



AMERICAN
UNIVERSITY OF BEIRUT

MAROUN SEMAAN FACULTY OF
ENGINEERING & ARCHITECTURE

Modeling the Interaction of Crude Oil Hydrocarbons with Polyethylene Microplastics in Aquatic Environments

Farah Ali Ahmad, Darine A. Salam

Department of Civil and Environmental Engineering, American University of Beirut, Beirut, Lebanon

BATTELLE

13th International Conference on Remediation of Chlorinated and Recalcitrant Compounds

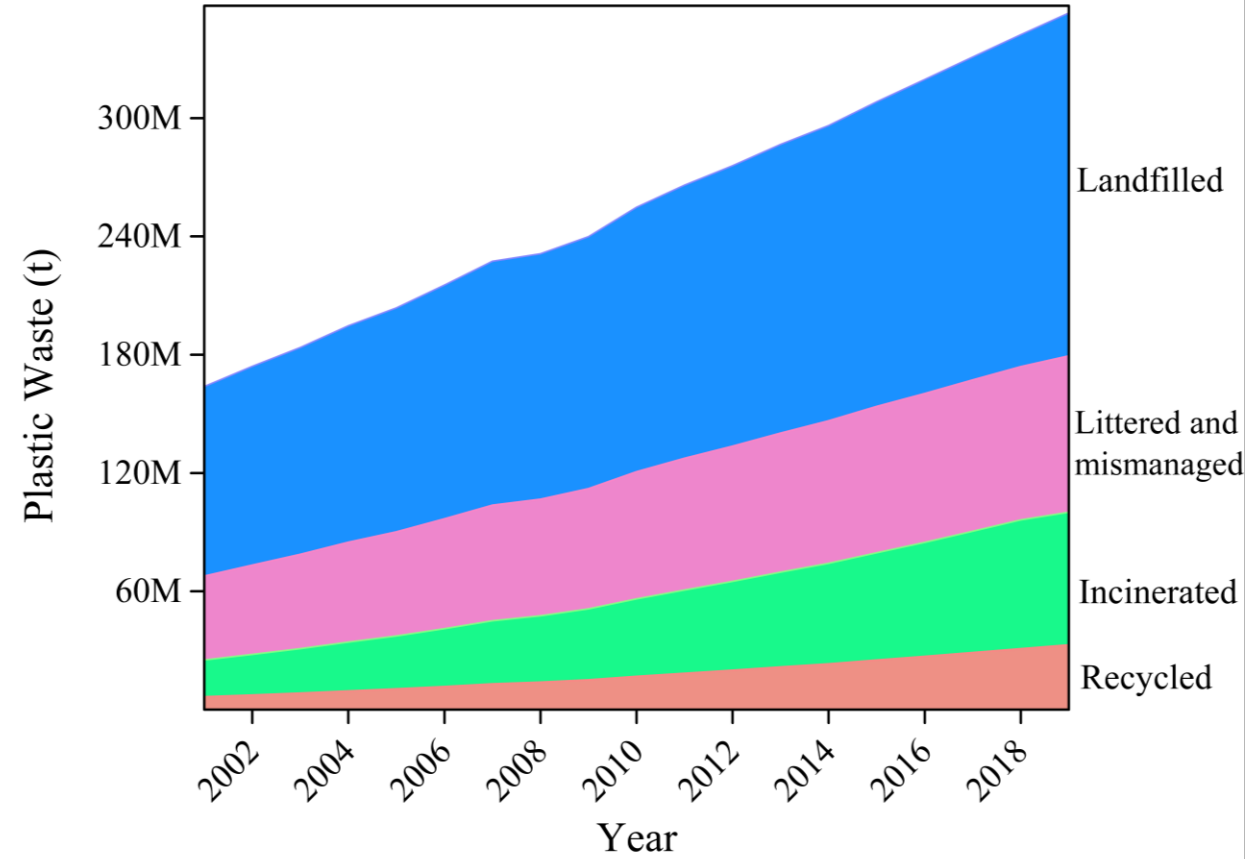
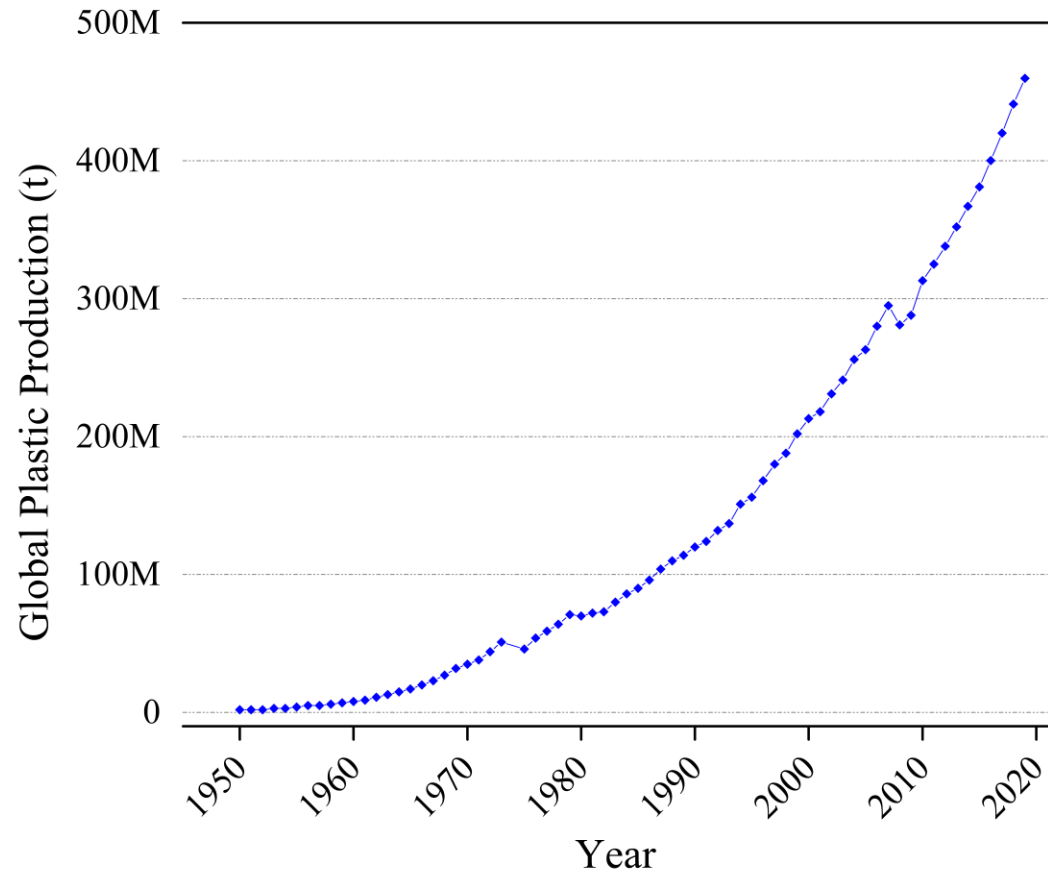
Session: B10: Microplastics, Pharmaceuticals, and Other Emerging Contaminants

