Performance of Anaerobic Sediment-Capping Systems: Role of Material Type in Designing Effective Bioactive Caps

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Anaerobic biodegradation processes in sediment capping systems

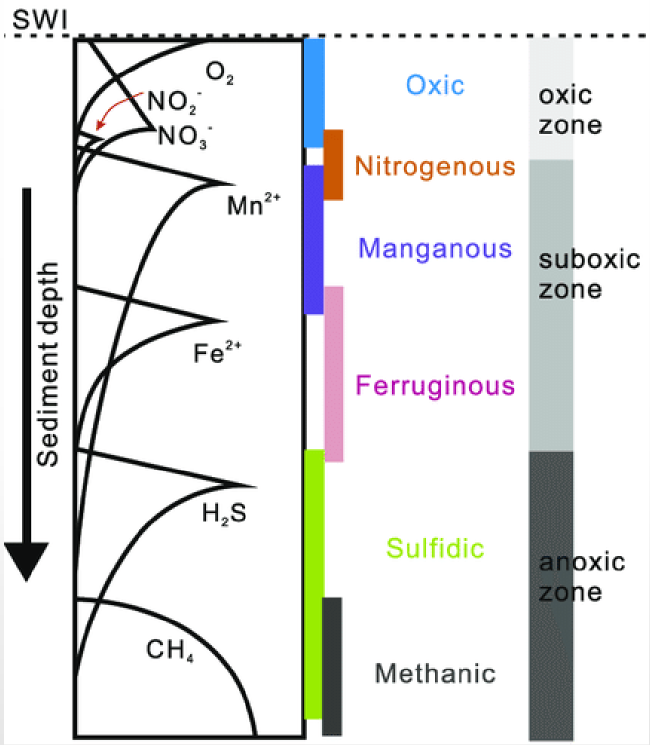


Image adapted from Canfield and Thamdrup, 2009

Sediment environment is mostly anoxic, and each redox zone is characterized by a niche of microorganisms adapted to those specific conditions[1].

Biodegradation of naphthalene by sulfate-reducing cultures showed negligible reaction rates[2, 3].
Natural attenuation cannot be considered as exclusive technique to remedy contaminated sediments in anoxic conditions.

Capping is an efficient containment strategy.

Are anaerobic biodegradation processes affected by the presence of different capping material?

[1] Himmelheber D.W. et al. Microbial colonization of an in-situ sediment cap and correlation to stratified redox zones. Environmental Science and Technology, 2009.
[2] Kummel S. et al. Anaerobic naphthalene degradation by sulfate reducing *Desulfobacteraceae* from various anoxic aquifers. FEMS, 2015.
[3] Kummel S. et al. Hydrogen isotope fractionation as a tool to identify aerobic and anaerobic PAH biodegradation. Environmental Science and Technology, 2016.

Performance of anaerobic sediment capping systems

Experimental Hypothesis

Capping materials, such as sand and PAC, influence naphthalene degradation kinetics in anaerobic systems

Experimental Systems

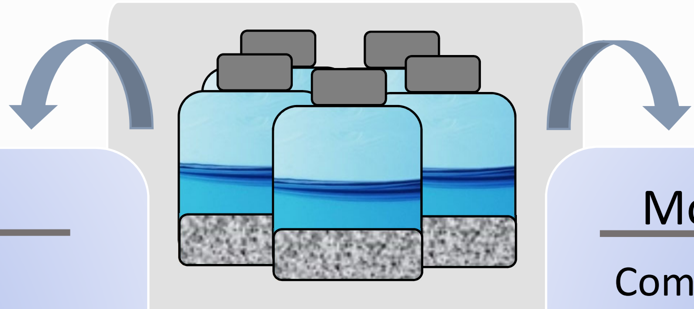
- Microcosms amended with U-^{13}C naphthalene
- Microcosms amended with U-^{14}C naphthalene

Appraise Capping Performance

- Monitor total naphthalene decrease
- Monitor ^{13}C enrichment
- Monitor changes in microbial community
- Monitor naphthalene mineralization

Experimental setup - ^{13}C amended microcosms

Sulfate-reducing culture enriched from sediments contaminated by PAHs were used to prepare microcosms containing naphthalene (**20% ^{13}C labeled**) as the only carbon source and sulfate as the only electron acceptor.



Chemical Analysis

Analysis are to:

- ❖ Quantify total naphthalene
- ❖ Estimate abundance of ^{13}C naphthalene

Sulfide and sulfate are monitored through IC analysis.

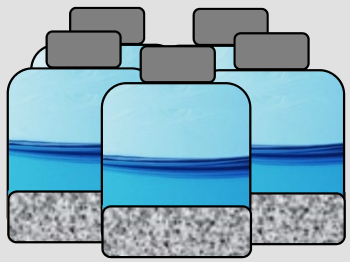
Molecular Analysis

Community analysis are performed in an external laboratory and collected data are used to:

- ❖ Analyze microbial community
- ❖ Identify naphthalene biodegraders

Experimental setup - ^{14}C amended microcosms

Sulfate-reducing culture enriched from sediments contaminated by PAHs were used to prepare microcosms containing naphthalene (**0.5% U^{14}C labeled**) as the only carbon source and sulfate as the only electron acceptor.



