Surfactant enhanced mobilization of polycyclic aromatic hydrocarbons from marine sediment by washing and flushing processes

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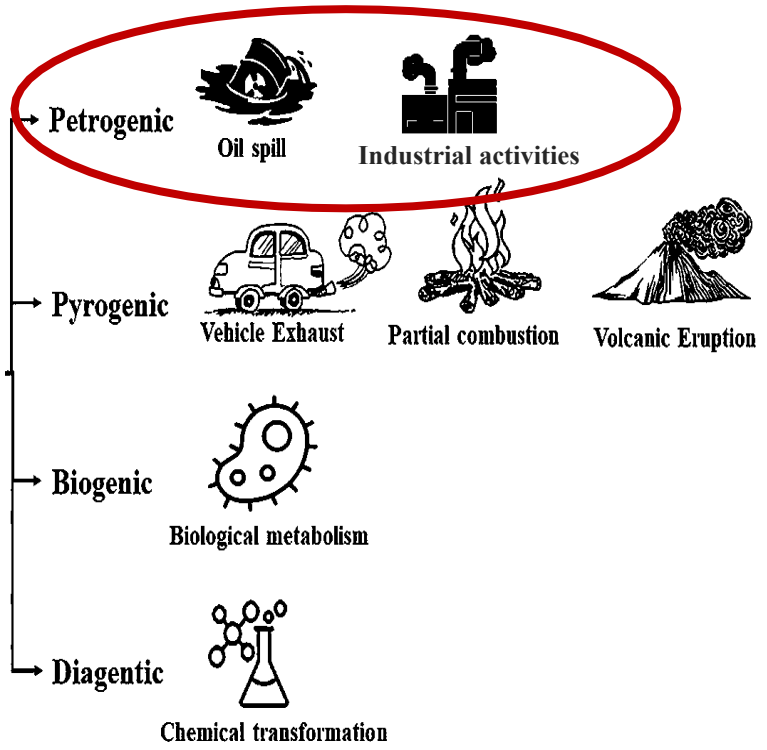
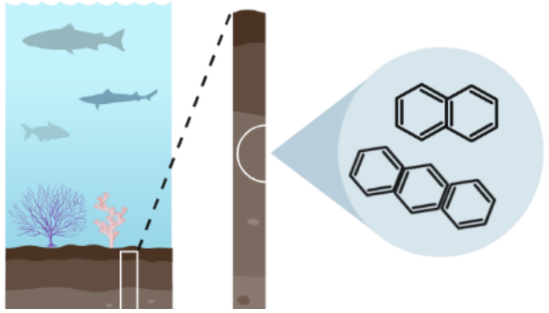
POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) CONTAMINATION

Major Sources of PAHs in marine sediments



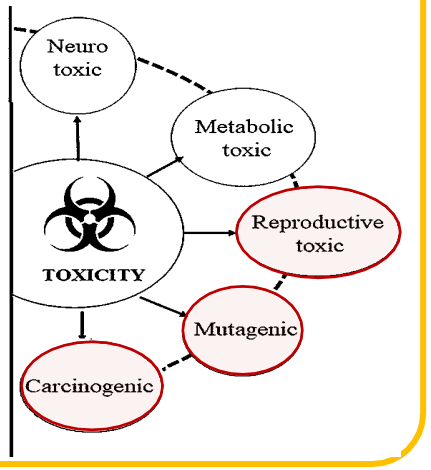
Adverse Effects

1) Environment



- Strong adsorption
- Persistent contamination sources
- Slow release in water
- Bioaccumulation

2) Human Health



Site Management

1) Site Requalification

In-situ capping to block the diffusion of pollutants

Bioremediation for a cost-effective PAHs removal

2) Treatment of polluted sediment

After dredging operations, the dredged matrix can be used for several applications:

- civil construction projects
- beach resurfacing
- land reclamation of swamp areas

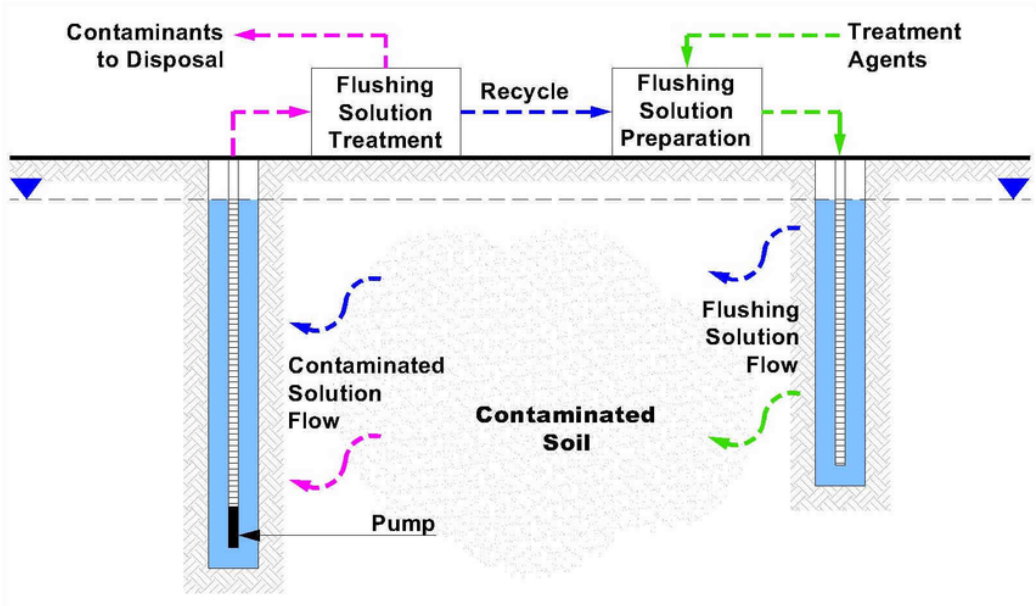
If contaminated, **the remediation of the sediment is absolutely necessary**

SURFACTANT-ENHANCED REMEDIATION (SER)

Ex-situ washing (a) or **In-situ flushing** (b) processes enhanced with **surfactant solutions** *for the mobilization* and *mass transfer* of organic compounds to the aqueous phase.

(a)

(b)

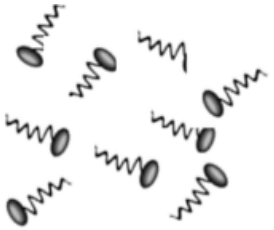


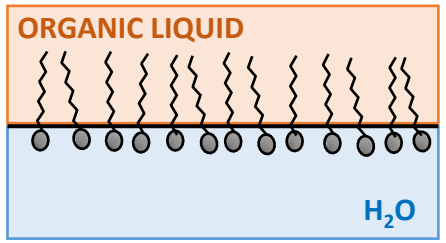
SURFACTANTS

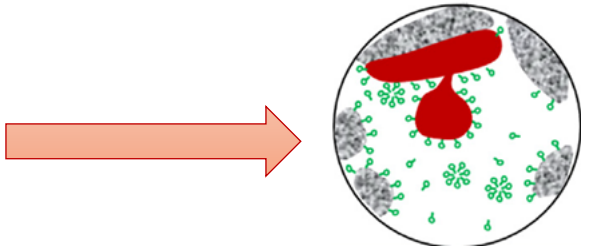
Polar head group

Hydrophobic alkyl chain

Adosrption on interfaces
between immiscible phases
(L-A, L-S or L-L)



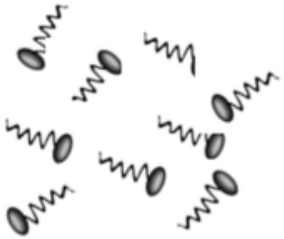


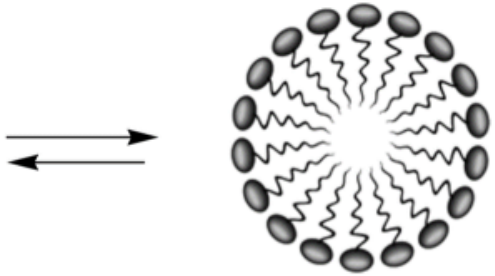


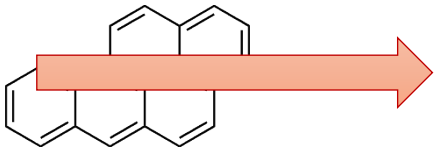
REDUCTION IN INTERFACIAL TENSION

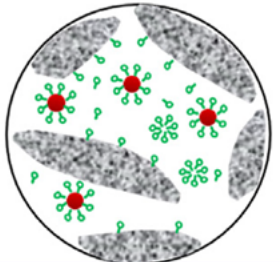
DISPLACEMENT AND MOBILIZATION OF ORGANIC PHASE

Micelles Formation
(when Cs ≥ CMC)