Denver, Colorado

June 2024



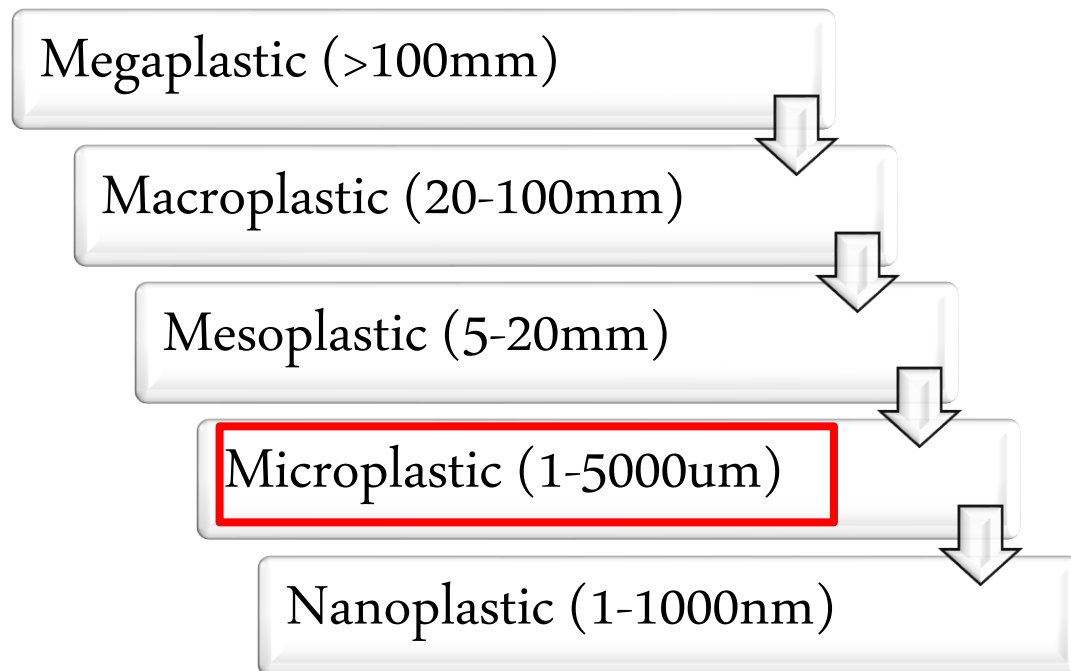
Plasticene Era



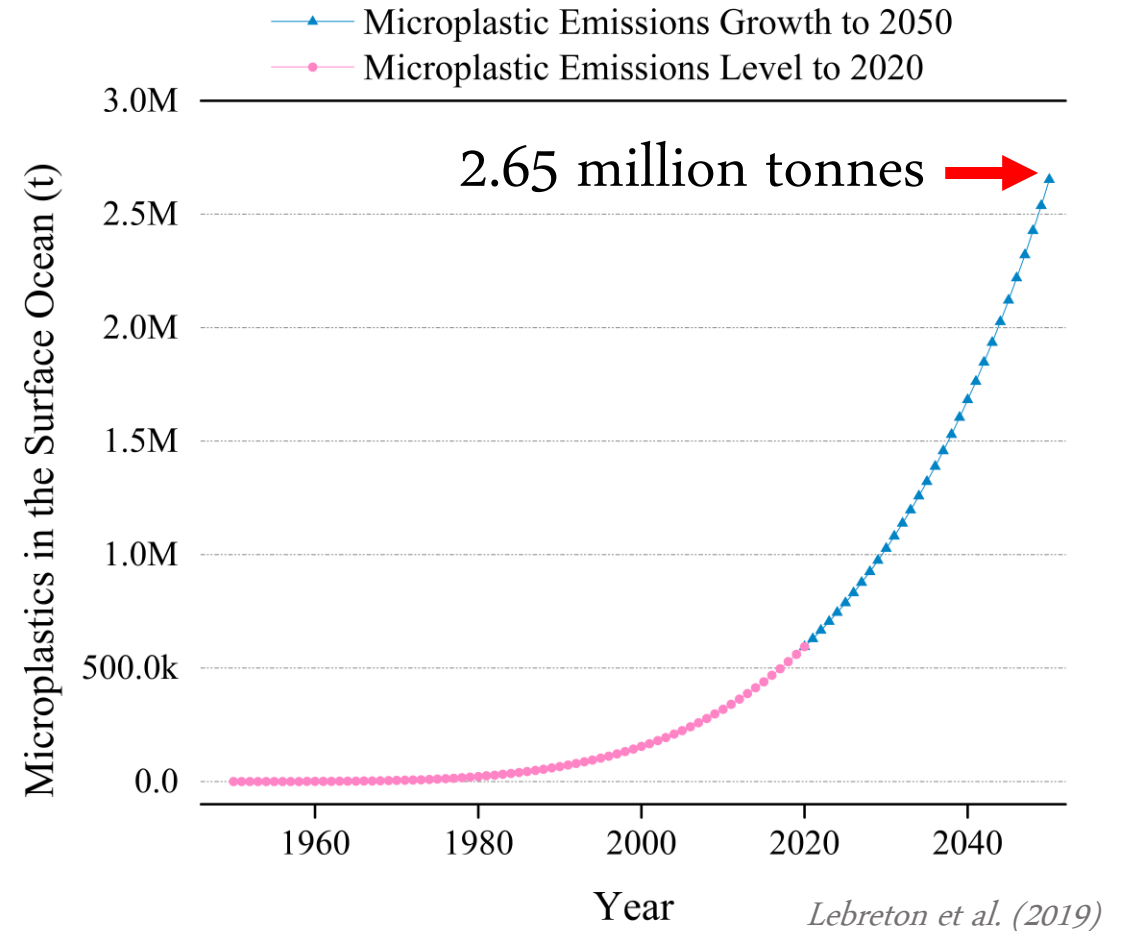
OECD (2022)

Defining Microplastics

- Insoluble synthetic solids
- 92% of plastic debris at sea
- **Polyethylene** and polypropylene are the most dominant



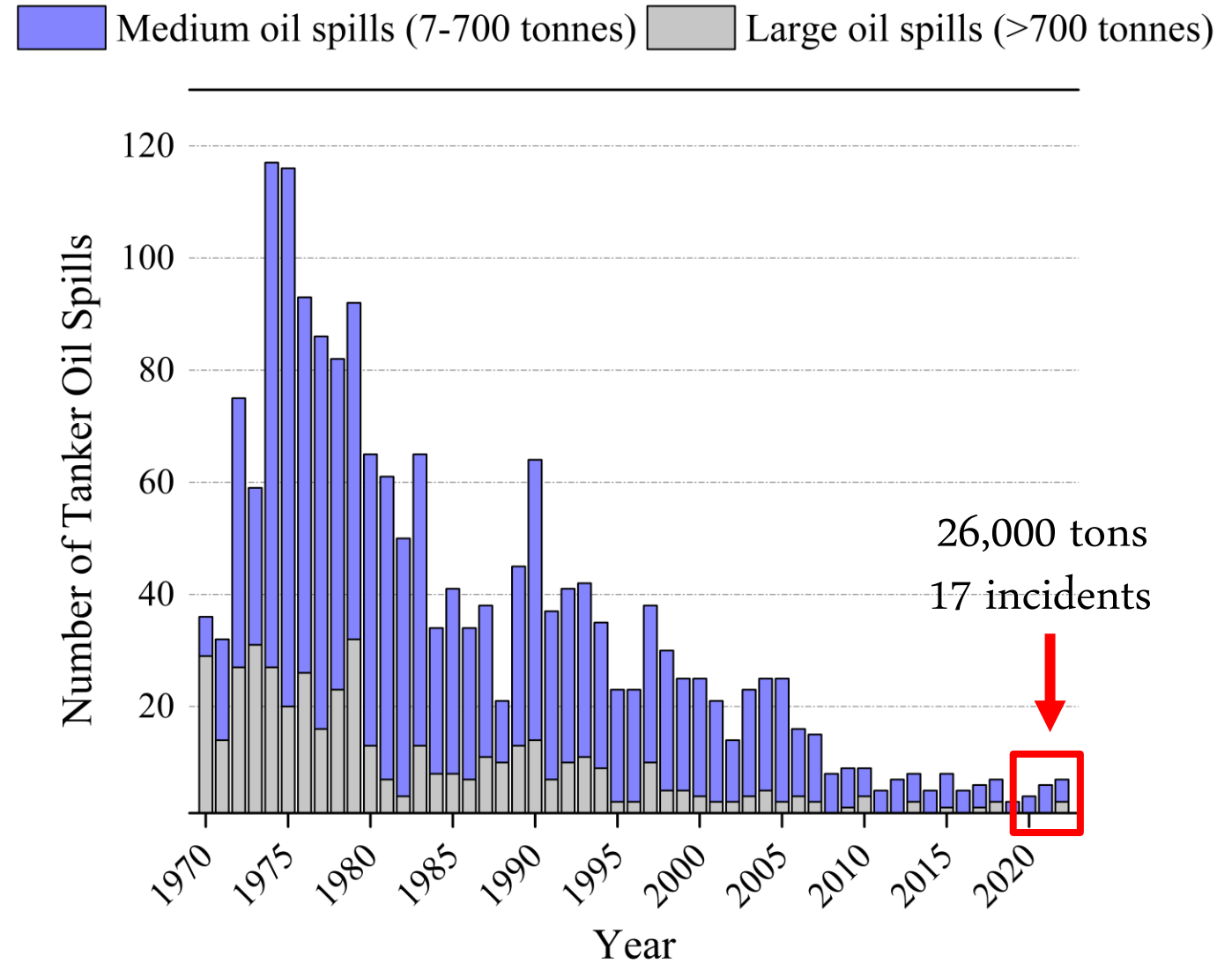
Debroy et al. (2022)



