

Rapid transfer of per- and polyfluoroalkyl substances through submarine canyons: sources, pathways and implications

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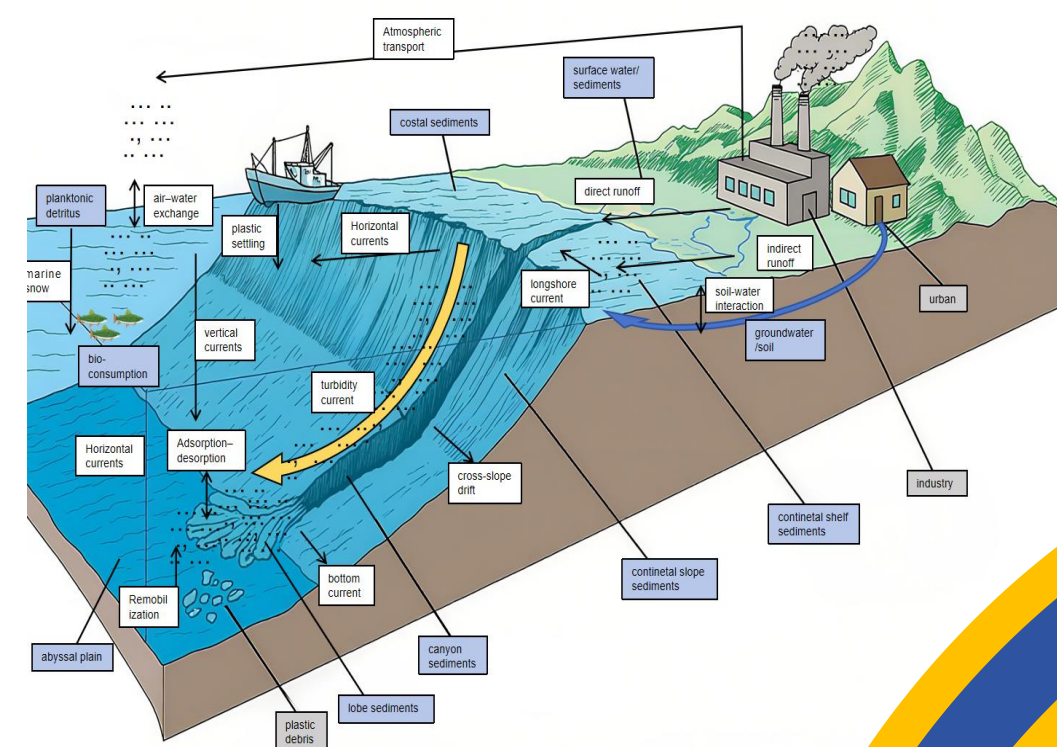
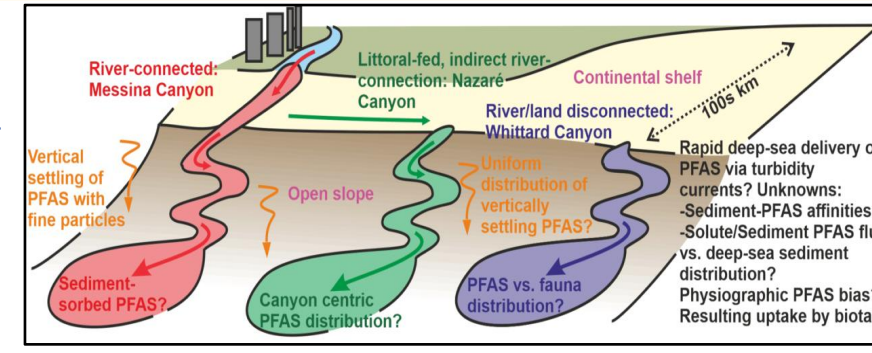
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Research Hypotheses

- PFAS enter the ocean via dissolved and particle-bound transport, controlled by chain length, organic matter, fine particles, minerals, salinity, and hydrodynamics.
- PFAS are preferentially preserved in fine-grained, low-reworking settings such as canyon levees, overbank deposits, lobes, and trench axes.
- In deep-sea sediments, PFAS bind strongly to organic- and metal-rich clays, especially long-chain compounds.
- Higher PFAS levels occur within canyons, particularly on levee crests, and are reflected in benthic organisms across habitats.