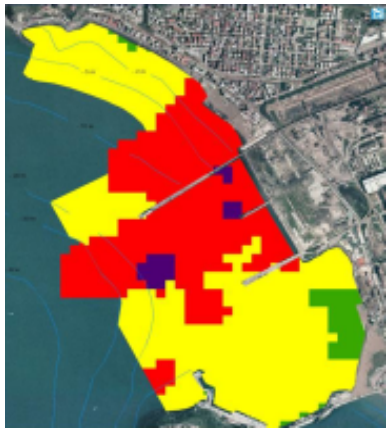
INCREASE IN THE APPARENT SOLUBILITY OF INSOLUBLE COMPOUNDS

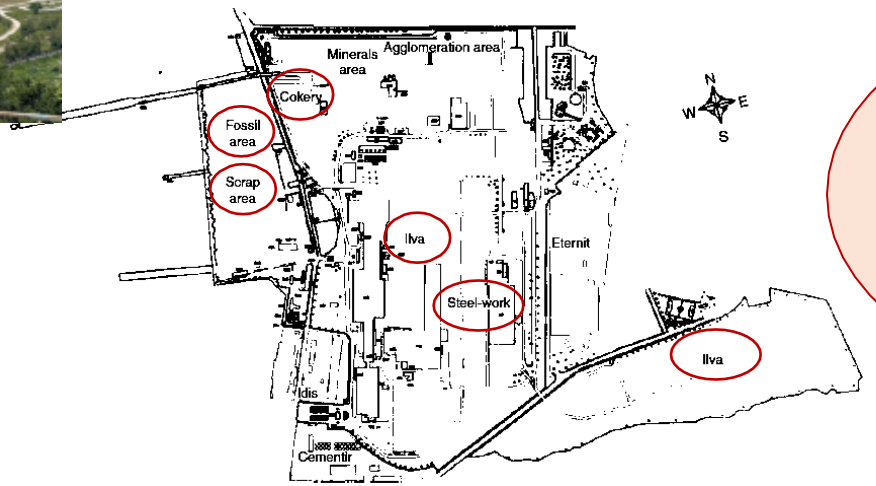
PSEUDOSOLUBILIZATION OF ORGANIC COMPOUNDS

AIM OF THE WORK

Remediation process study for the mobilization of PAHs from an historically polluted sediment by surfactants solution in washing and flushing operations

- National Priority Site (NPS) of Bagnoli-Coroglio
- Hystorical contamination due to industrial activities of «ex ILVA» steel plant (decommissioned in 1992)



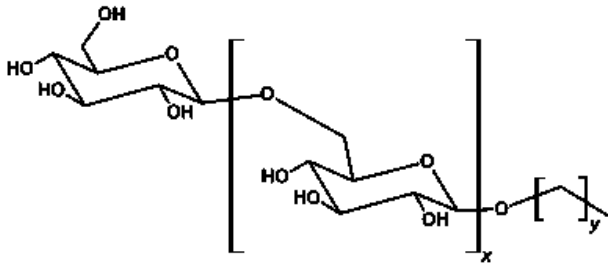


- Heavy Metals
- Hydrocarbons
- BTEX
- **PAHs**

SURFACTANTS

Supplied by CHIMEC

APG 1 – APG 2



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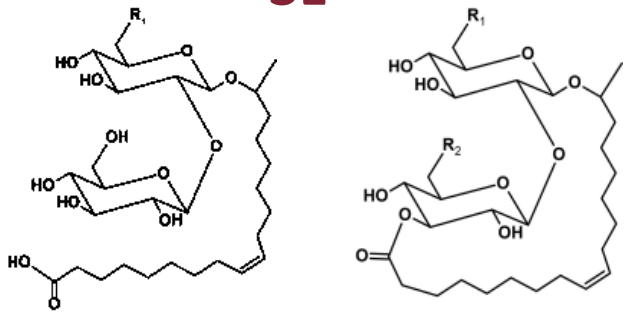
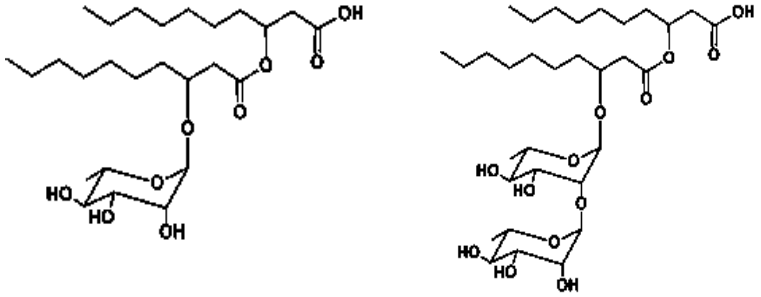
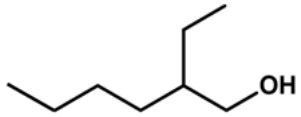


RL 1 – RL 2



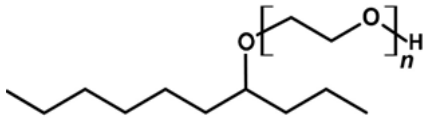
APG 2a

2-ethylhexyl alchool



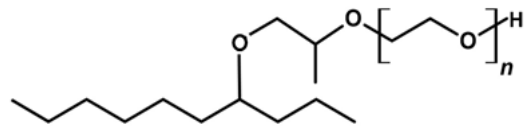
APG 2b

Polyethoxylated co-surfactant



APG 2c

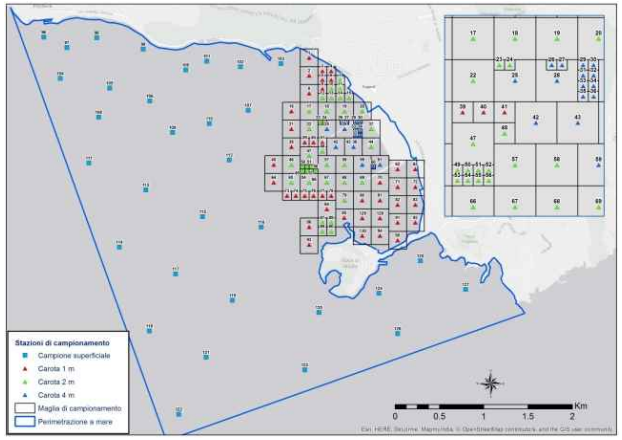
Polyethoxylated propoxylated co-surfactant



Material	APG1	APG2	APG2a	APG2b	APG2c	SL	RL1	RL2
CMC (%wt)	0.06[a]	0.007[a]	0.065[b]	0.035[b]	0.037[b]	0.0125[a]	0.0013[a]	0.0173[a]

WORK ORGANIZATION – EXPERIMENTAL PATHWAY

Sediment Sampling



Sediment Characterization
Determination of PAHs contamination level

Batch Test #1
PAHs mobilization from the sediment by the effect of surfactant solution
[Cs = 5x CMC]

Batch Test #2
Study of the effect of surfactant concentration on PAHs mobilization
[Cs = 1 – 3 – 5%]