Background Information

Crude oil

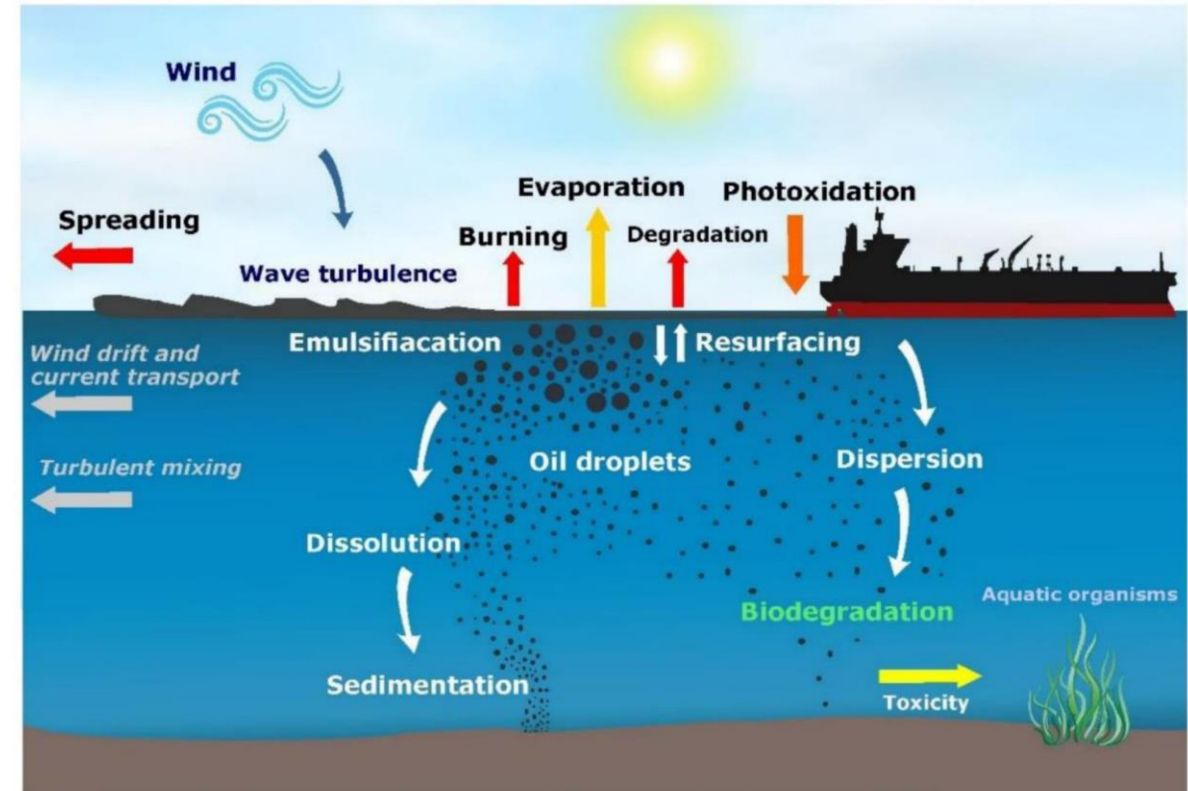
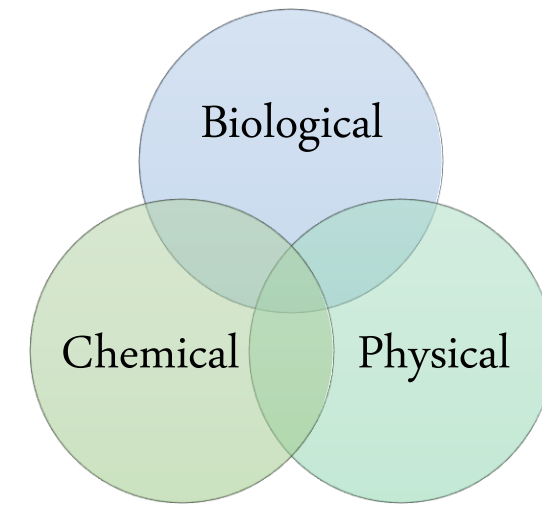
- Primary global energy source
- Potential spills
- Environmental threats & water contamination



International Tanker Owners Pollution Federation (ITOPF)

Background Information

- Spilled oil undergoes a complex series of physical, chemical, and biological changes
 - Non-polar organic contaminants
 - Hydrophobic expulsion from water
 - Adhere to microplastics
- Impact the partitioning of crude oil components
 - Affect the mass balance of these components



Objectives

1

Quantify the uptake of crude oil hydrocarbons by microplastics in water

2

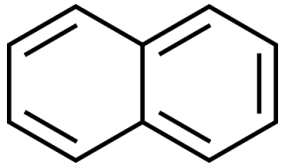
Identify the type of interactions occurring through kinetic and isotherm modeling

3

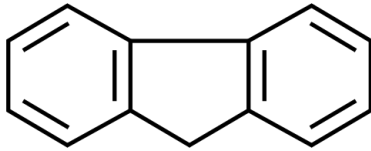
Enhance the understanding of the potential fate of spilled oil in aquatic environments

Target Hydrocarbons: Polycyclic Aromatic Hydrocarbons and Alkanes

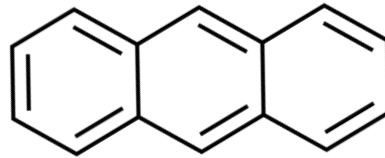
Target PAHs



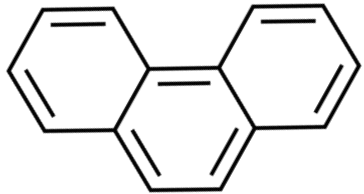
Naphthalene



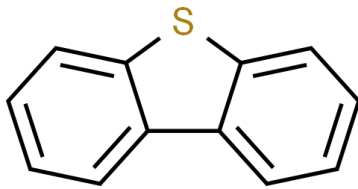
Fluorene



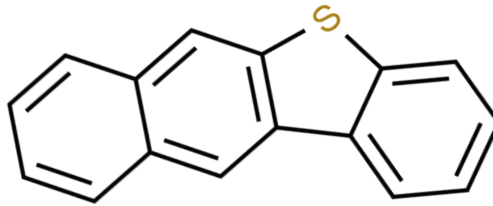
Anthracene



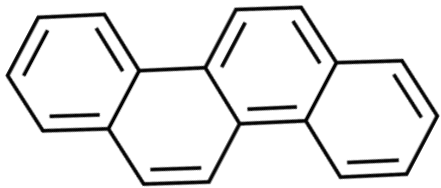
Phenanthrene



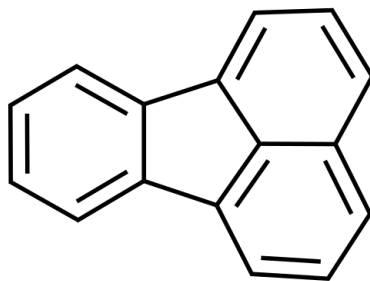
Dibenzothiophene



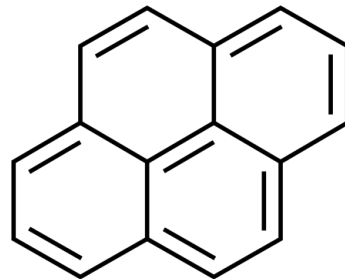
Naphthobenzothiophene



Chrysene

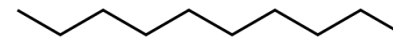


Fluoranthene



Pyrene

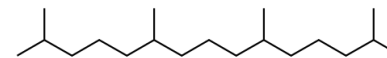
Target Alkanes and Isoalkanes



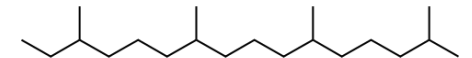
Decane (nC10)