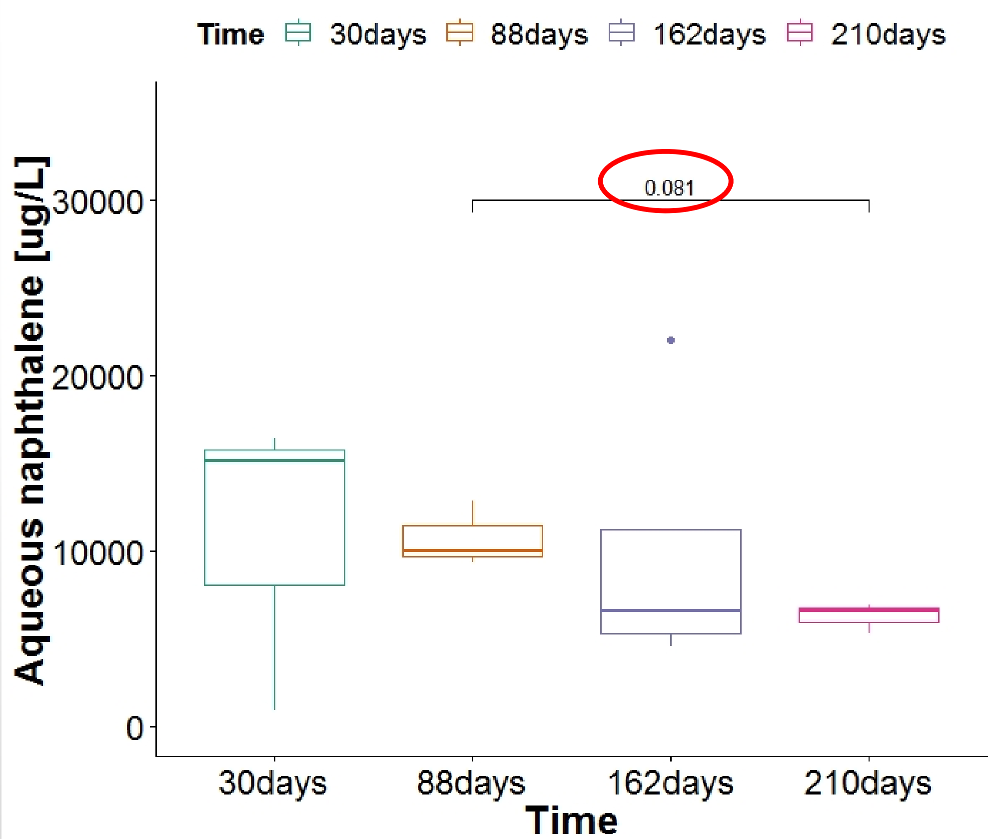
Chemical analysis (molecular analysis not possible with ^{14}C isotope)

$^{14}CO_2$ in the headspace of microcosms is collected via syringe and "base trapped" in an aqueous alkaline solution.

^{14}C is quantified using a liquid scintillation counter to:

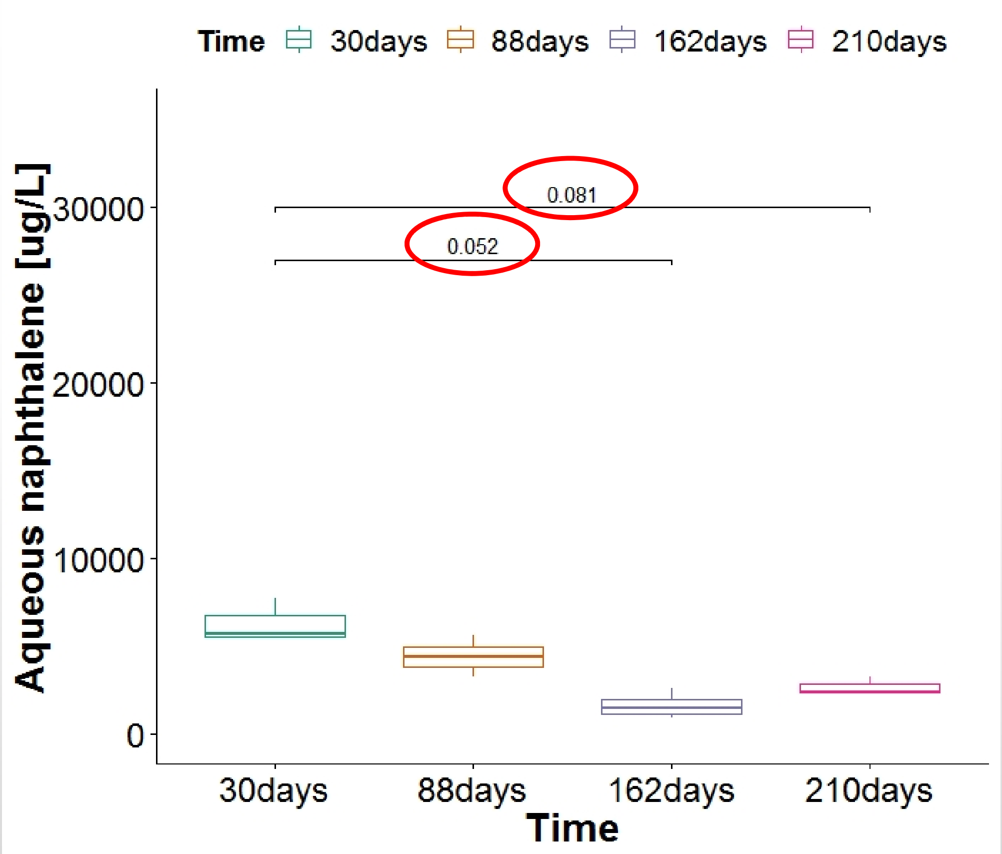
- Quantify total $^{14}CO_2$ production
- Evaluate remaining radio-labeled naphthalene in solution
- Estimate mineralization kinetics

Naphthalene decrease – PAC microcosms



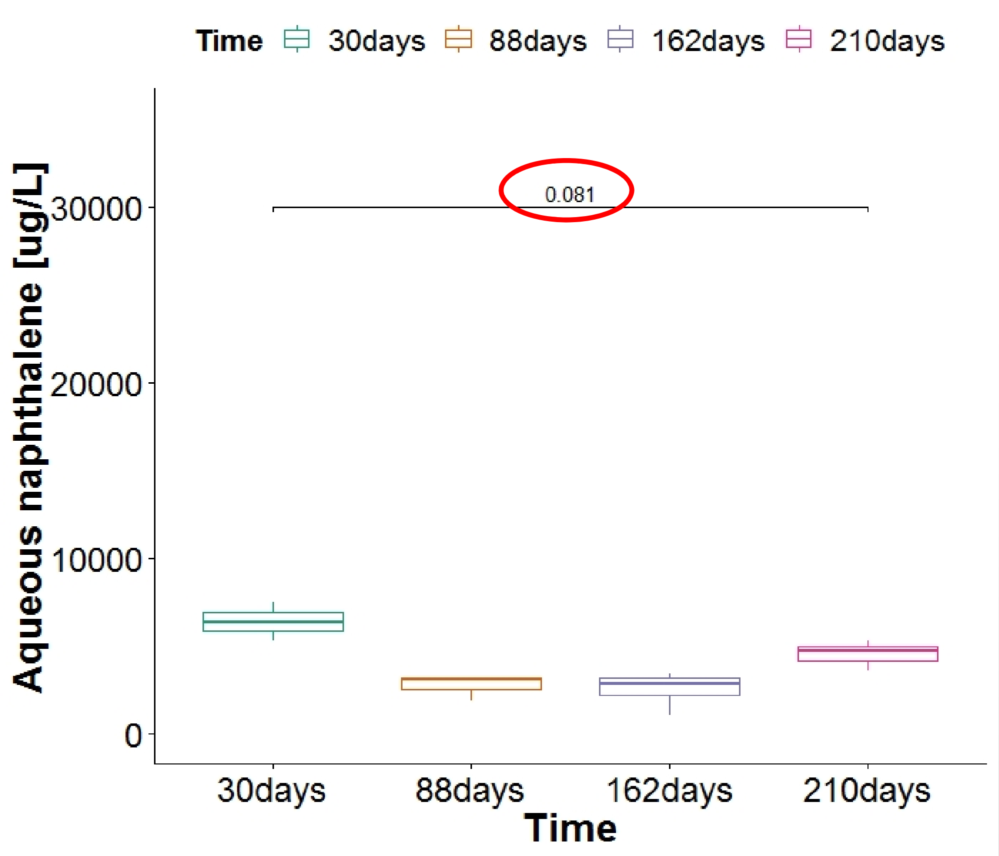
- Significant difference between 210 days and previous samplings (88 days)
- The variations at 30days and 162 days limit statistical inference, likely due to the slow adsorption kinetics onto PAC
- Sterile microcosms do not show statistically significant decrease of naphthalene concentrations [Kruskal-Wallis test p value > 0.1]