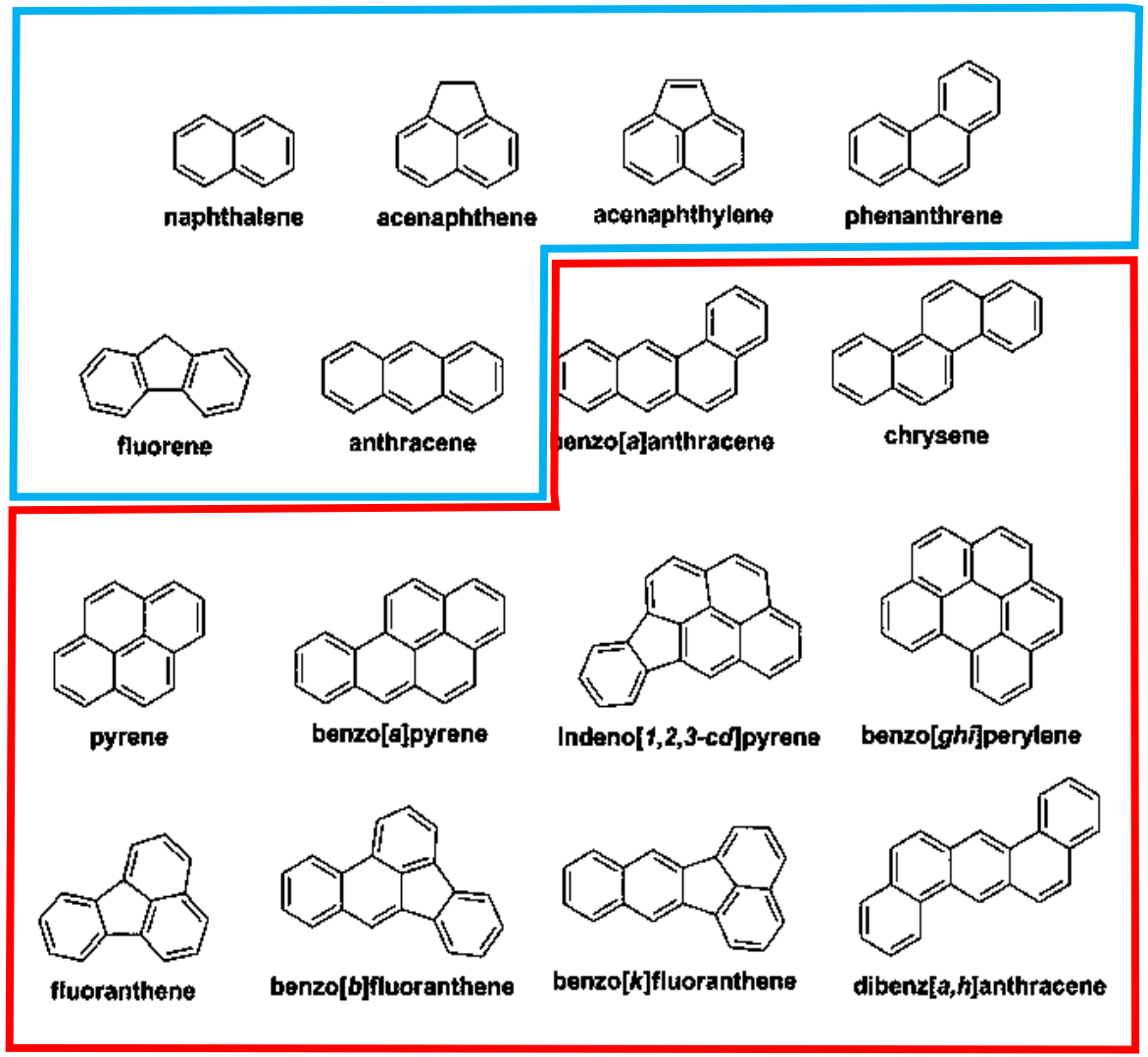
Column Experiment
Lab-scale flushing process simulation
[Cs = 1%
Q = 0.5 mL/min]

SEDIMENT CHARACTERIZATION

Contaminant	Molecular weight (g mol $^{-1}$)	Concentration (µg g^{-1})
Naphthalene	128.17	52.8
Acenaphthylene	152.2	19.4
Acenaphtene	154.21	43.7
Fluorene	166.22	51.4
Phenanthrene	178.23	238.7
Anthracene	178.23	70.4
Fluoranthene	202.26	695
Pyrene	202.26	427.9
Benzo(a)anthracene	228.29	282.2
Chrysene	228.29	145.6
Benzo(b+j)fluoranthene	252.32	332.6
Benzo(k)fluoranthene	252.32	92.6
Benzo(a)pyrene	252.32	636.3
Indeno(1,2,3-cd)pyrene	276.34	217.0
Dibenzo(a,h)anthracene	278.35	60.0
Benzo(g,h,i)perylene	276.34	142.1
∑ PAHs		3507.8

15% LIGHT PAHs

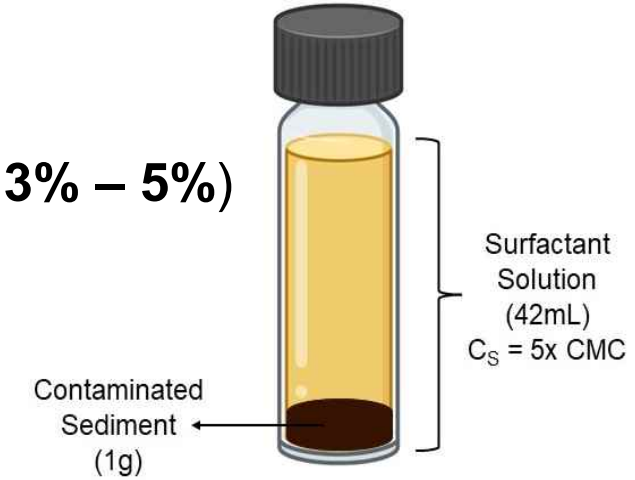
85% HEAVY PAHs

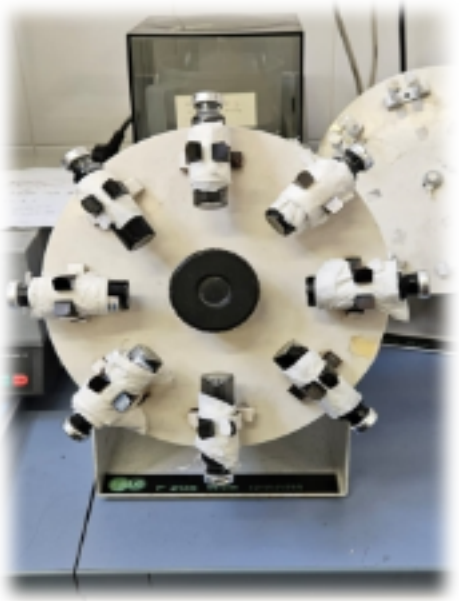


BATCH TESTS: Experimental Set-Up

- **Preliminary evaluation of surfactants' ability in PAHs mobilization**
- **Effect of surfactant concentration**

- 42mL Batch Reactors
- 1g of sediment
- 42mL of surfactant's solution (**Cs = 5x CMC – 1% – 3% – 5%**)
- Reference test: H_2O washing
- 48h rotatory stirring
- Centrifuge of samples: 10 min at 3000 rpm
- GC-MS analysis

