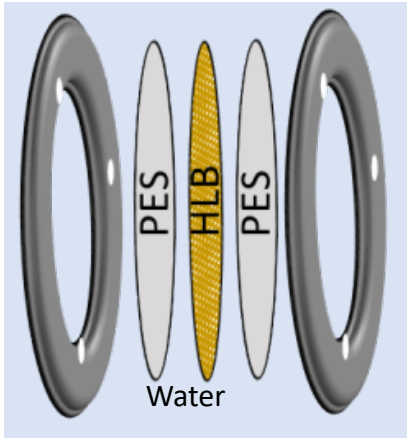
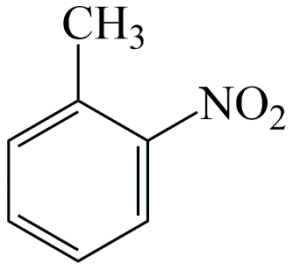
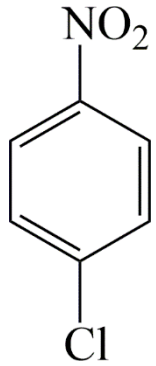
Lab experimental set up

- POCIS deployed in spiked water (7L)
- Water sampling over time
- Extraction of PES and HLB over time
- Sacrificial setup
- Duplicates with blanks and controls

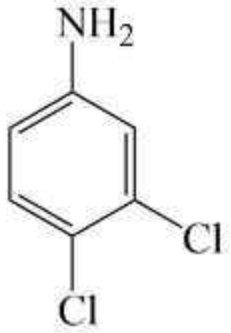




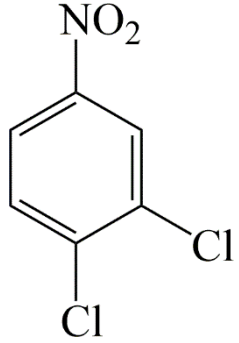
2-nitrotoluene
(2-NT)



4-chloronitrobenzene
(4-CNB)



3,4-dichloaniline
(3,4-DCA)



3,4-dichlonitrobenzene
(3,4-DCNB)

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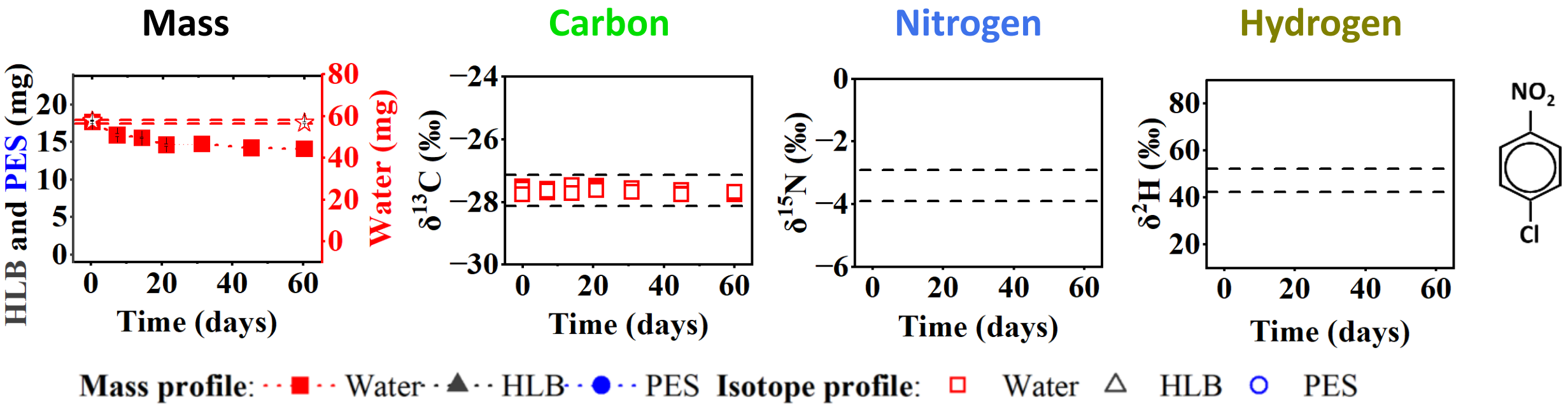
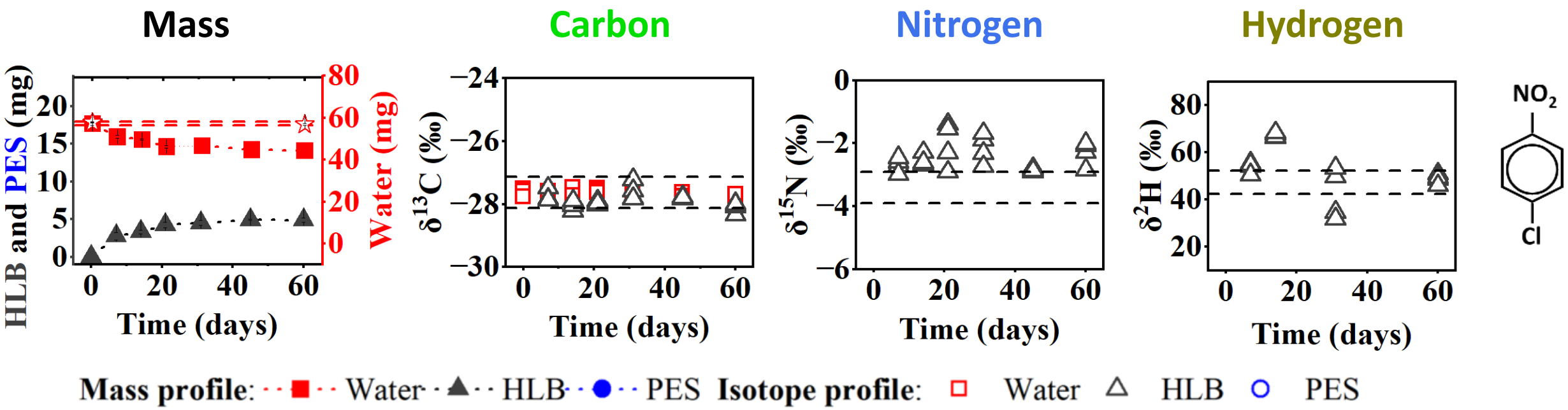
Suchana et al. 2022, STOTEN