Naphthalene decrease – Sand microcosms



- Significant difference between 162 days [95%confidence], 210 days [92%confidence] and previous samplings (30 and 88 days)
- Higher significance of the differences compared to PAC microcosms, likely because of limited variability due to faster sorption onto sand
- Overall, sterile microcosms do not show statistically significant decrease of naphthalene concentrations [Kruskal-Wallis test p value > 0.1]

Naphthalene decrease – Media Free microcosms



- Overall naphthalene concentration decreases after 210 days [92% confidence mean comparison with 30 days], however a clear decreasing trend is not observed

- Significant naphthalene decrease observed in media free sterile microcosms, suggesting participation of processes different than biodegradation

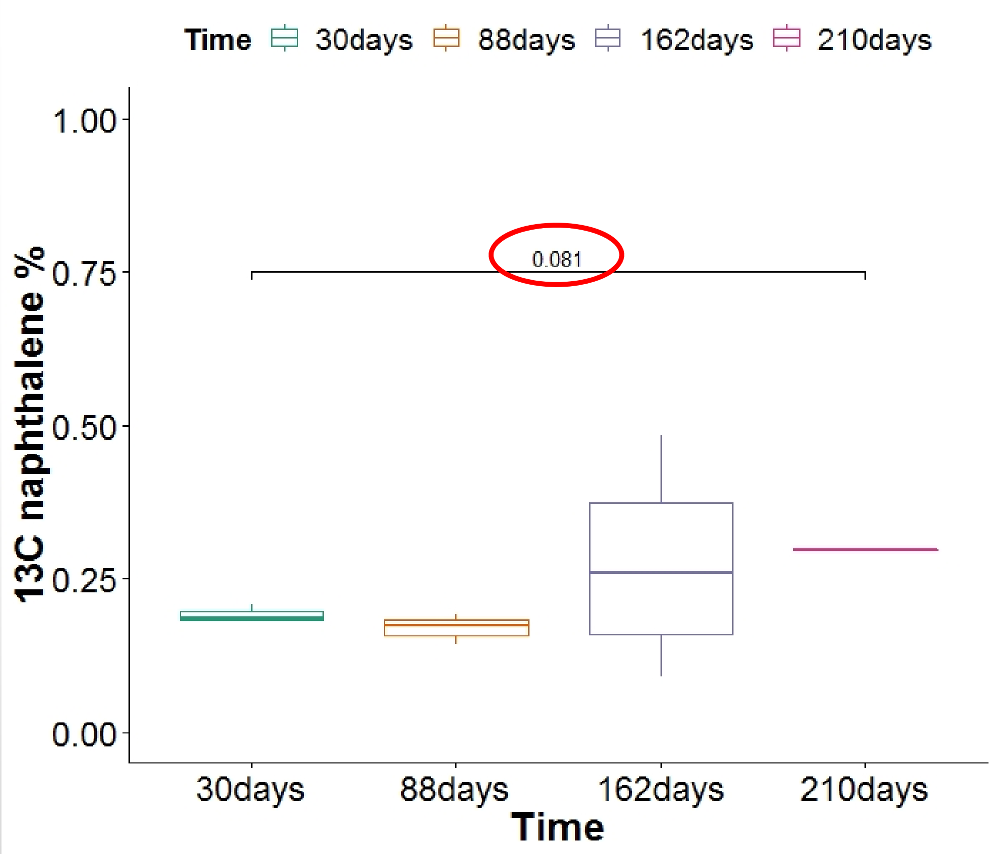
Naphthalene decrease – Comparison of preliminary kinetics

Total naphthalene concentrations were modeled to a first order kinetic, and a simple linear regression was used to compare significance of decrease with different treatment

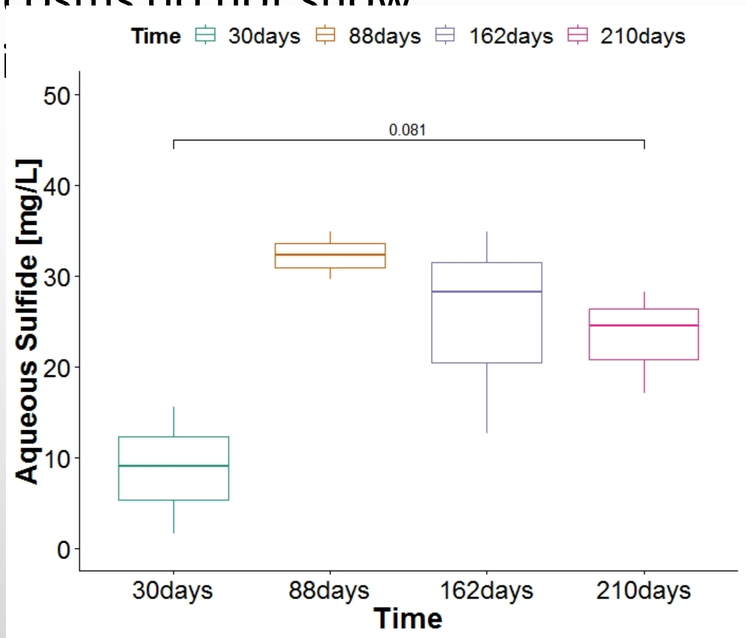
	PAC	Sand	Media Free
First order decay constant [day^{-1}]	$4.9 \cdot 10^{-3}$	$6.6 \cdot 10^{-3}$	$2.3 \cdot 10^{-3}$
p-value	0.023	0.006	0.296