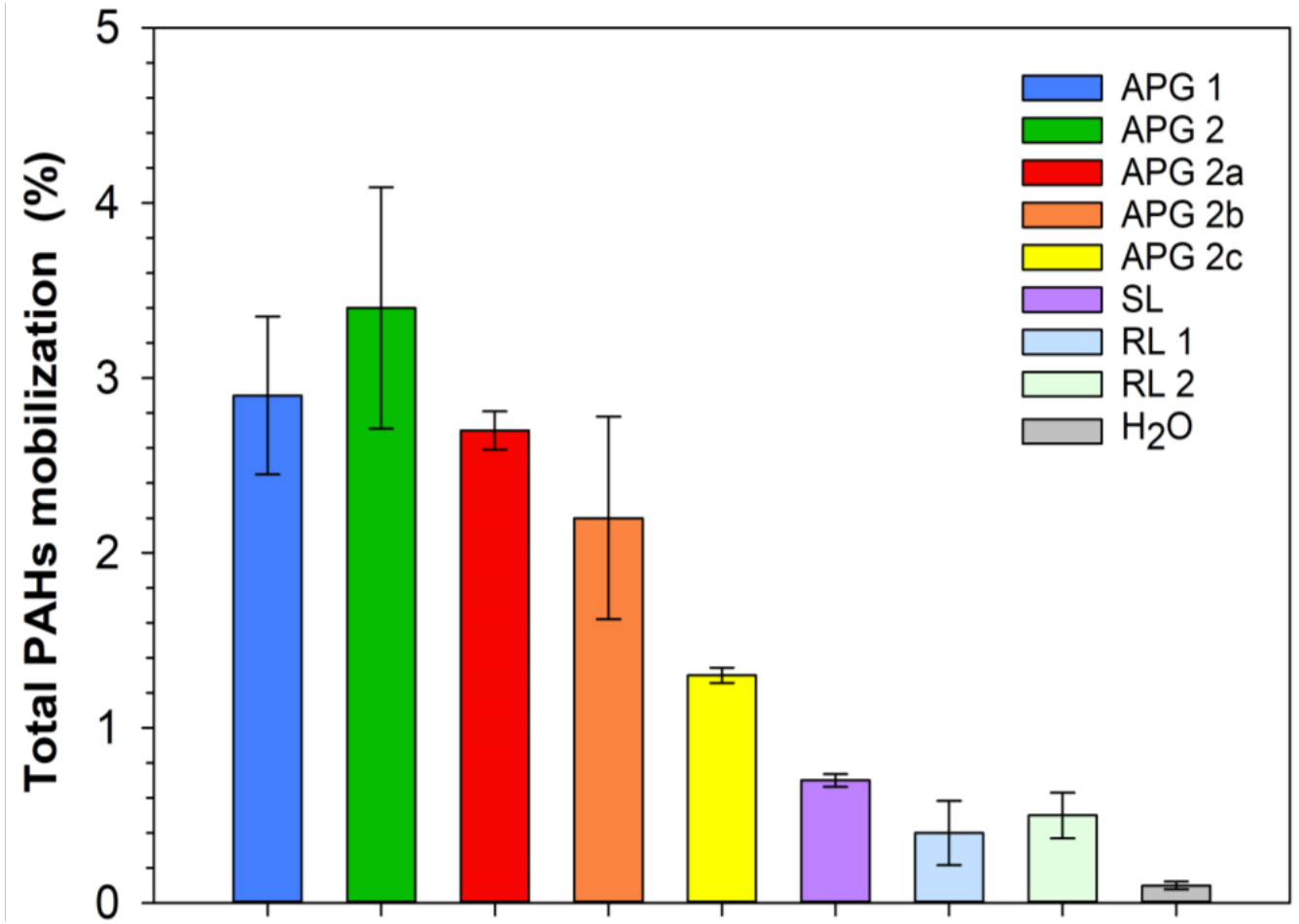




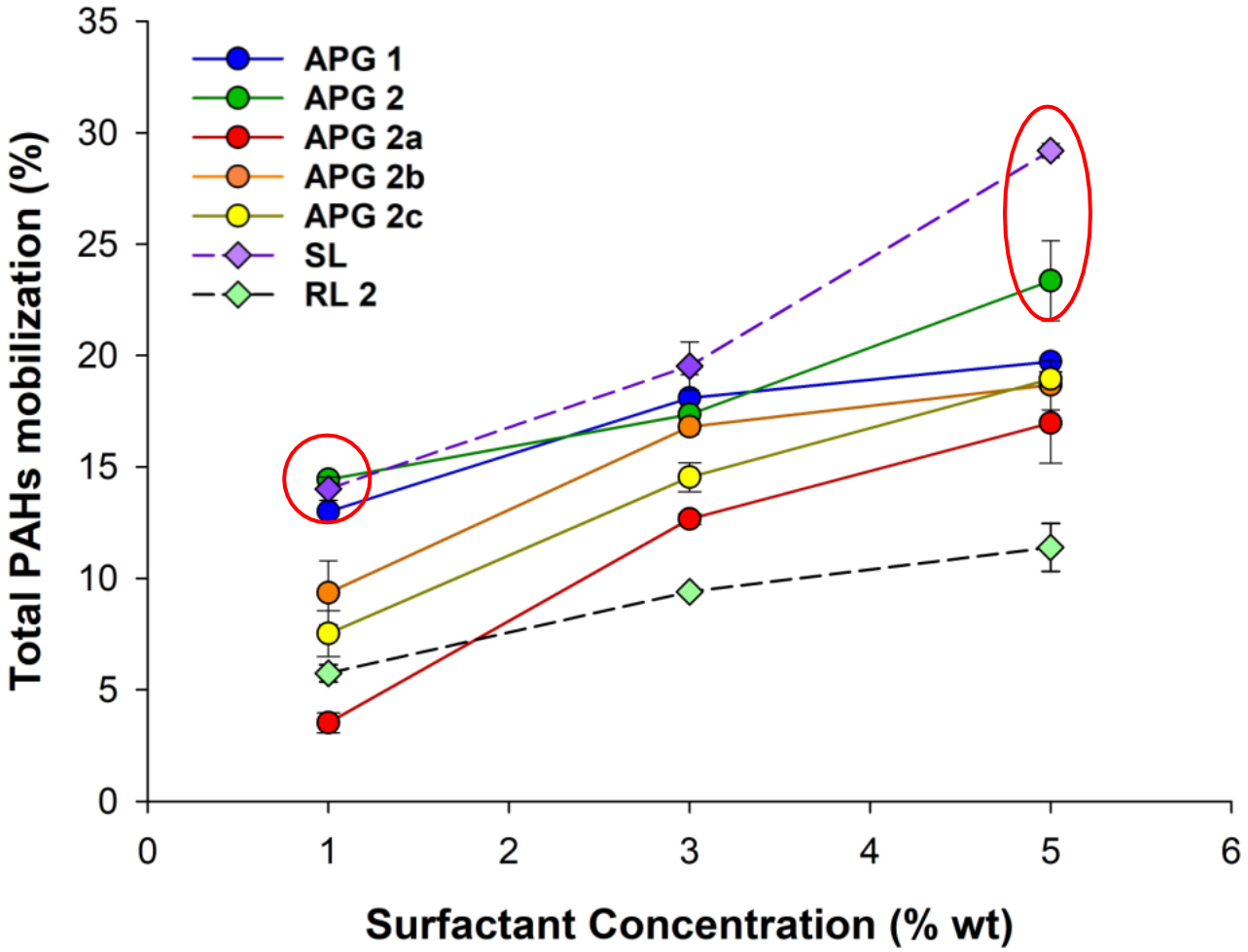
Material	APG1	APG2	APG2a	APG2b	APG2c	SL	RL1	RL2
C_S= 5x CMC (%wt)	0.3	0.035	0.325	0.175	0.185	0.0625	0.0065	0.0865

BATCH TEST #1: PAHs mobilization evaluation

- Significant increase in PAHs mobility
- PAHs mobilization was:
  - 20-35 times greater than H_2O for synthetic surfactants
  - 5-10 times greater than H_2O for biosurfactants
- Synthetic APG 2 and biological SL have resulted as the most effective among their respective classes (synthetic and biosurfactants)