Sorption- and diffusion-induced isotope fractionation



Suchana et al., available in Chemrxiv

Sorption- and diffusion-induced isotope fractionation



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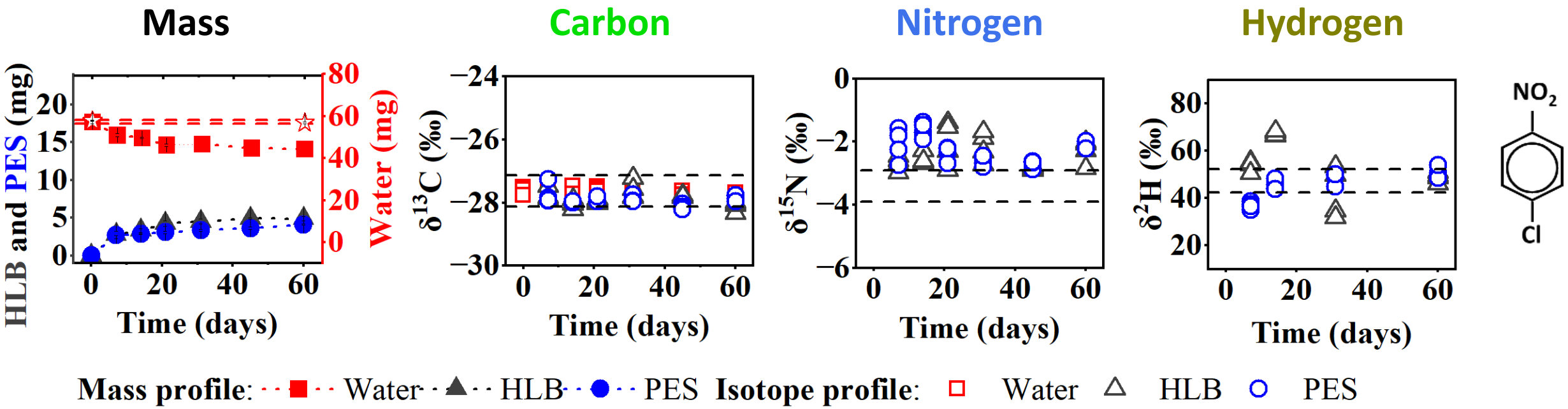
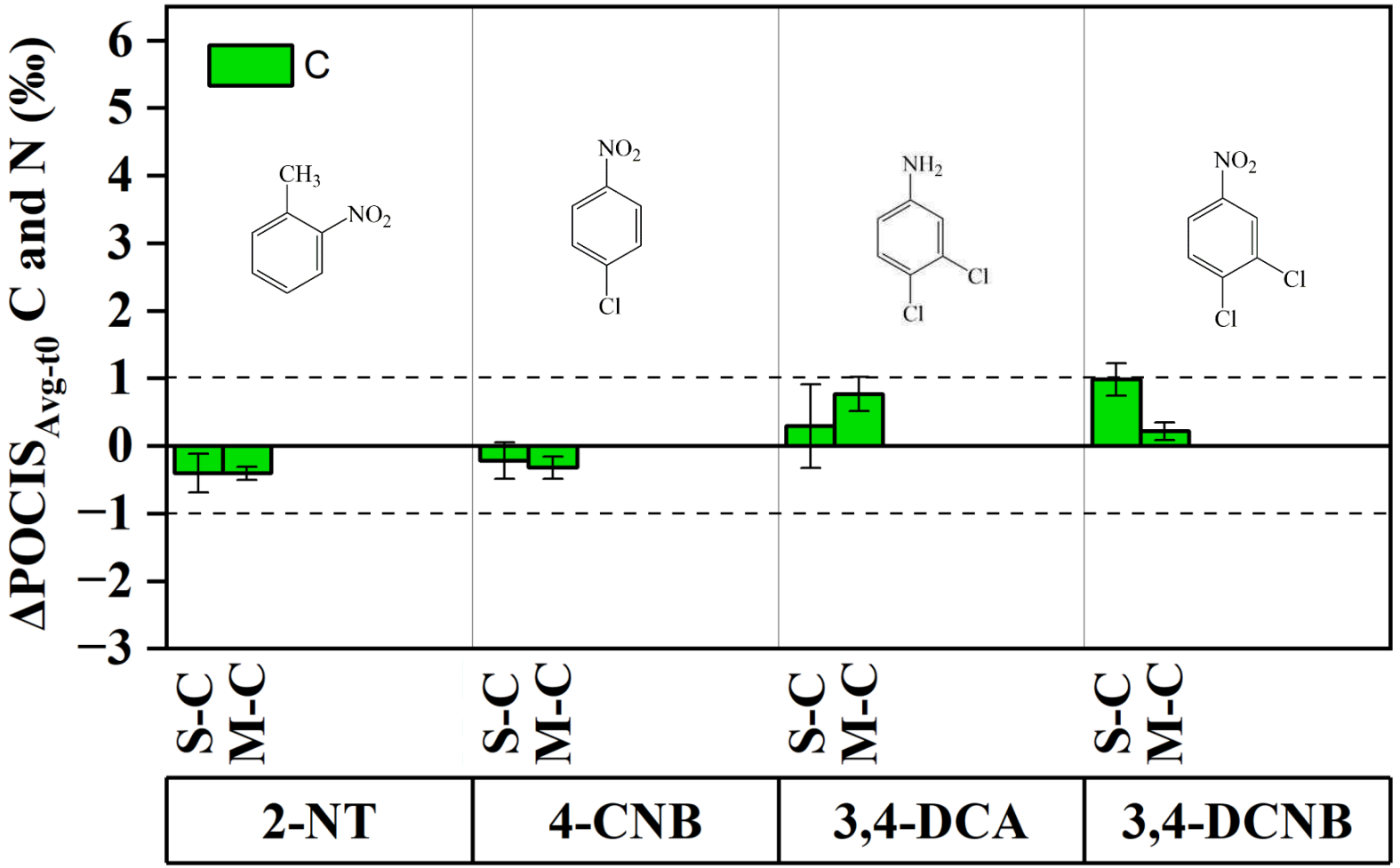
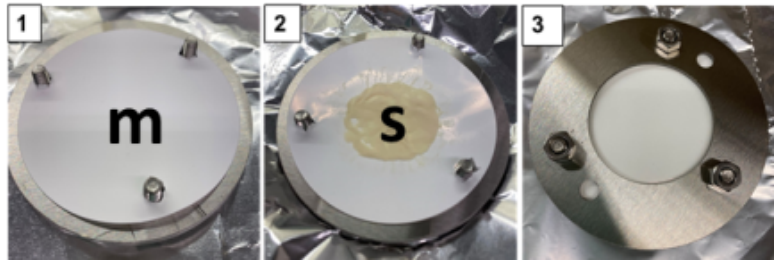