Pentatriacontane (nC35)

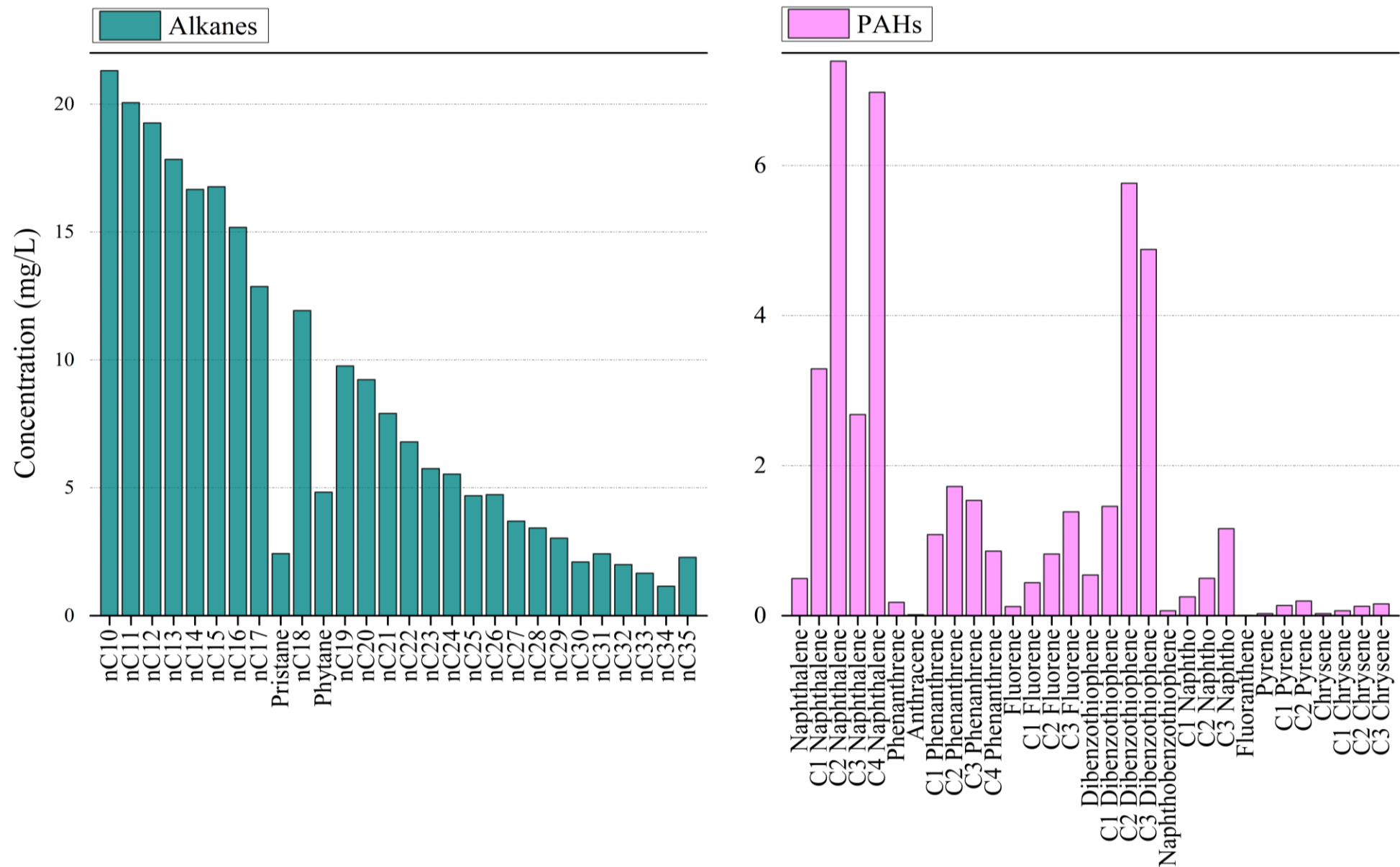


Pristane



Phytane

Target Hydrocarbons: Light Arabian Crude Oil Composition



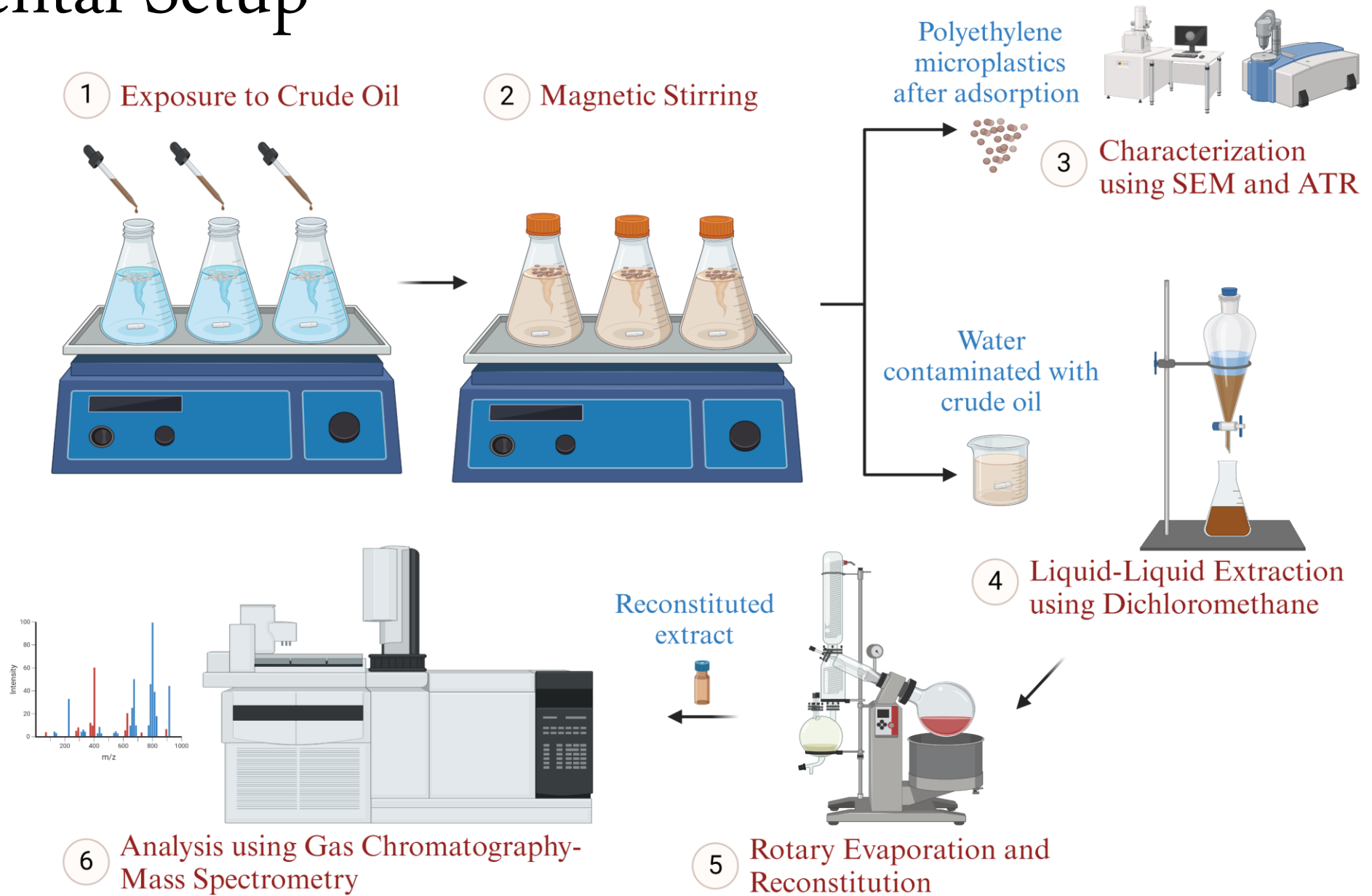
Experimental Workflow

- Preliminary experiments: Setup validation
- Characterization: Analysis of surface morphology and composition
- Behavior on different sizes of microplastics
- Kinetic experiments: Investigation of adsorption rates
- Isotherm Experiments: Assessment of maximum adsorption capacity