BATCH TEST #2: Surfactant concentration effect

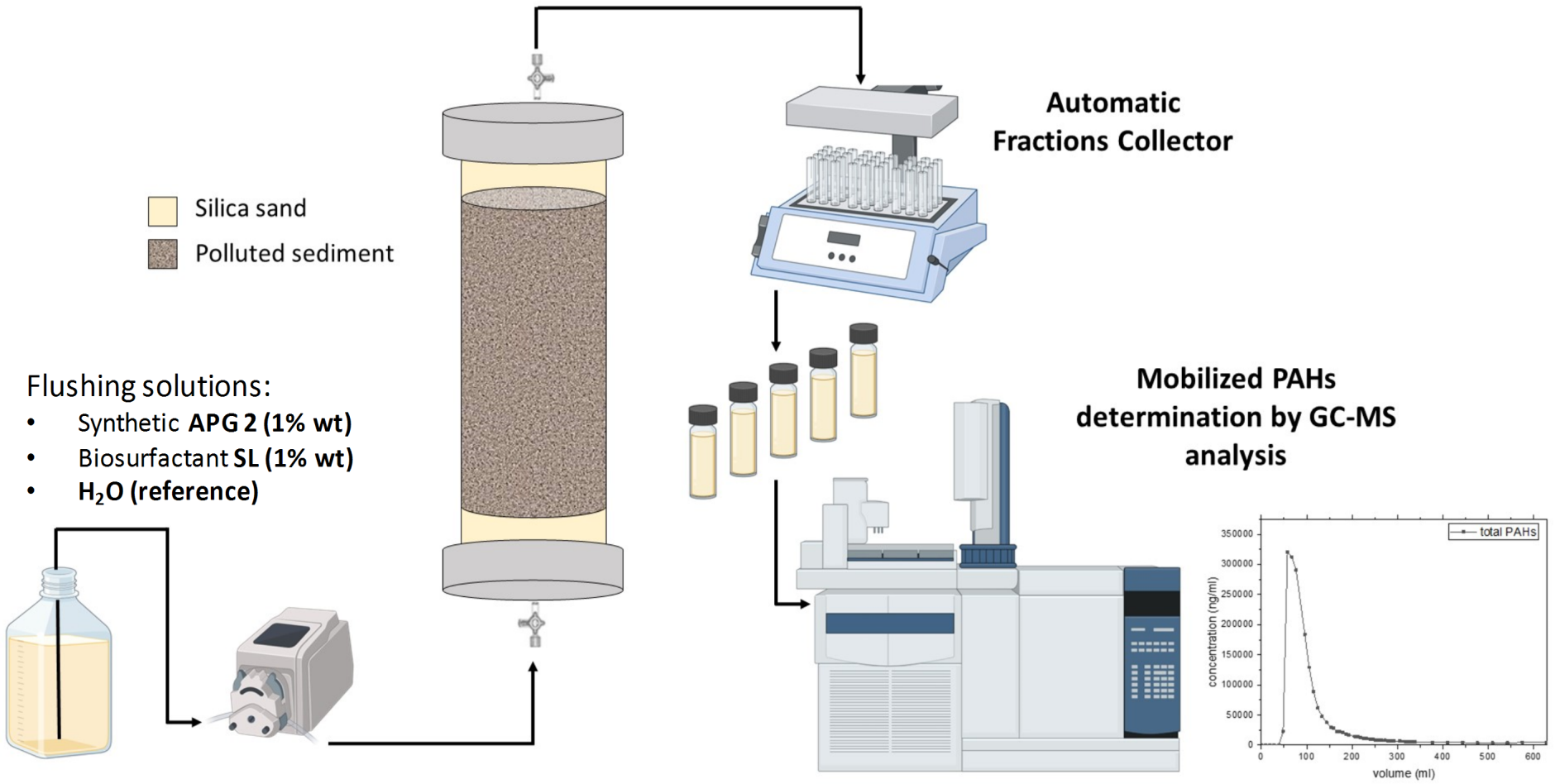


- PAHs mobilization increases as the surfactant concentration increase

- APG 2 and SL were the most promising surfactants <u>at both lowest (1% wt) and greater concentrations (5% wt) tested</u>

Selected as flushing agents for continuous experiments

CONTINUOUS CONFIGURATION COLUMN TEST: Experimental Set-Up



PMMA Columns

h = 14cm ; id = 2.8cm

Flushing Solutions:

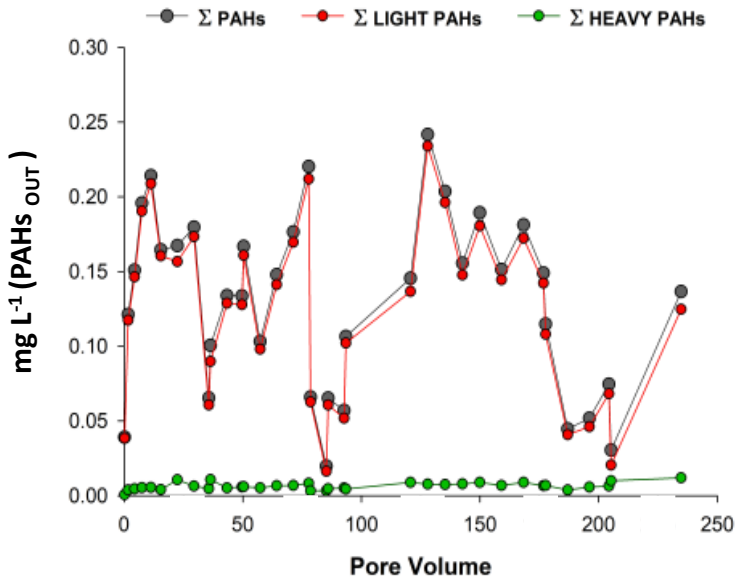
- APG 2 (1% wt)
- SL (1% wt)
- H_2O (reference)

Q = 0.6 mL min^{-1}

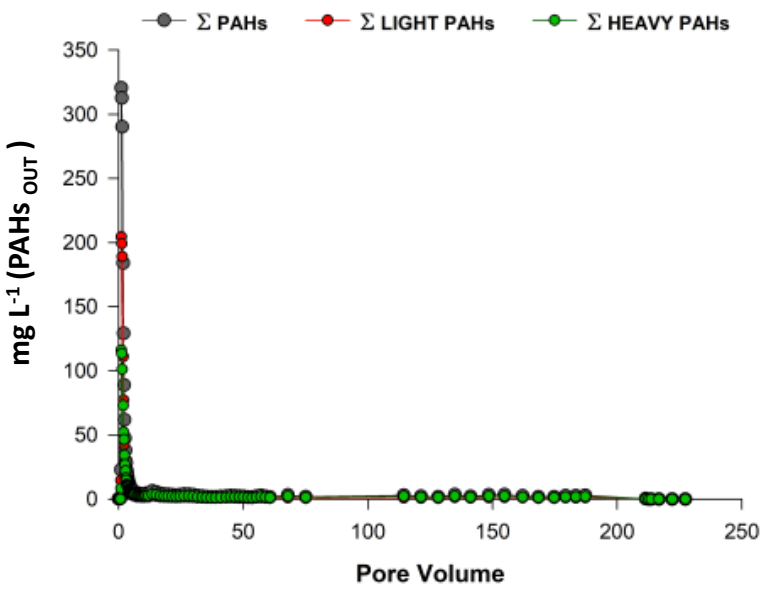
Working time: **14 days**

CONTINUOUS CONFIGURATION COLUMN TEST: Results

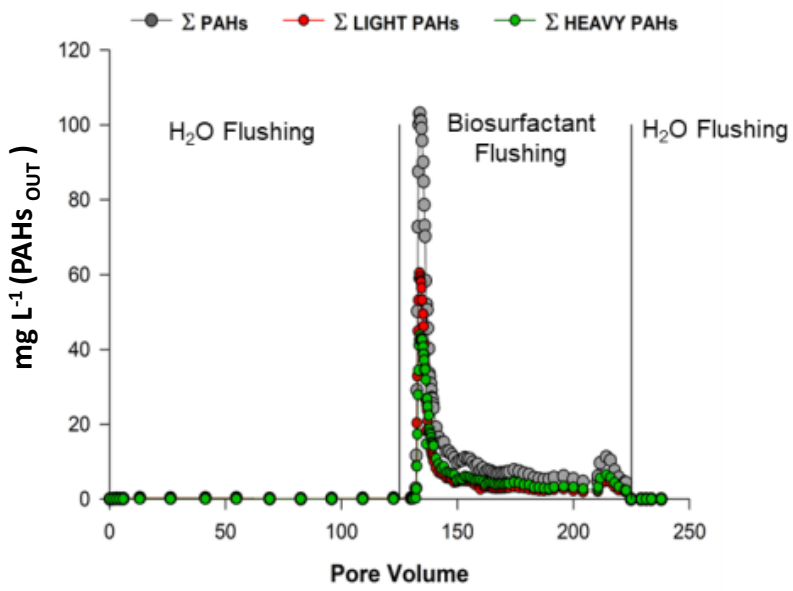
H_2O (reference)