- Significant sorption in both sorbent and membrane
- Concentration and isotope equilibrium after 30 days
- Recommended deployment time of POCIS for CSIA is minimum 30 days

Suchana et al., available in Chemrxiv

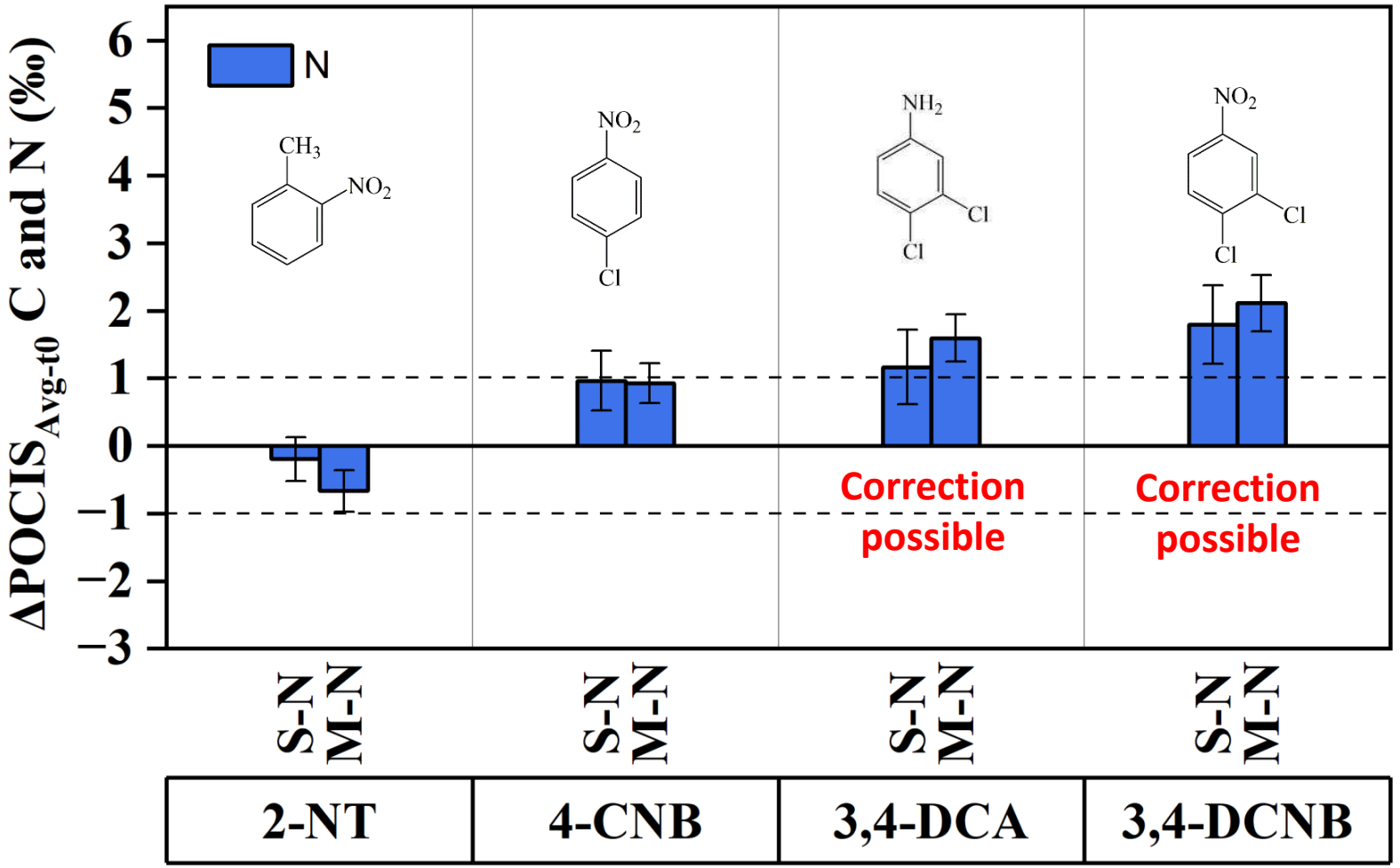
Negligible Carbon shift after 30 days

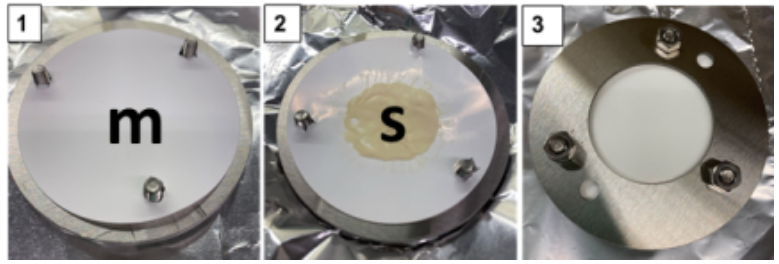




Mostly negligible shifts in sorbent and membrane

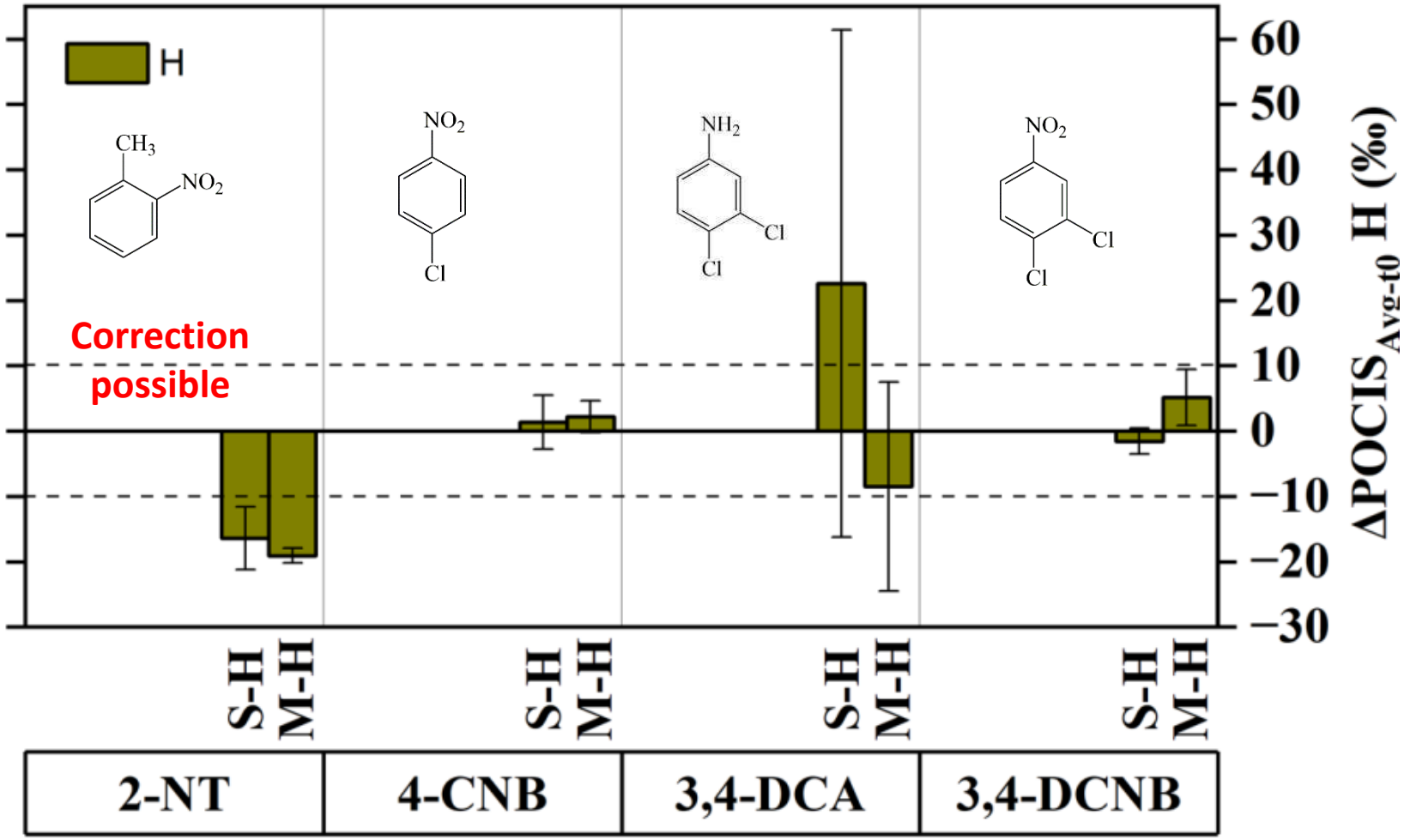
Negligible/reproducible Nitrogen shift after 30 days

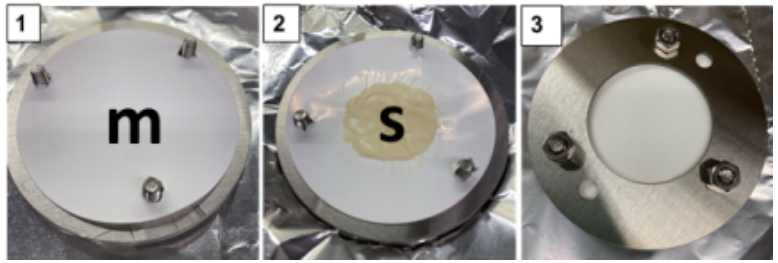




Reproducible and similar shifts in sorbent and membrane

Negligible/reproducible Hydrogen shift after 30 days





High variability for 3,4-DCA, possibly due to H-bonding

Goal

Evaluate the potential of POCIS to enable CSIA at trace level environmental concentrations

Specific objectives

1. Evaluate sorption- and diffusion-induced isotope fractionation
2. Performance evaluation under field conditions

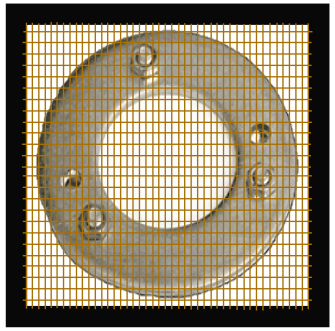
Field deployment

60 days deployment in constructed wetlands

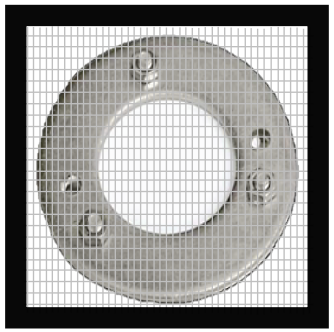
4L grab sample for SPE

Vs.

POCIS



Vs.