- PAC and sand amended microcosms show decay constant statistically different than zero [p-value < 0.05]
- Decay constant not statistically significant for media free system
- Higher decay constant estimated for PAC system

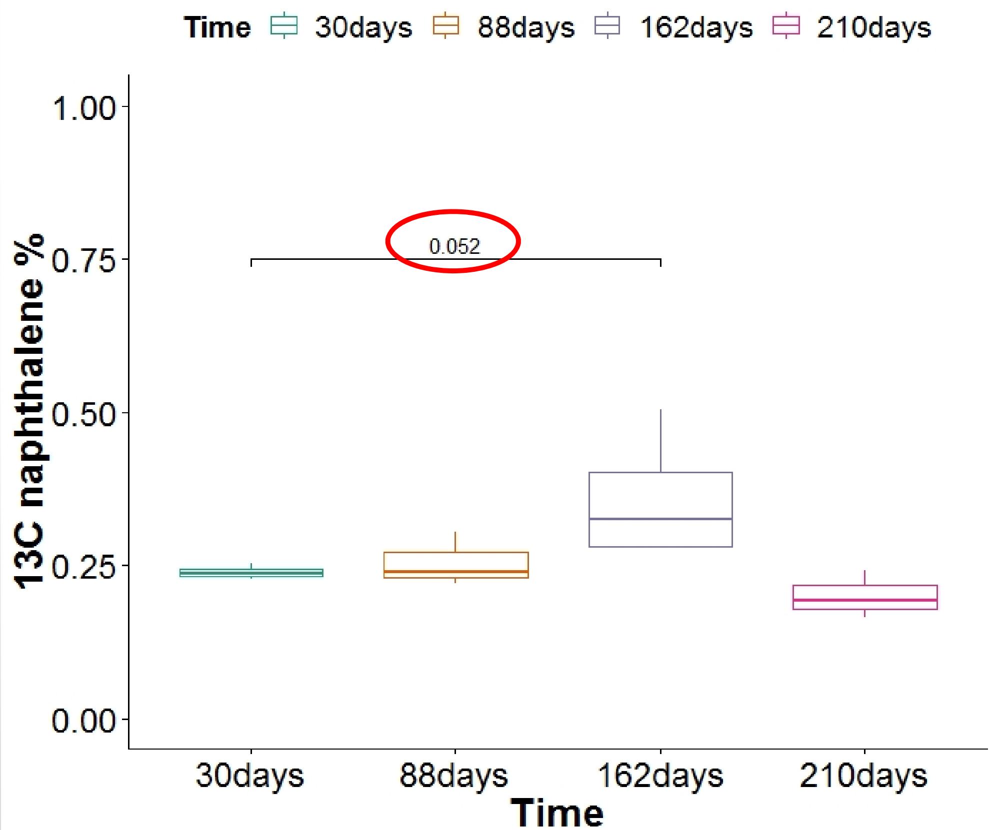
^{13}C enrichment – PAC microcosms



- ^{13}C naphthalene enriched [92% confidence] after 210 days incubation
- Sterile microcosms do not show statistically si
Wallis test p-va
- Sulfide produced in biologically active microcosms



^{13}C enrichment – Sand microcosms



- ^{13}C naphthalene percentages significantly enriched [95% confidence] after 160 days incubation
- High variabi
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- Sterile micr
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- Sulfide
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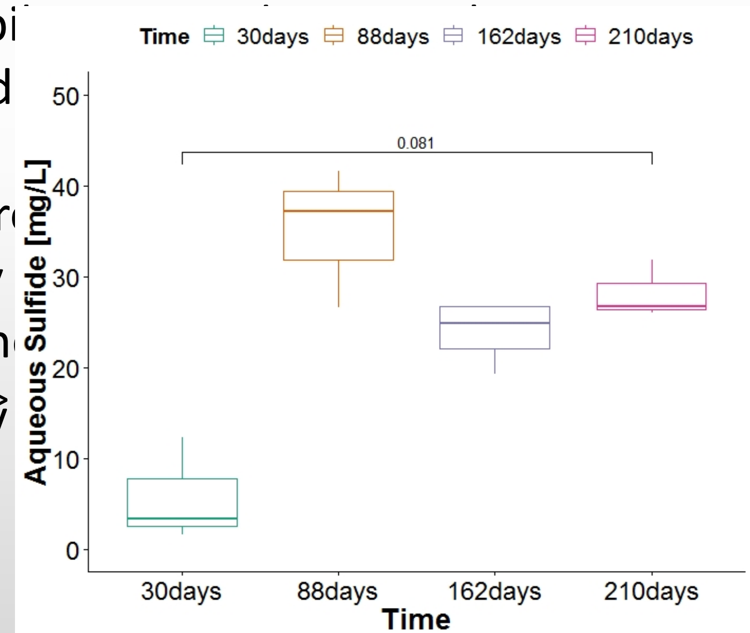
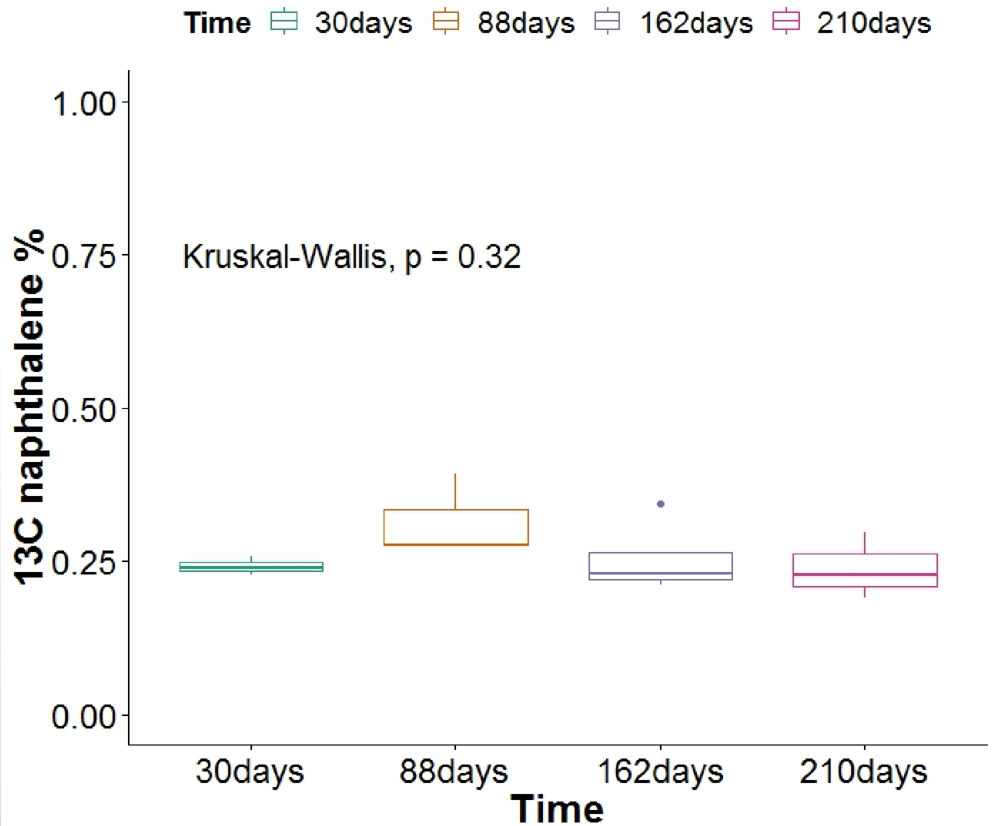