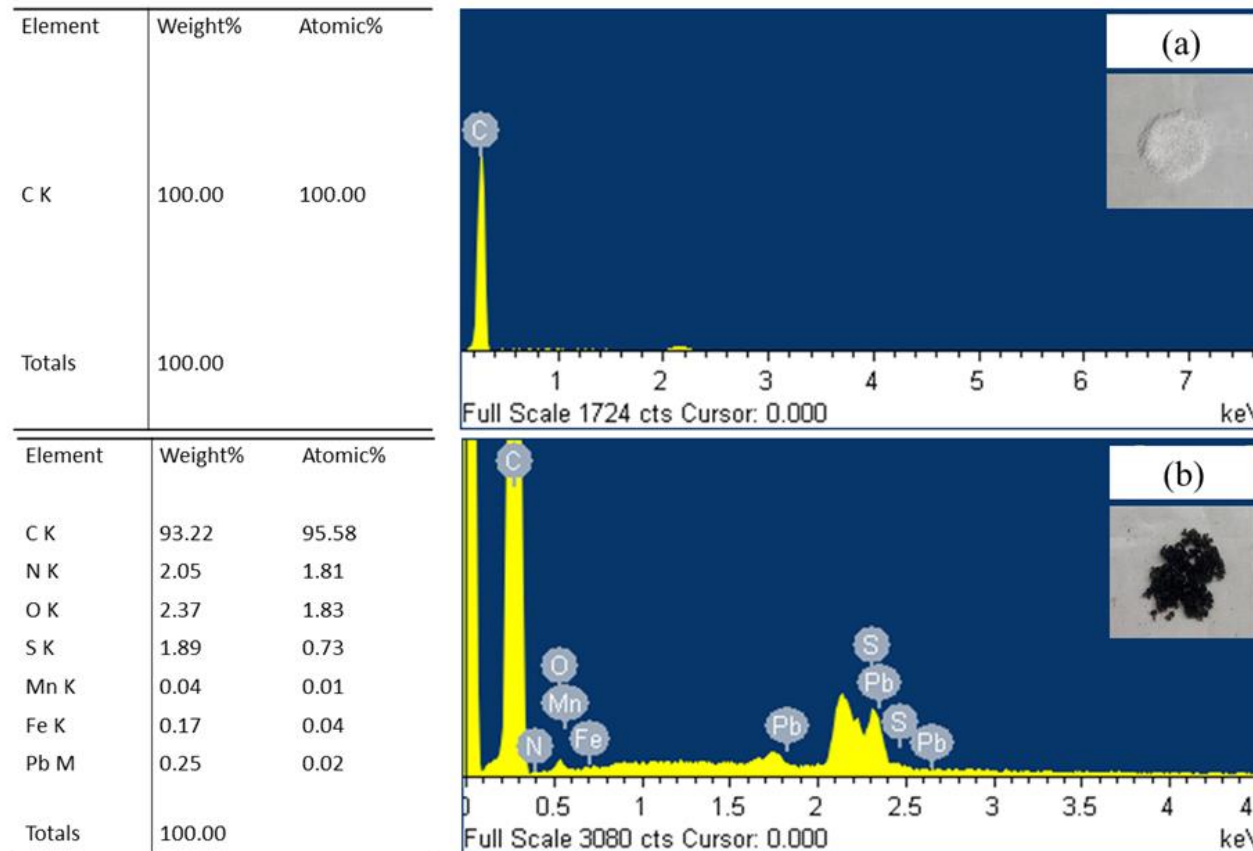
Experimental Conditions

		Preliminary Experiments	Microplastics' Size Experiments	Kinetic Experiments	Isotherm Experiments
Microplastics 		0.2 g.L ⁻¹ and 1g.L ⁻¹	1g.L ⁻¹	1g.L ⁻¹	1g.L ⁻¹
Crude oil 		704 mg.L ⁻¹	704 mg.L ⁻¹	704 mg.L ⁻¹	17.61 - 2641.2 mg.L ⁻¹
Microplastics size range 		300-600 µm	180-300 µm 300-600 µm 600-5000 µm	300-600 µm	300-600 µm
Time 		120 hours	120 hours	0 - 168 hours	168 hours
Temperature 		25 °C	25 °C	25 °C	25 °C
pH 		Neutral	Neutral	Neutral	Neutral

Experimental Setup



Characterization: Scanning Electron Microscopy- Energy Dispersive X-ray Spectroscopy



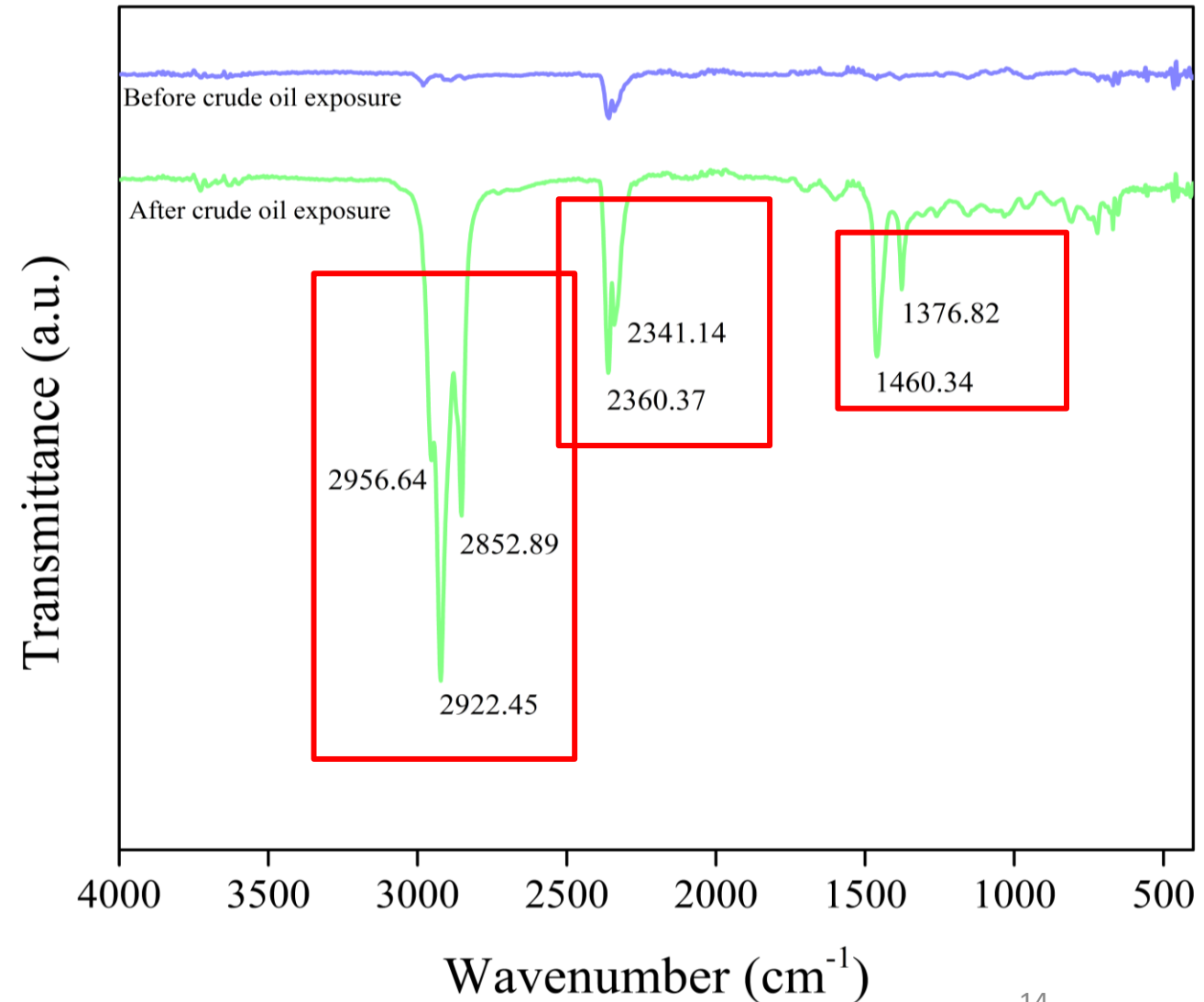
Polyethylene microplastics
before exposure to crude oil