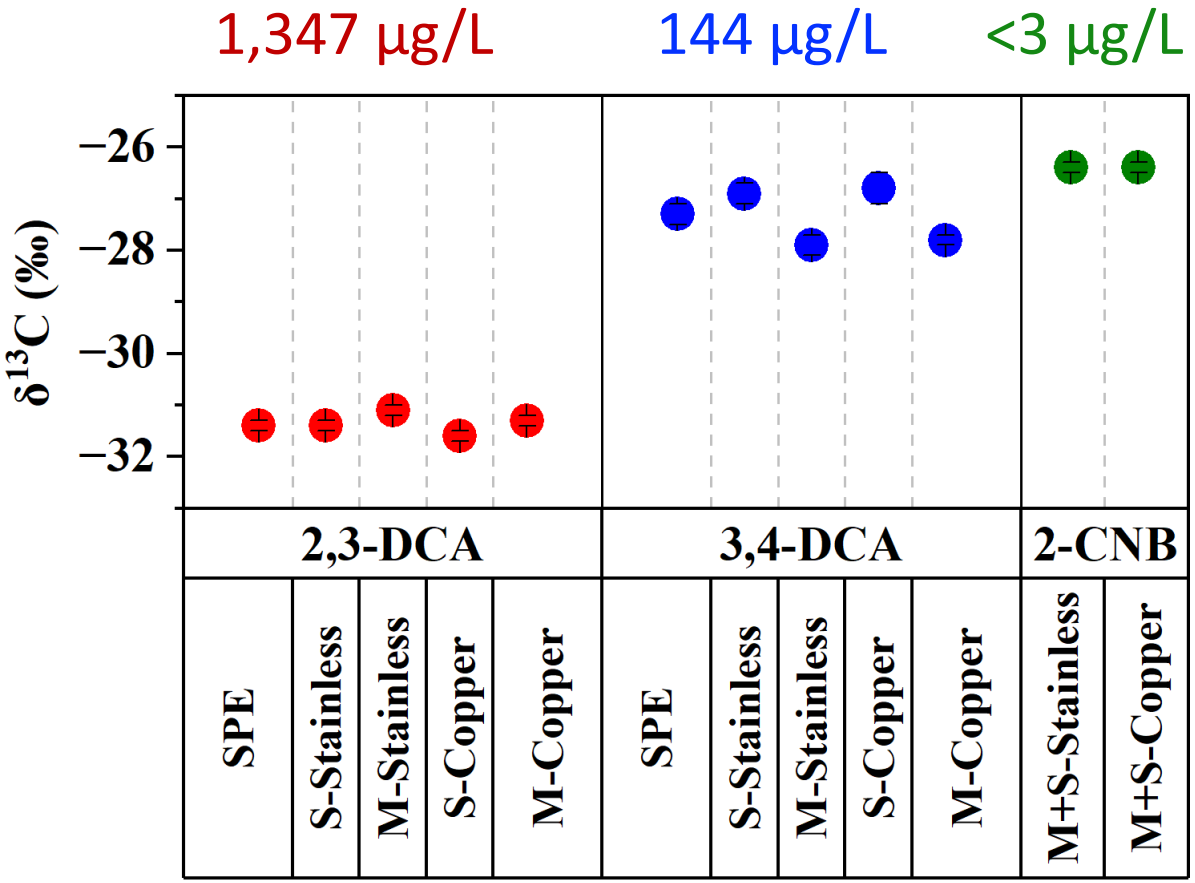


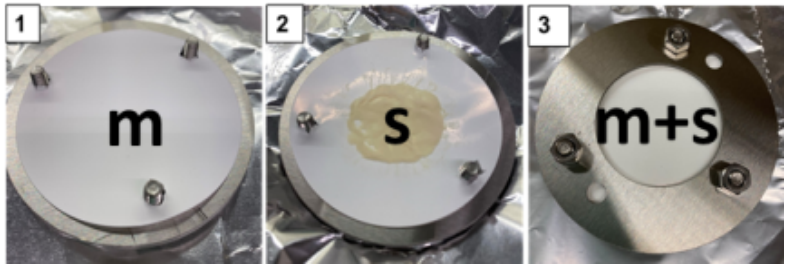
Copper

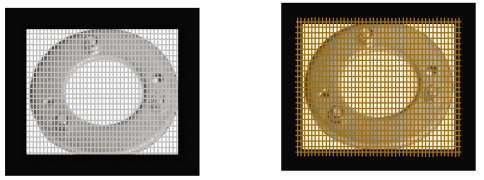
Stainless steel

Suchana et al. 2023, ACS Analytical Chemistry

POCIS and SPE give comparable Carbon signature