APG 2

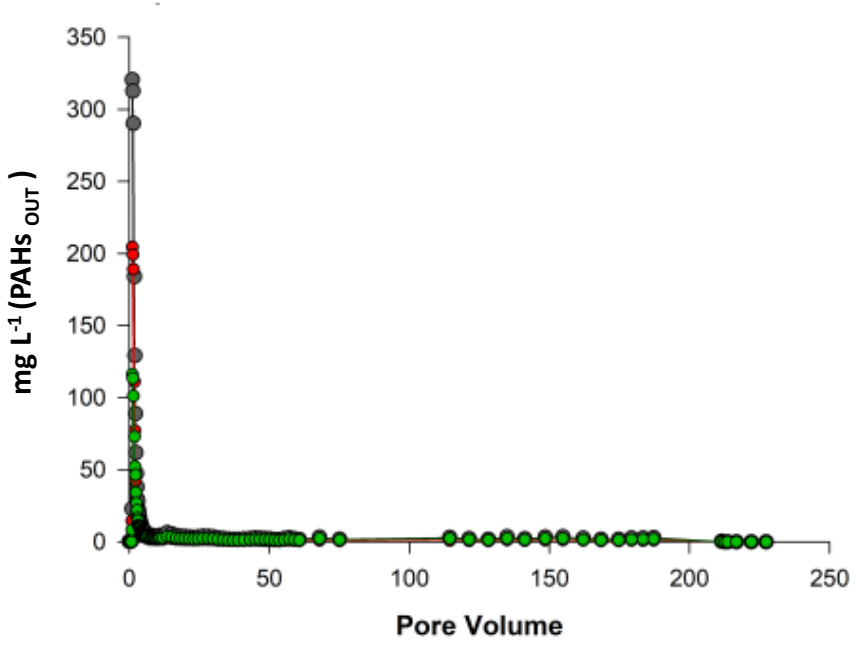


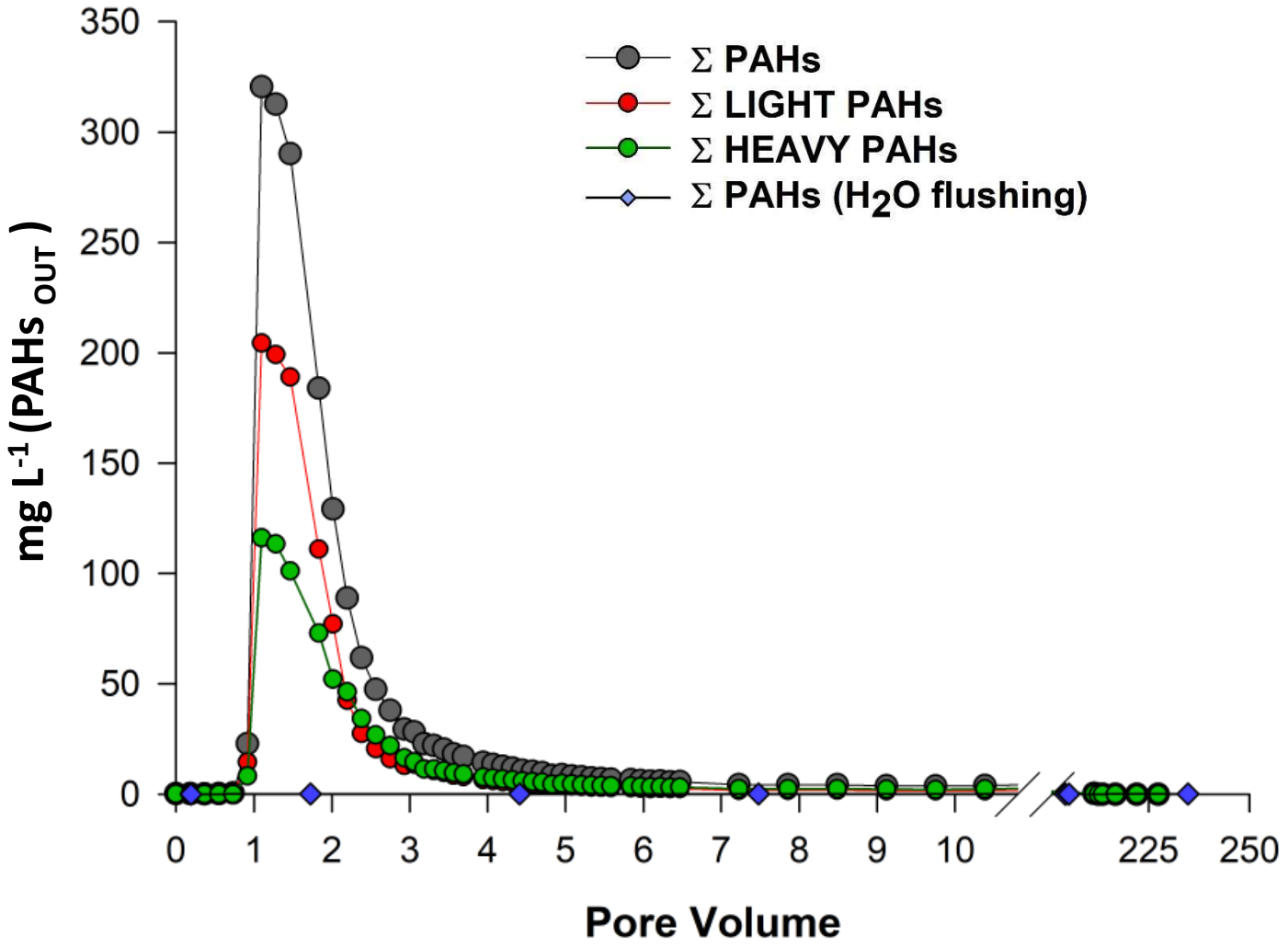
SL



CONTINUOUS CONFIGURATION COLUMN TEST: Results

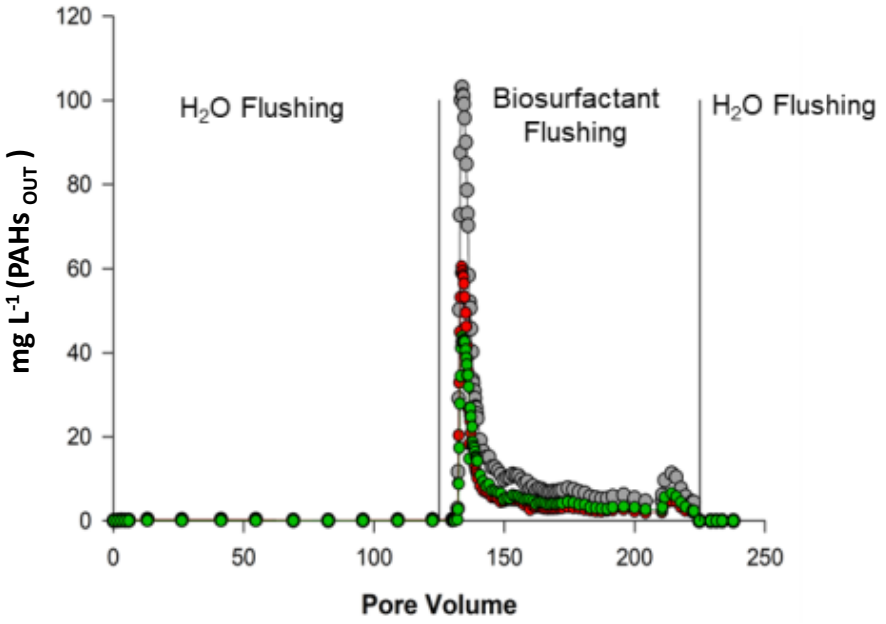
APG 2

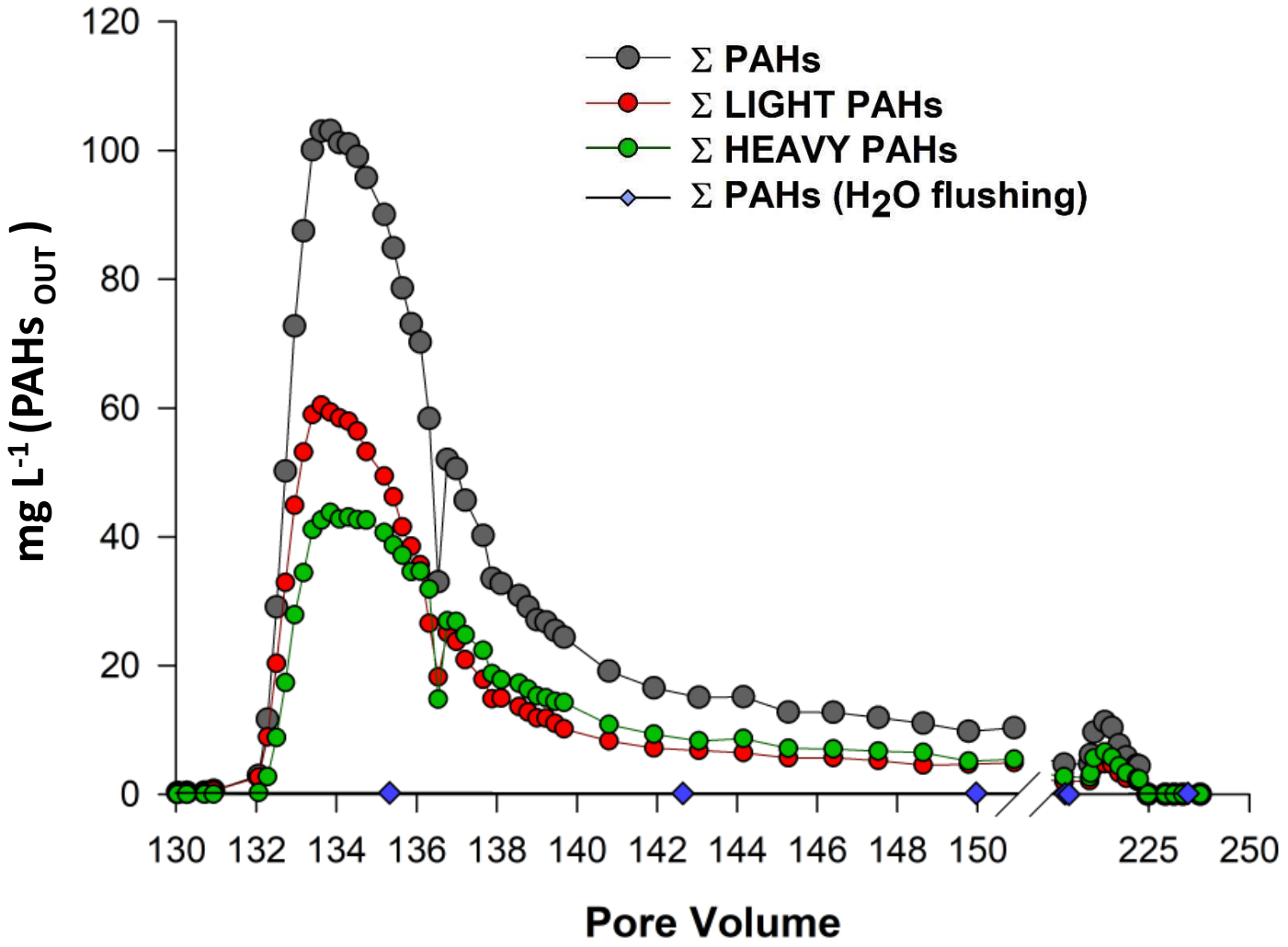