^{13}C enrichment – Media Free microcosms



- ^{13}C naphthalene percentages do not change after 210 days of incubation [Kruskal-Wallis test p value > 0.1]

- Inconstant a
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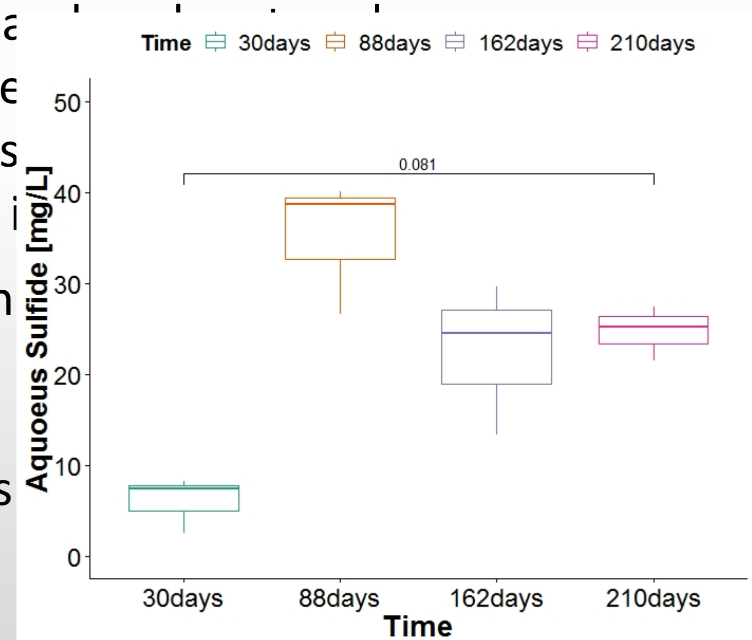
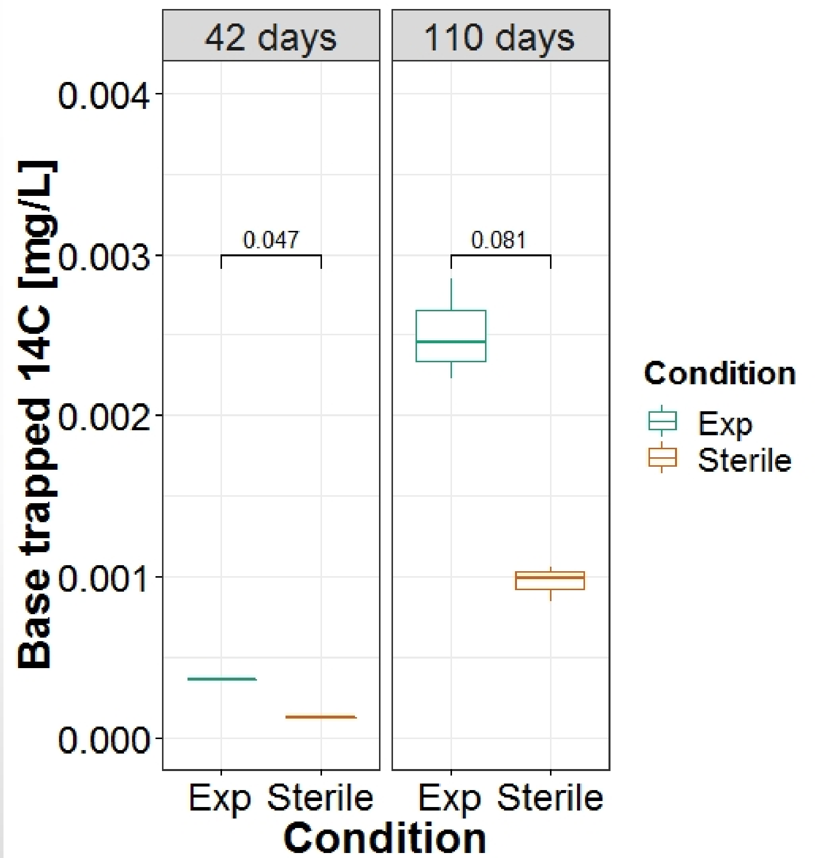
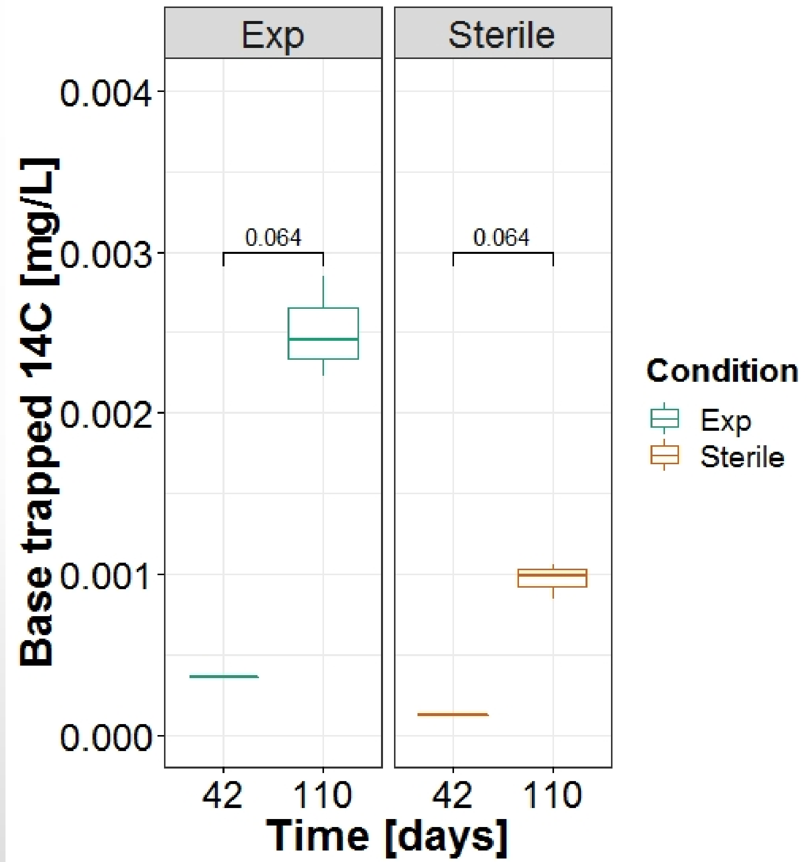
- Sulfide produced in biologically active microcosms