Polyethylene microplastics
after exposure to crude oil

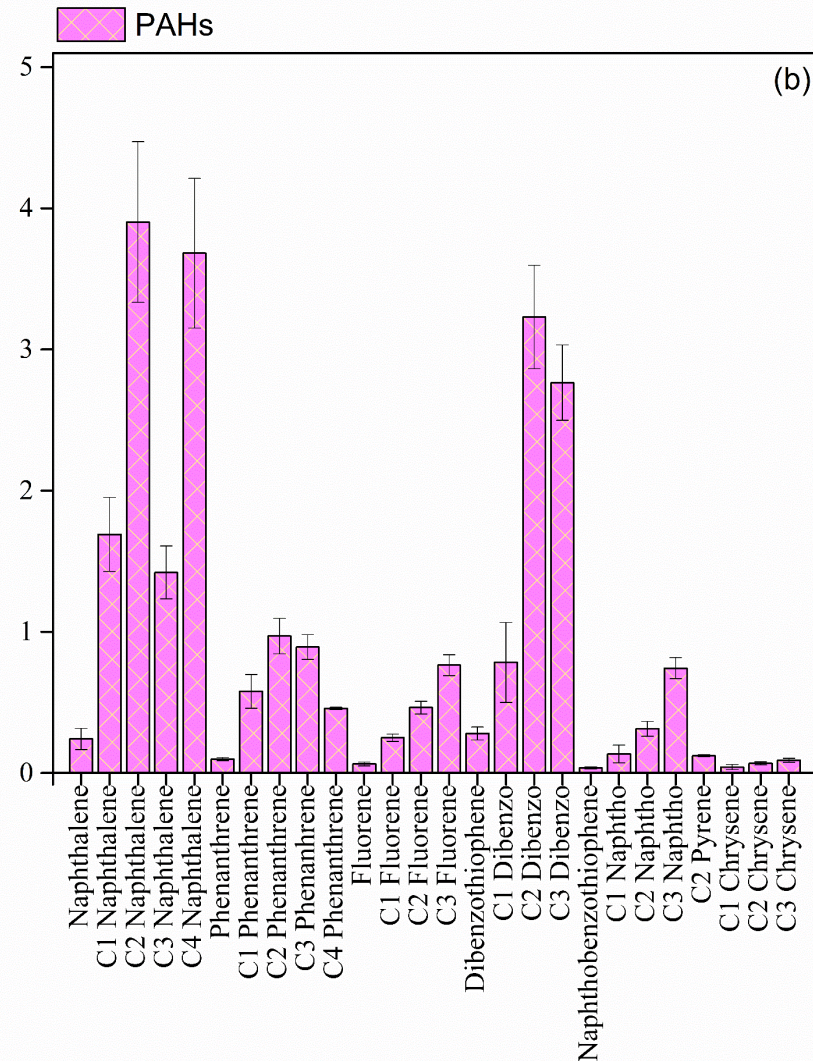
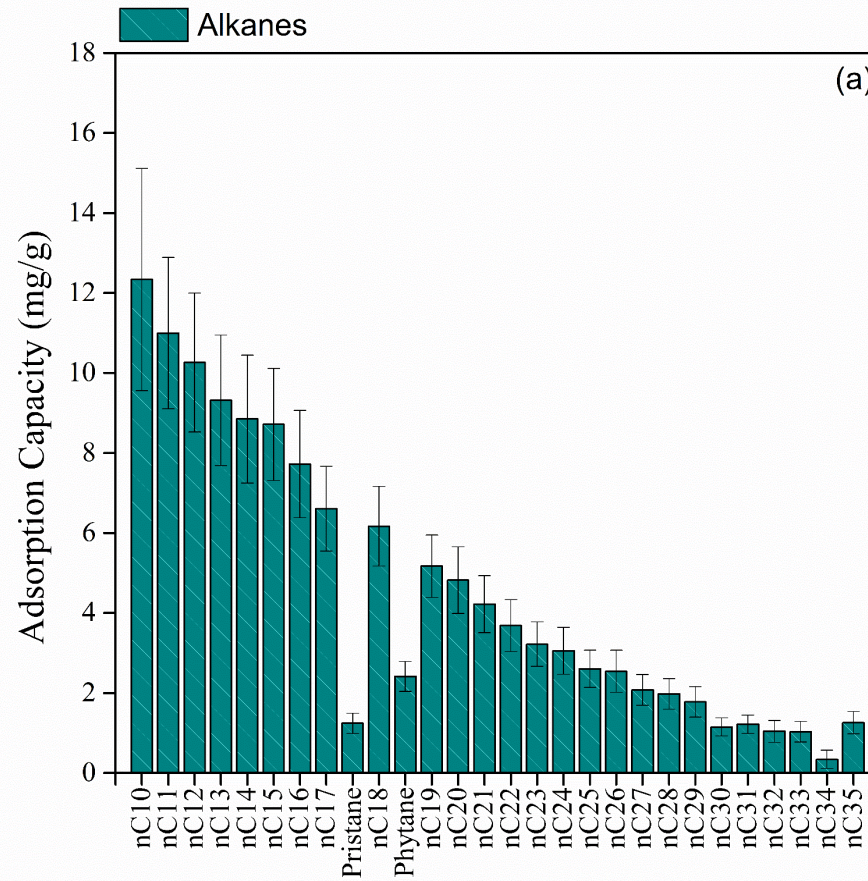
Characterization: Attenuated Total Reflectance

- Spectral profiles of hydrocarbons arise mainly from **stretching** and **bending** vibration modes in **C-H** bonds of

- ✓ Saturated methylene groups (CH_2)
- ✓ Terminal methyl ($-\text{CH}_3$) group
- ✓ Aromatic functional groups