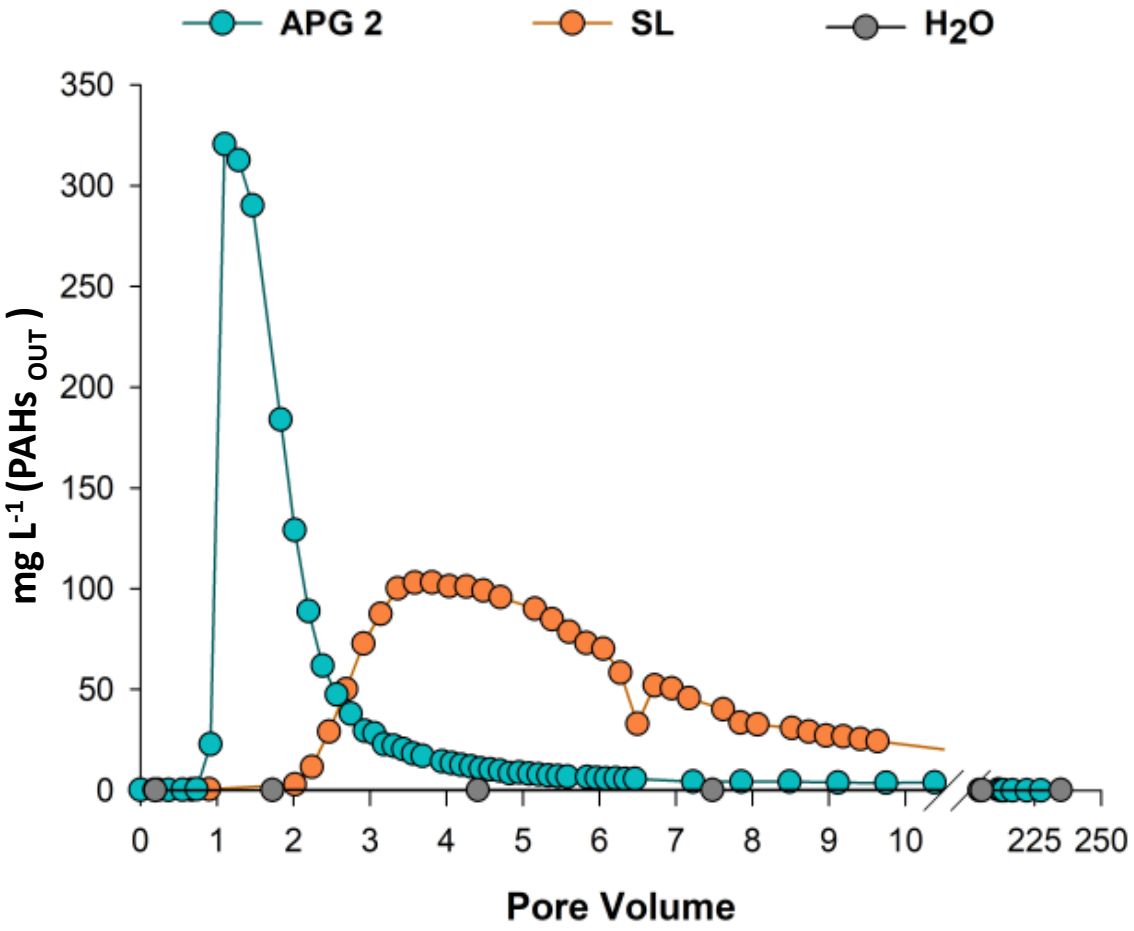
CONTINUOUS CONFIGURATION COLUMN TEST: Results

SL





CONTINUOUS CONFIGURATION COLUMN TEST: Results



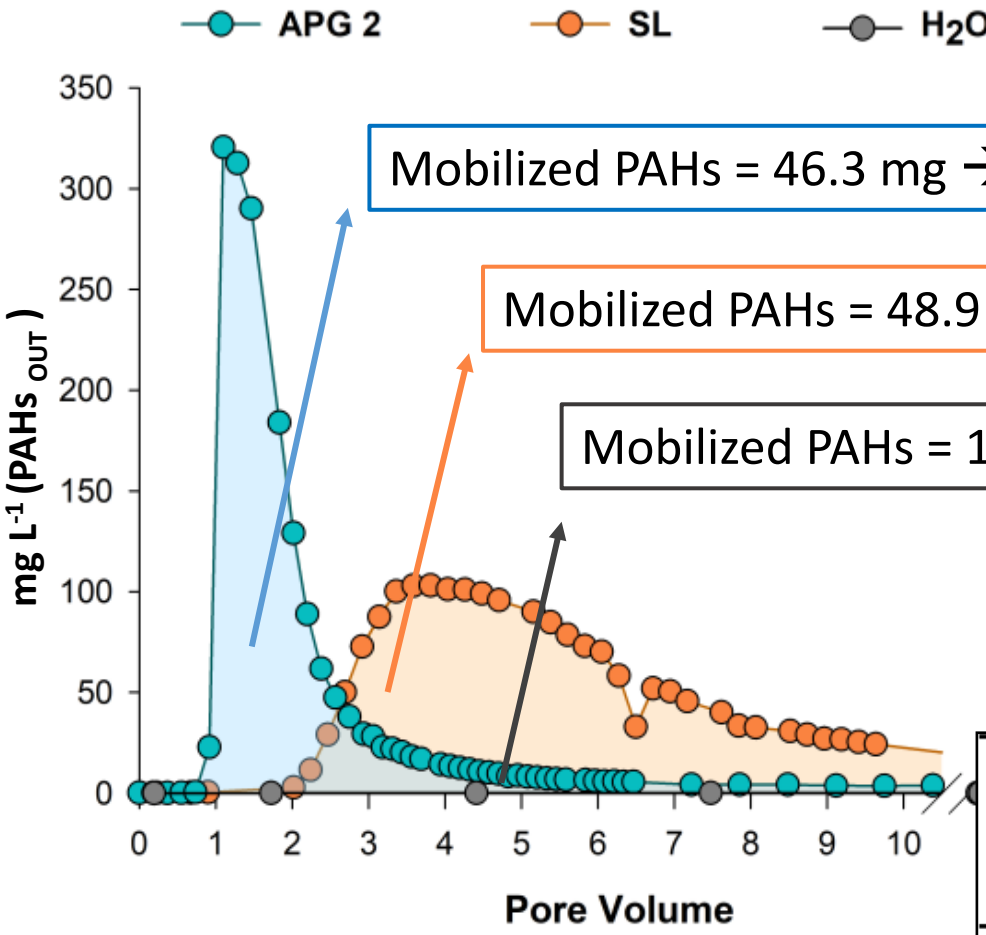
APG 2

- Sharp PAHs concentration profile
- Direct and intense activity on contamination