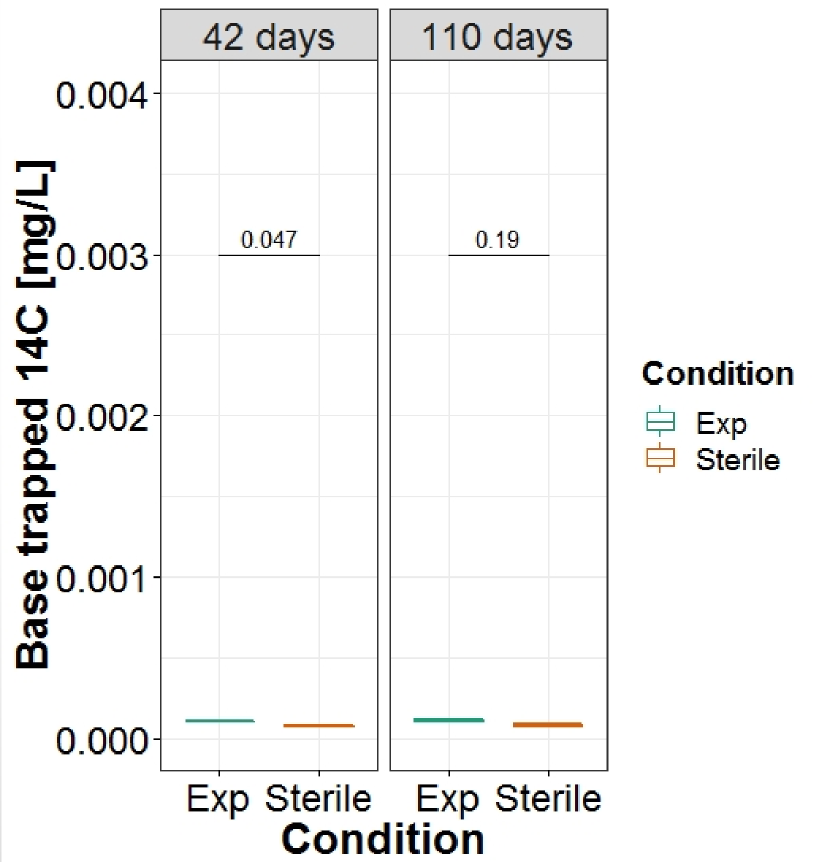
^{14}C accumulation - PAC microcosms



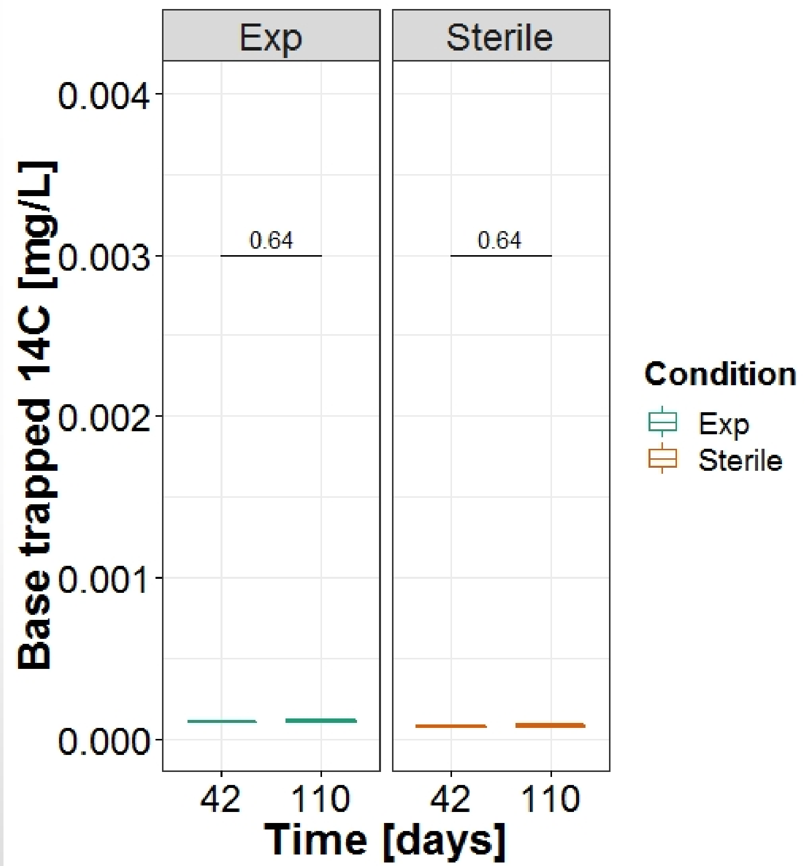


- Base trapped ^{14}C significantly differ between experimental and sterile microcosms at each time point [95% and 92% confidence]
- Higher ^{14}C in biologically active microcosms, although detected in both experimental and sterile conditions