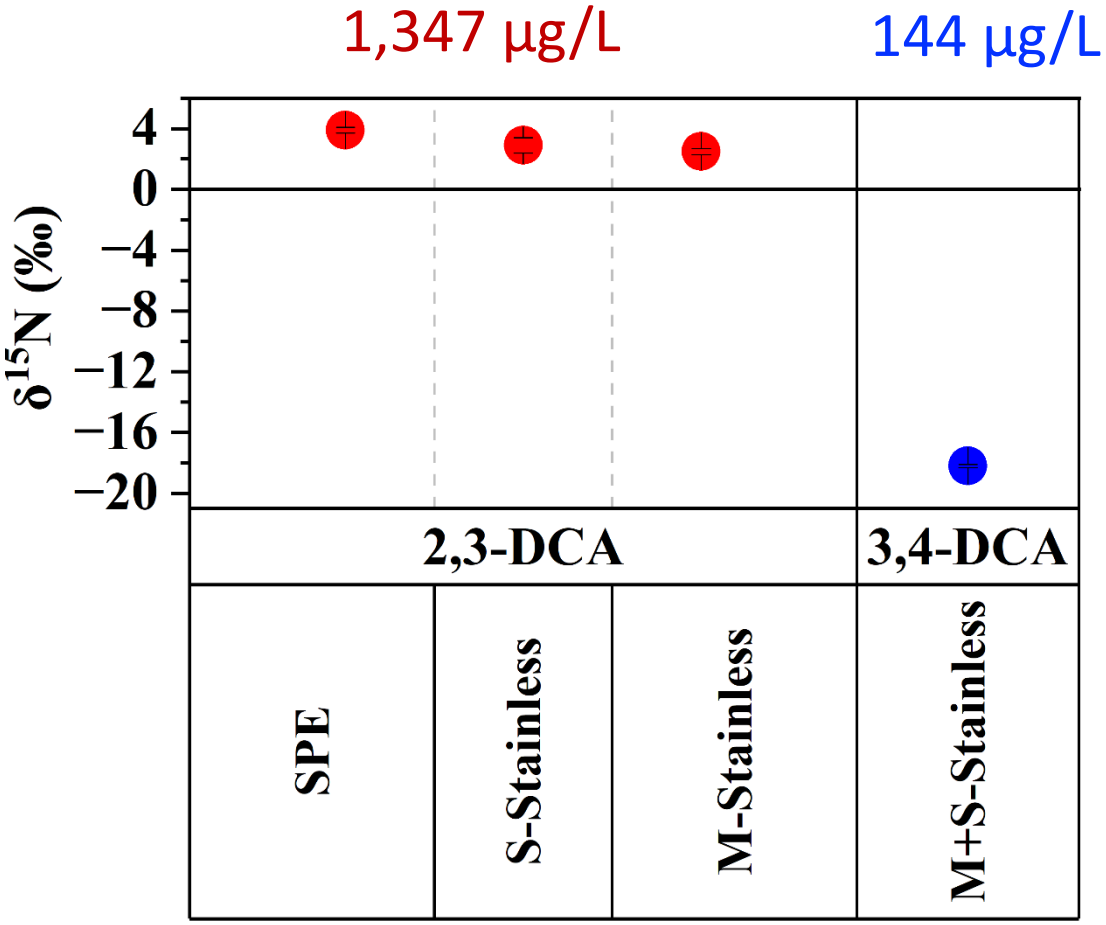


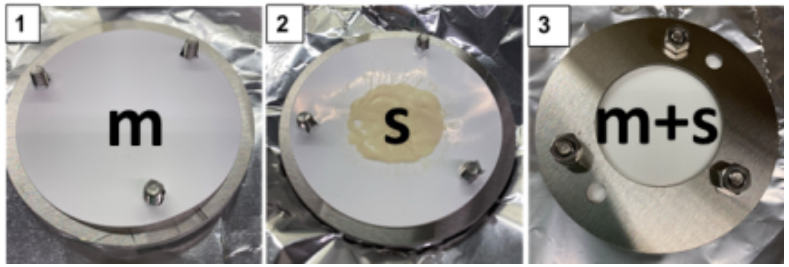


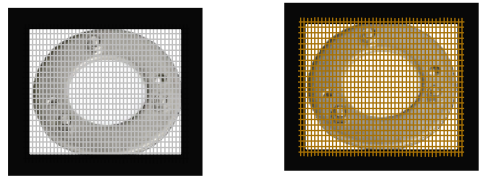
Stainless Copper

- POCIS and SPE are comparable
- Sorbent and membrane are similar
- Detection limit$_{M+S}$ lower than 4L SPE