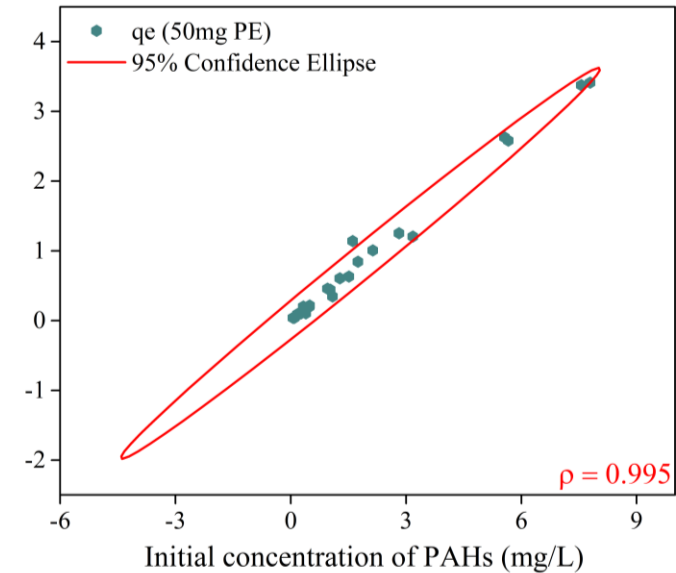
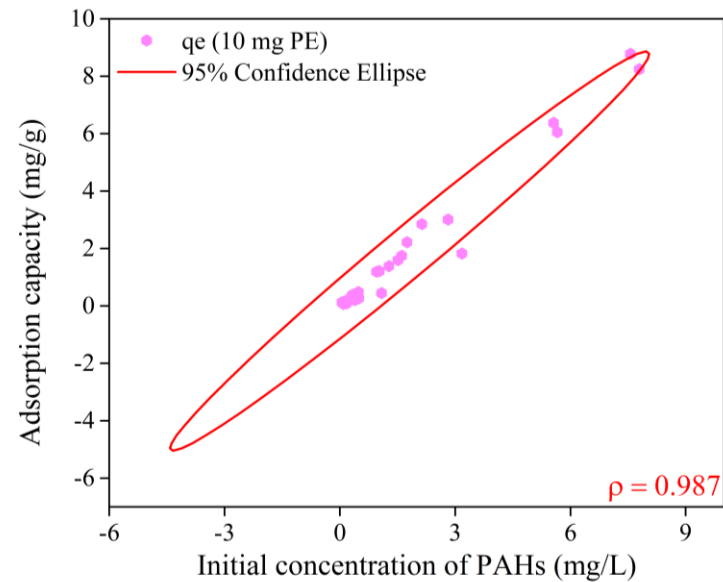
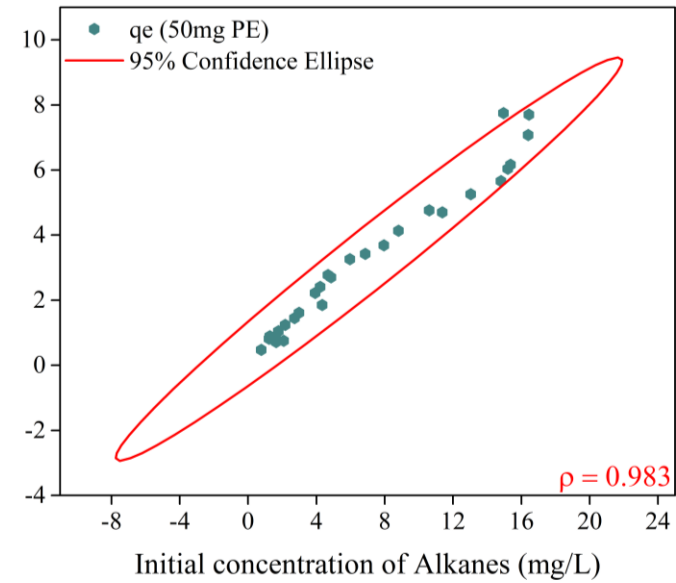
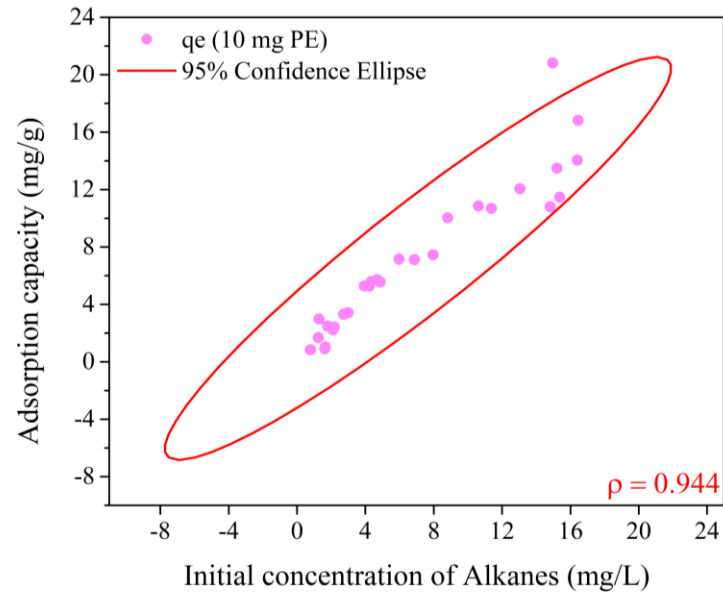


Adsorption Capacity of Individual Hydrocarbons

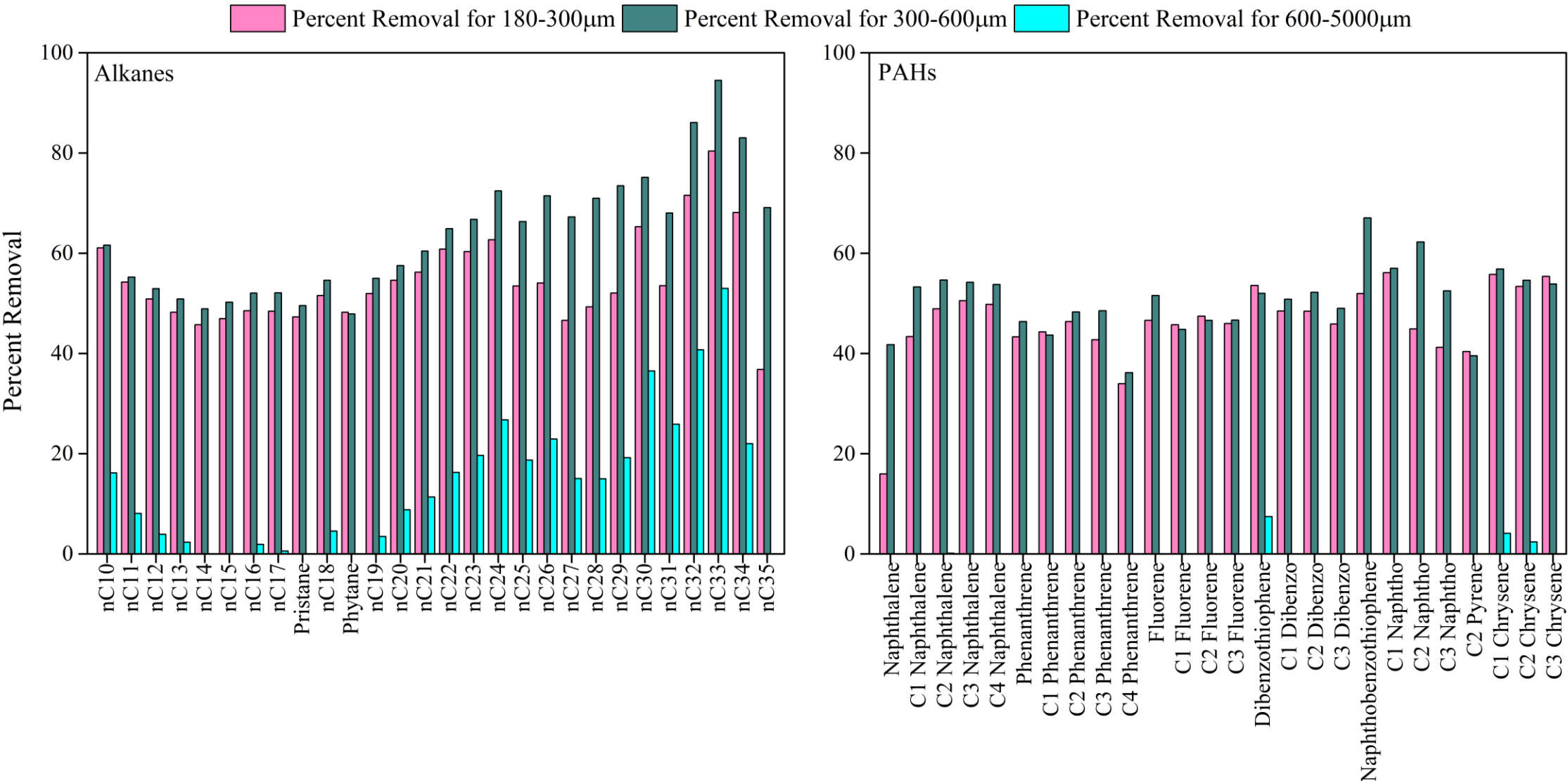


$$\text{Adsorption Capacity } (q_e) = \frac{(C_i - C_e).V}{m}$$

Correlating Initial Concentration of Hydrocarbons to Adsorption Capacity



Effect of Microplastics' Size on Percent Removal



Adsorption of Crude Oil Hydrocarbons on Microplastics: Kinetic Models

Pseudo-first order:

$$q_t = q_e(1 - e^{-K_1 t})$$

Pseudo-second order:

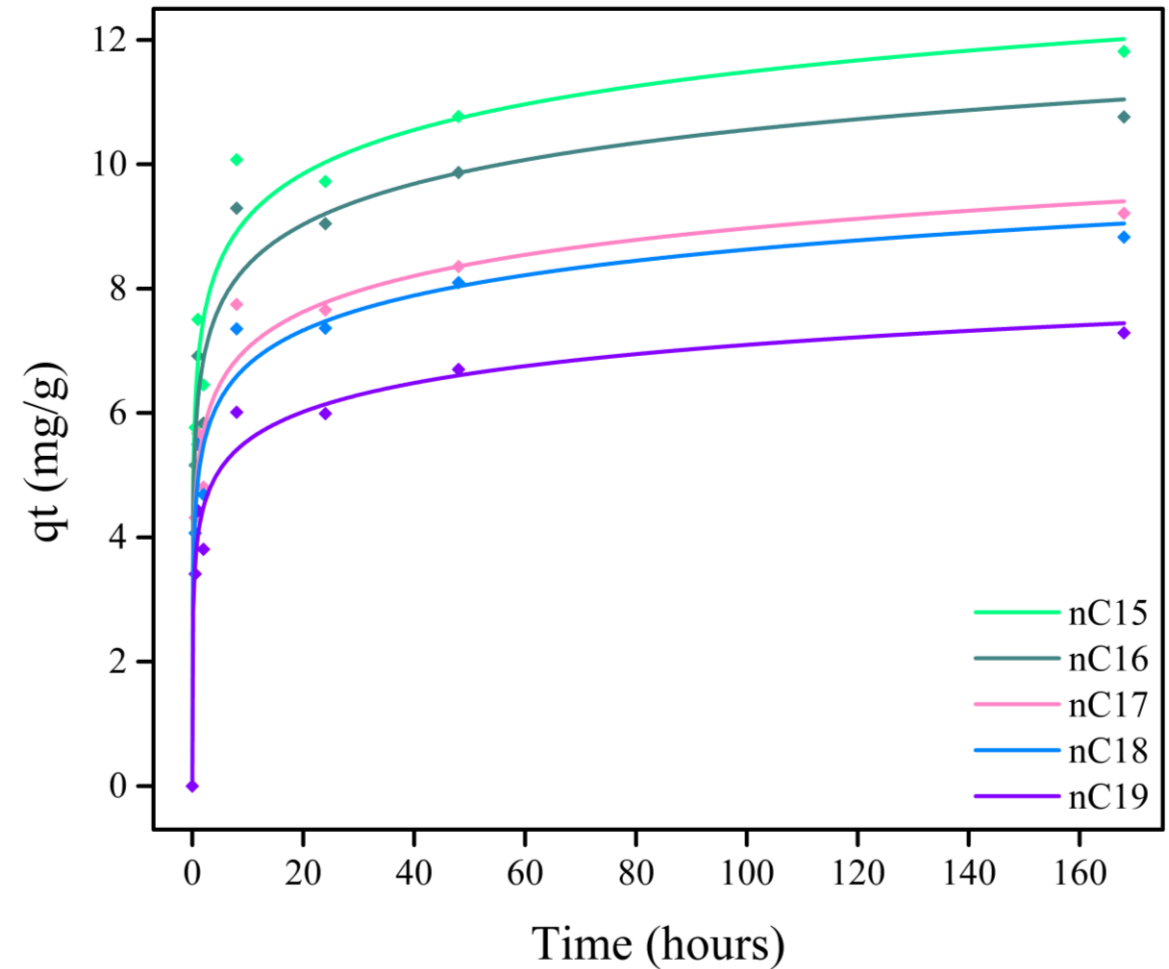
$$q_t = \frac{q_e^2 K_2 t}{1 + K_2 q_e t}$$

Elovich:

$$q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t)$$

Intraparticle diffusion:

$$q_t = K_{diff} t^{\frac{1}{2}} + C$$

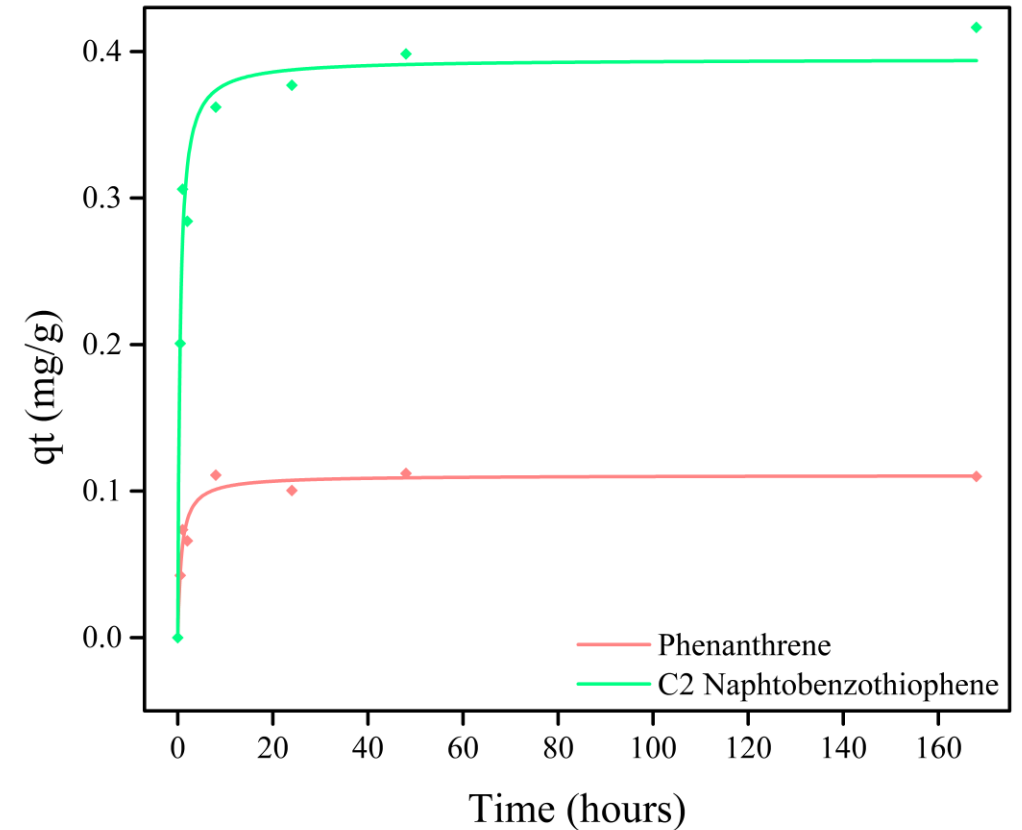


Elovich > PSO > PFO > IPD

Influenced by **chemical** adsorption interactions

Adsorption of Crude Oil Hydrocarbons on Microplastics: Kinetic Models

- All target hydrocarbons adhered to the Elovich model
- Except for
 - Phenanthrene: PSO > PFO
 - C2 Naphtobenzothiophene: PSO > Elovich



Adsorption of Crude Oil Hydrocarbons on Microplastics: Isotherm models

Langmuir

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$$

nC10

nC27-nC29

nC33-nC35

C₀₋₁ Naphthalene

C_{0,1,4} Phenanthrene

C₃ Fluorene

C₀₋₃ Naphtobenzothiophene

C_{1,3} Chrysene

Monolayer adsorption behavior

Freundlich

$$q_e = K_F C_e^n$$

nC11-nC21

C_{2,3,4} Naphthalene

C_{2,3} Phenanthrene

C₀₋₂ Fluorene

C₀₋₃ Dibenzothiophene

C₂ Pyrene

C₂ Chrysene

Multilayer adsorption behavior

Temkin

$$q_e = \frac{RT}{b} \ln(K_T C_e)$$

nC22-nC26

nC30-nC32

Monolayer adsorption behavior

Discussion and Limitations

- ✓ An experimental challenge was to determine the maximum adsorption capacity for the compounds occurring at relatively low concentrations in the crude oil
- ✓ It was hard to attribute the adsorption behavior solely to the size, the weight, and the hydrophobicity of the molecules
- ✓ The varying concentrations of the different crude oil compounds and their competitive interaction within the mixture mostly dictated their adsorption behavior

Conclusions

- ✓ Microplastics affect the post-spill mass balance of crude oil hydrocarbons in water
- ✓ Favorable adsorptions for all the target components
- ✓ $Q_m = 364.7 \text{ mg.g}^{-1} \rightarrow 5.75 \text{ mg of hydrocarbons/m}^2 \text{ of PE surface between 300 and 600 um}$
- ✓ Interactions may influence the spreading rates and natural dispersion processes
- ✓ Predictive models should incorporate the adsorption of hydrocarbon components onto microplastics
- ✓ Contribute to more accurate and comprehensive models of the fate of hydrocarbon contamination arising from oil spills

Thank You