^{14}C accumulation - Sand microcosms

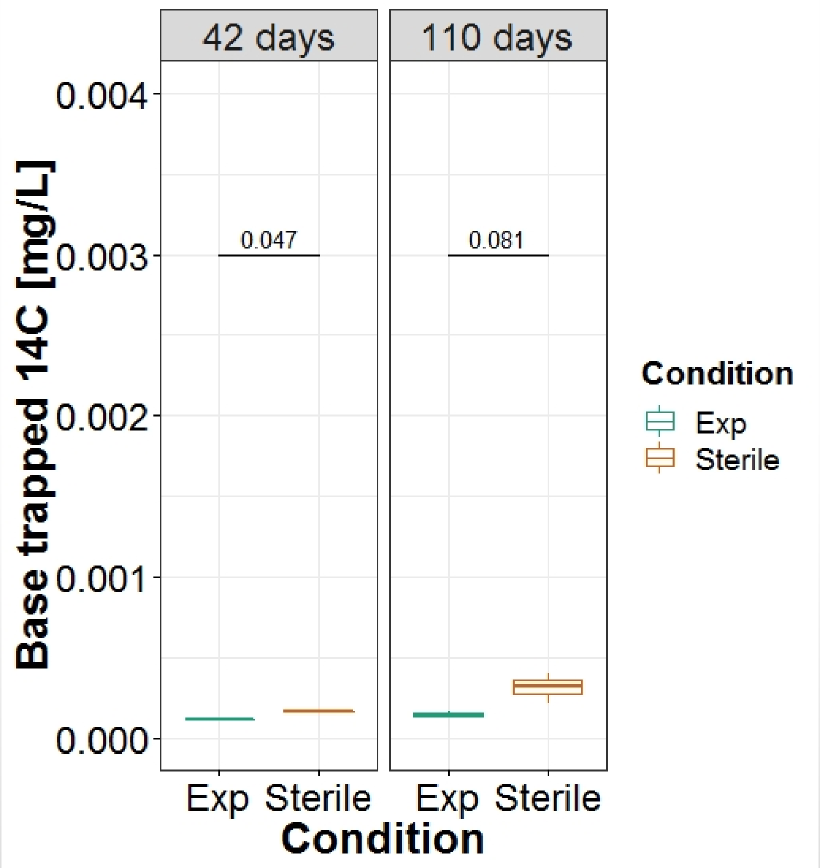


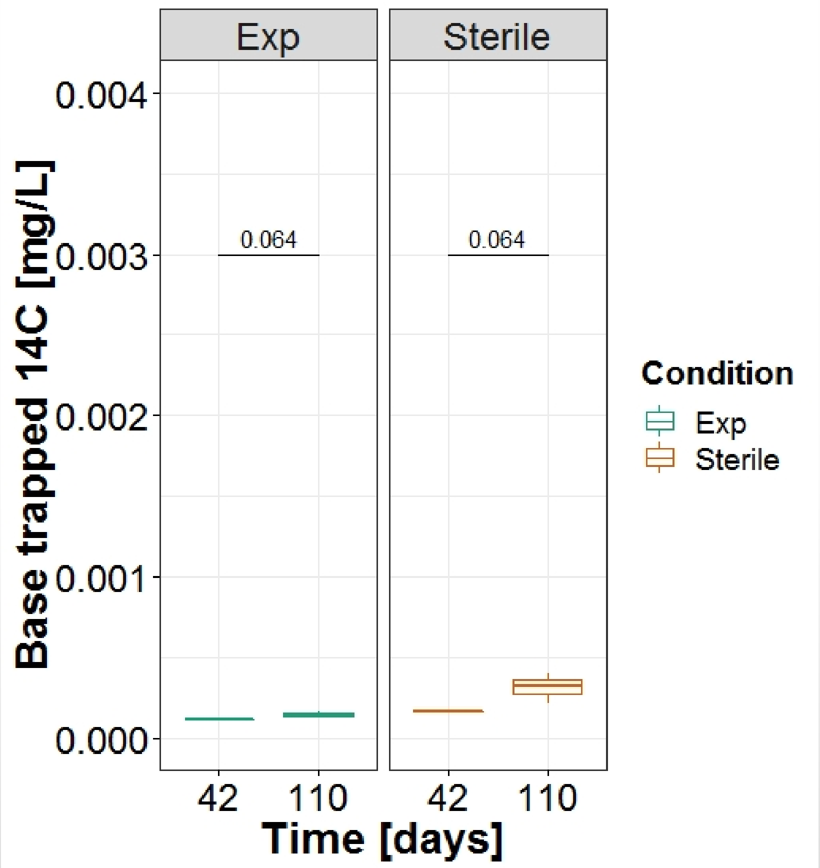
- Concentrations of ^{14}C differ between experimental and sterile microcosms at each time point [95% and 80% confidence]



- ^{14}C observed in both experimental and sterile conditions, with no statistically significant difference