SL

- Smooth PAHs concentration profile
- Less intense but more gradual activity on contamination

CONTINUOUS CONFIGURATION COLUMN TEST: Results



Flushing Solution	starting mg PAHs	$C_{OUT\ max}$ (mg L^{-1})	Mobilized mg PAHs	PV	∑ PAHs Removal	
					Continuous	*Batch*
H_2O	133.2	/	1.60	225	1.2 %	0.1%
APG 2 (1%)	165.9	325	46.3	4.5	27.9 %	14.9%
SL (1%)	167.3	105	48.9	40-60	29.4 %	14.7%

CONCLUSIONS

In the context of SER technology, this work provided for the development of an experimental protocol (batch tests followed by column experiments) for a lab-scale process study for the remediation of a historically contaminated sediment with an aged contamination source. In this regard:

- **THE EFFICIENCY AND APPLICABILITY OF SEVERAL GREEN SURFACTANTS WERE EVALUATED**
- **A BENCHMARK FOR THE SELECTION OF THE MOST PROMISIONG SURFACTANT WAS PROVIDED**
- **A BENCHMARK FOR THE SELECTION OF BEST PROCESS CONDITION WAS PROVIDED**

- **Great effectiveness** of surfactants for the mobilization of recalcitrant and highly persistent compounds in situations of historical contamination.
- Great enhancement of PAHs mobilization than H_2O (**30 times greater than H_2O**).
- **Continuous configuration process allowed to a higher mobilization** than the classical batch-configuration washing process.
- **The mobilization occurred in a very small pores volume range**

THANK YOU FOR THE KIND ATTENTION

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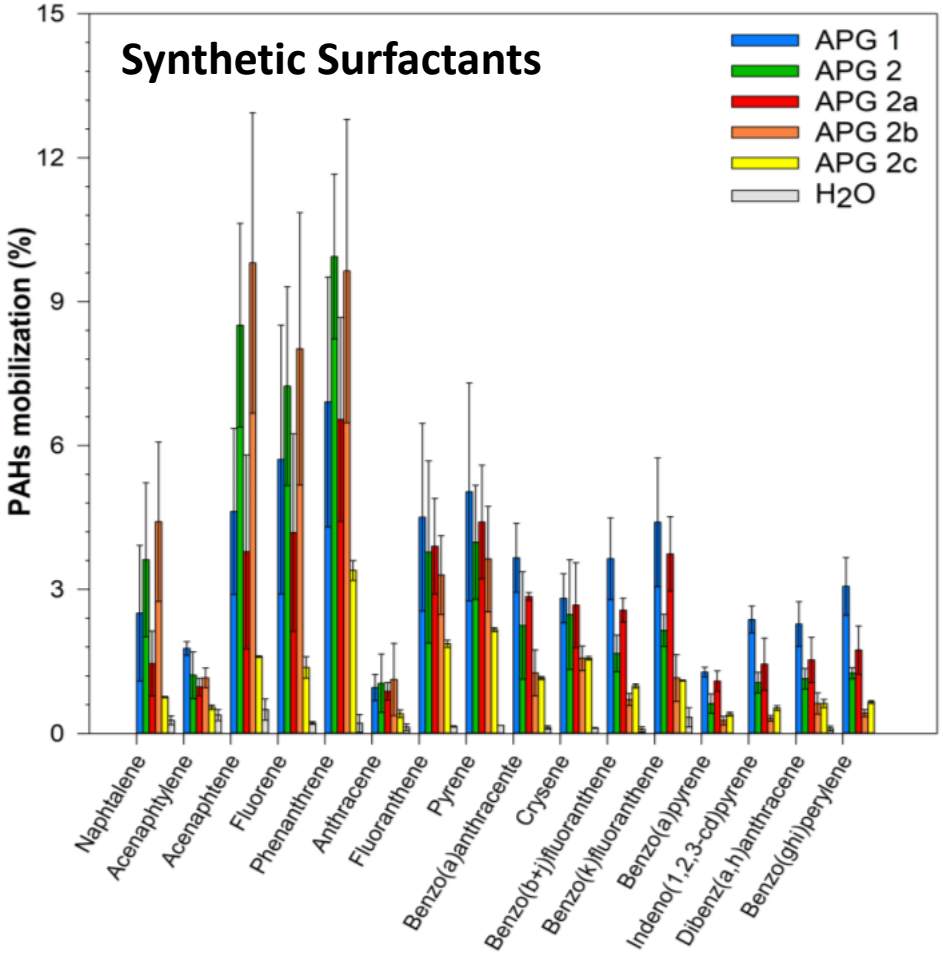
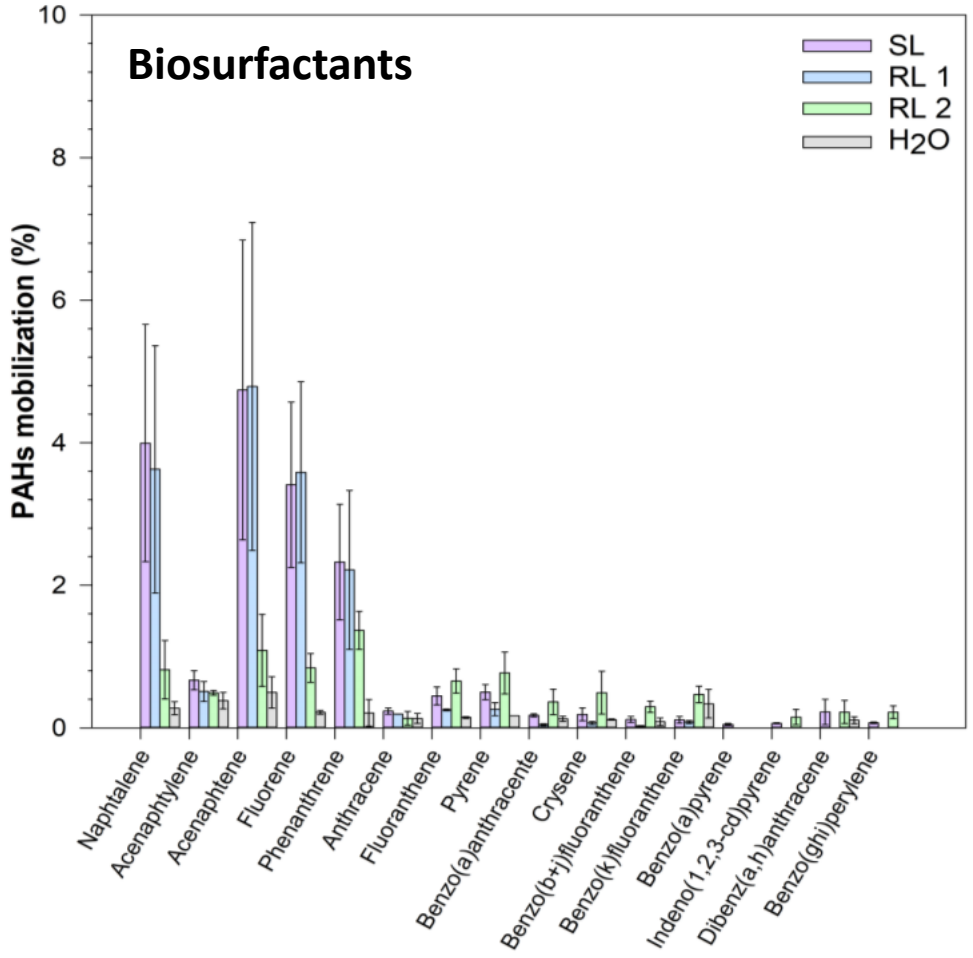
Backup Slide for a possible question

BATCH TEST #1: PAHs mobilization – Single compound results





Backup Slide for a possible question

CONTINUOUS CONFIGURATION COLUMN TEST: Results