POCIS and SPE give comparable Nitrogen signature



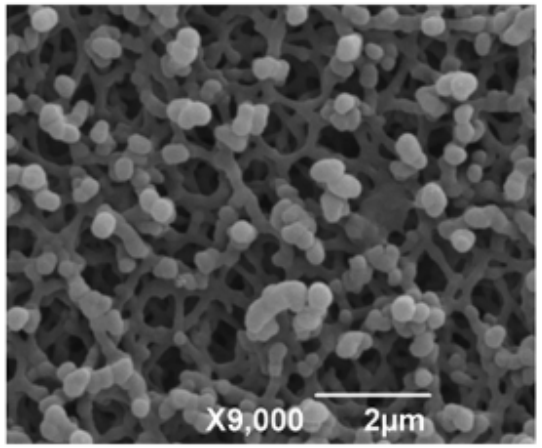


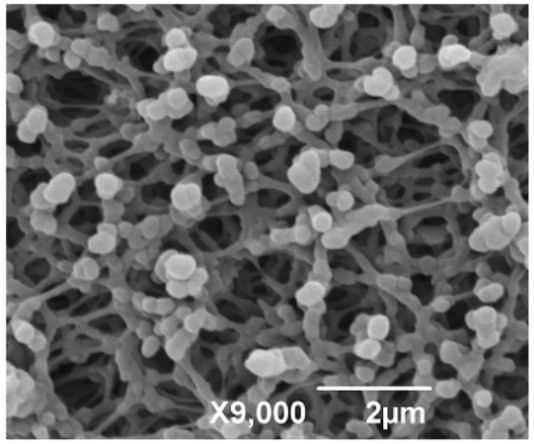


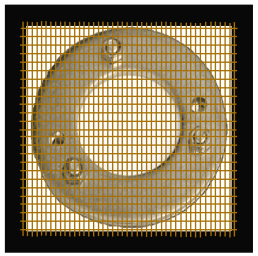
Stainless Copper

- Similar results as carbon

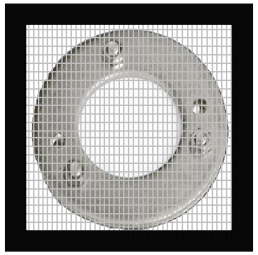
Biofilm on membrane does not affect isotope signatures



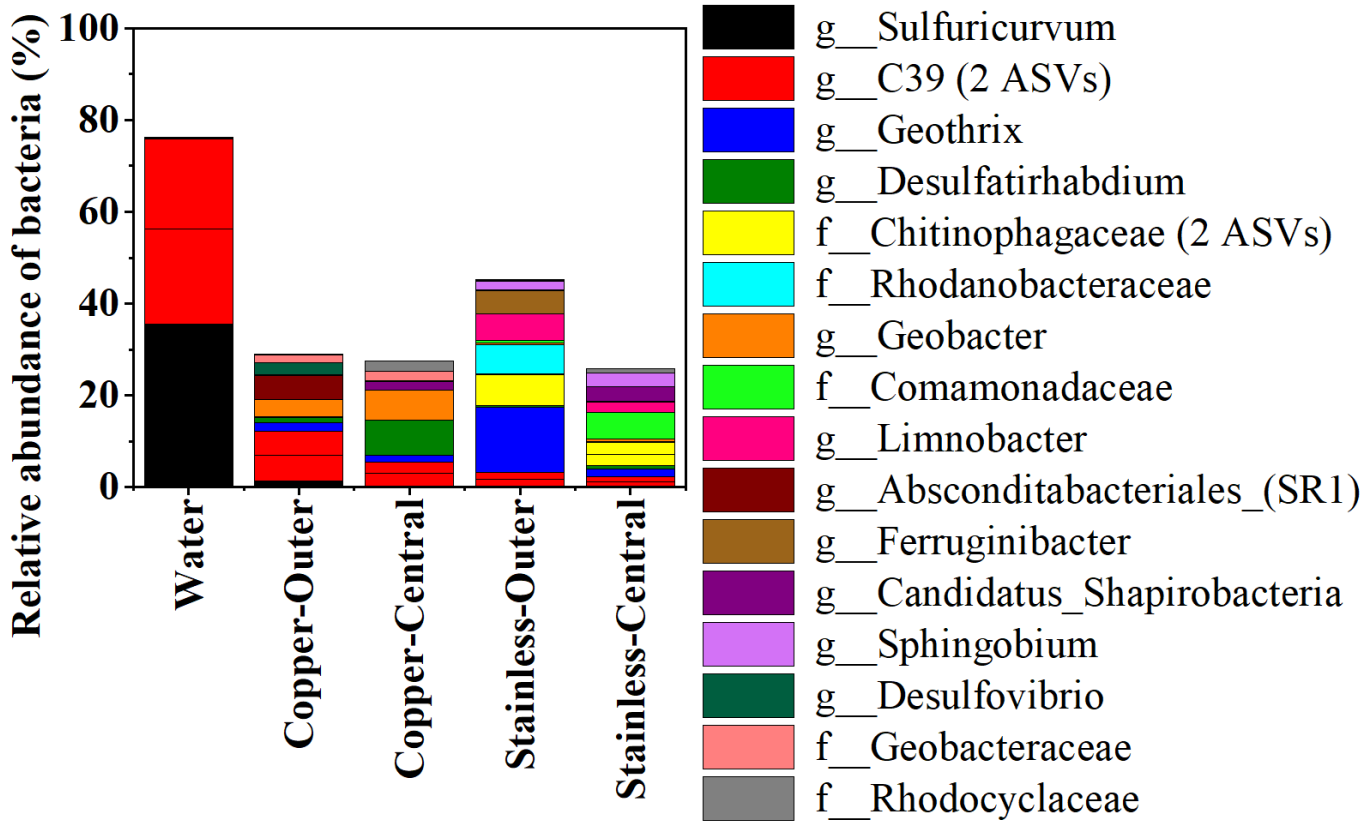




Stainless



Copper



Biofilm formation on membrane exposed part

Diverse and small abundance on membrane than in water

Take home messages

1. POCIS is suitable with CSIA for substituted chlorobenzenes

2. POCIS and SPE are comparable under field conditions

3. One POCIS is equivalent to ~10 L of water extraction by SPE

4. Potential for ng/L concentrations CSIA using multiple POCIS

Thank you!

Questions?

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