^{14}C accumulation - Media Free microcosms

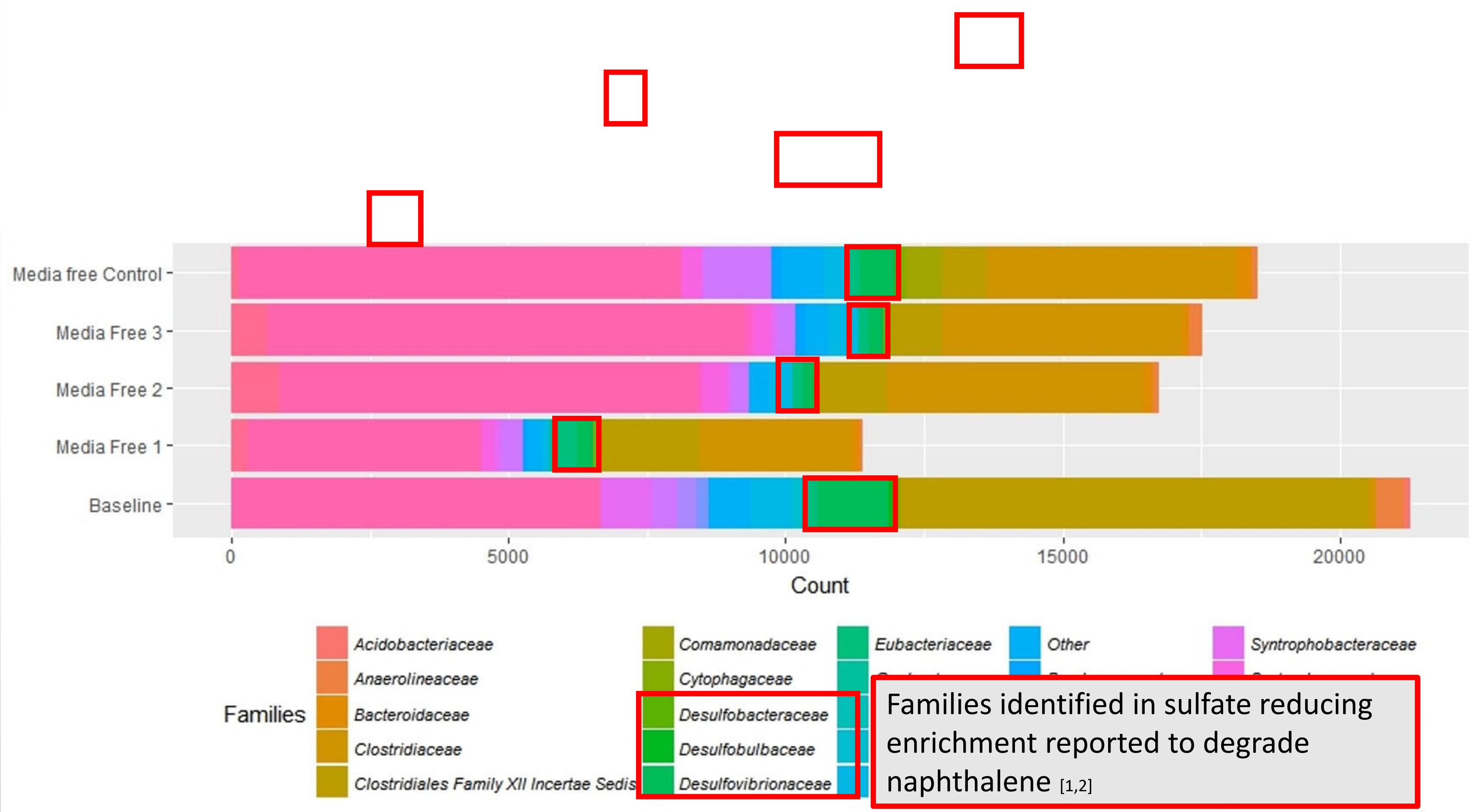




- Headspace ^{14}C accumulates in both experimental and sterile microcosms over time

- Accumulation of ^{14}C carbon is observed in both experimental and sterile conditions

Changes in the Microbial Community Composition



[1] Friedrich Widdel F. and Rabus R. Anaerobic biodegradation of saturated and aromatic hydrocarbons. Current Opinion in Biotechnology, 2001.
[2] Kummel S. et al. Anaerobic naphthalene degradation by sulfate reducing *Desulfobacteraceae* from various anoxic aquifers. FEMS, 2015.

Preliminary Conclusions

Naphthalene decrease

- Higher decay constants in presence of PAC

^{13}C enrichment

- Presence of biological activity in PAC and sand microcosms, with a more clear trend when PAC is present

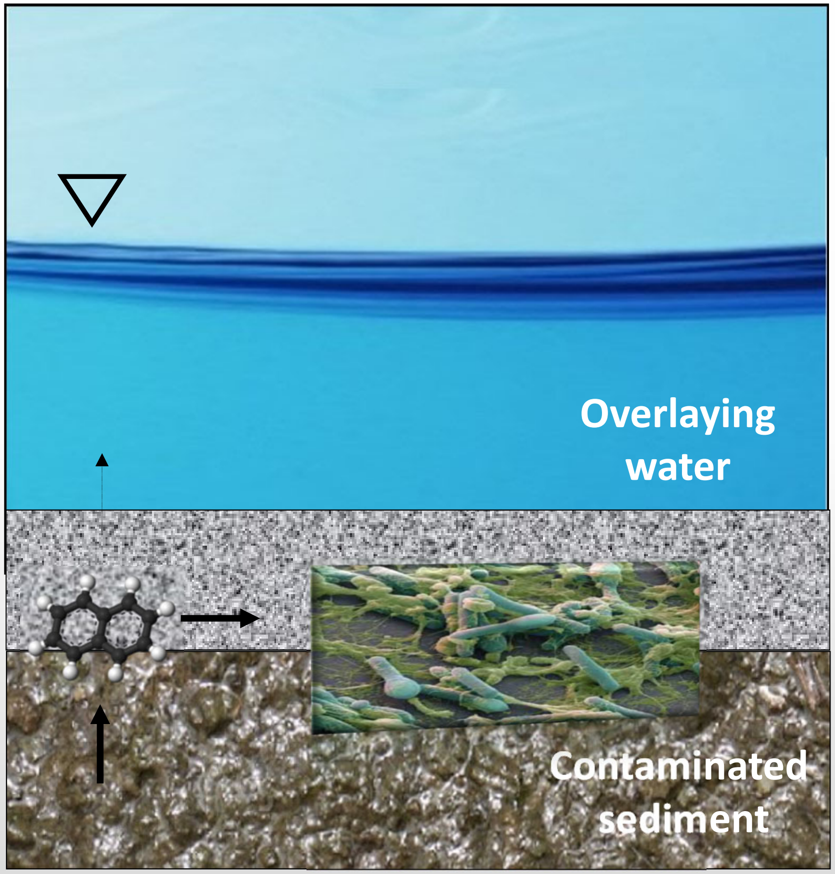
^{14}C accumulation

- Indication of highest mineralization kinetics in microcosms amended with PAC

Microbial Community

- Diverse microbial community develops in the pac system, maintaining a portion of families linked to naphthalene degradation enriched in the baseline

Project rationale



Design optimized capping systems to support natural biodegradation

Contaminants transformed in benign products

Minimize risk of exposure and reduce legacy pollutants

Thank you for your attention