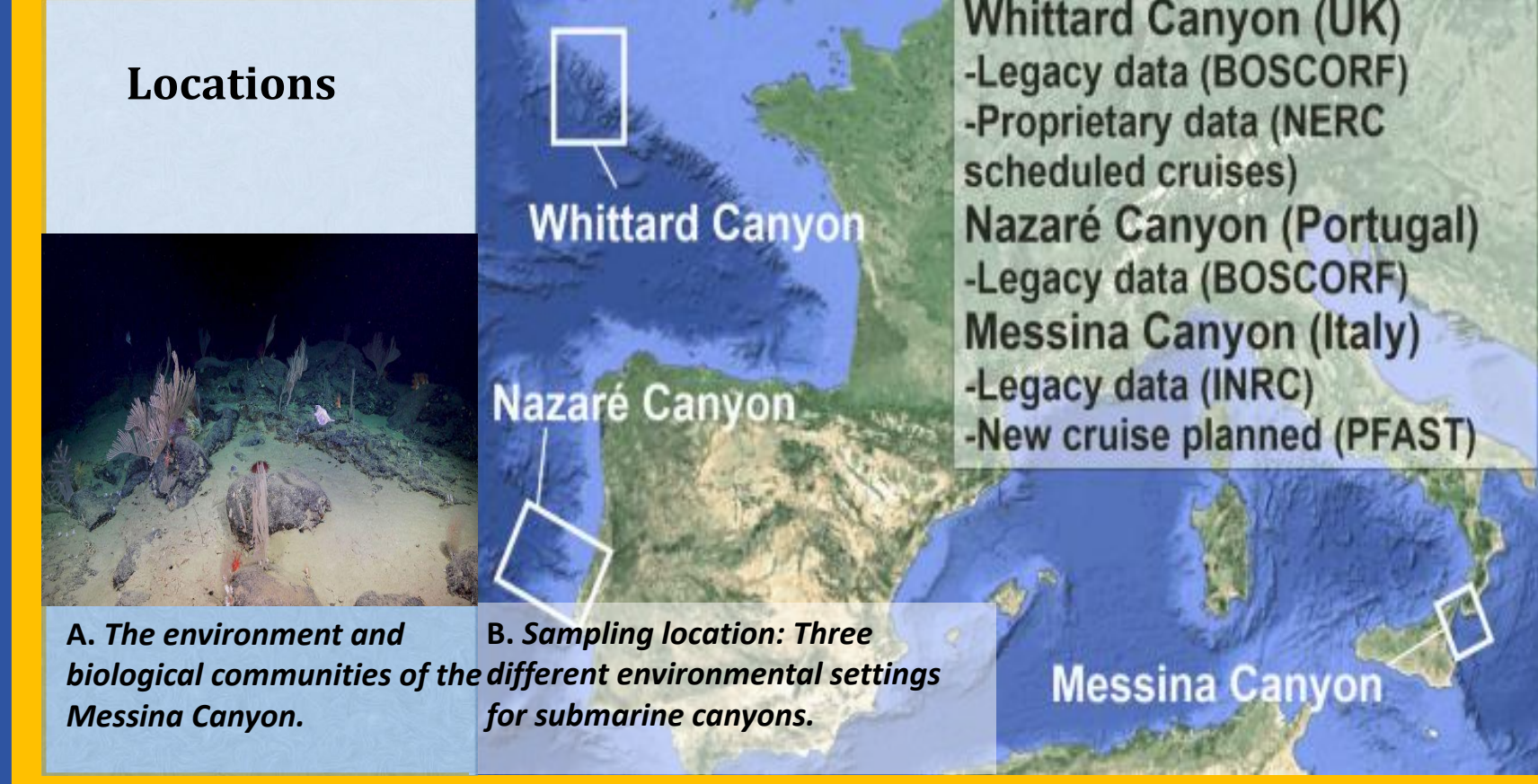
Three canyons with different sediment-supply modes.



Predicted pathway model for PFAS transport to the deep sea.

Process / flow type	Bed type	Bed type description	Interpretation	PFAS
Background	Heterogeneous setting	Grain size: clay, silt, sand. Sedimentary structures: structureless or laminated.	Suspension settling from water column.	Suspended particles settle slowly, are widely dispersed, and are easily disturbed and resuspended, and therefore do not represent the most efficient transport pathway.
Low-density turbidity current	Low-density turbidite	Grain size: silt to lower medium sand. Sedimentary structures: plane parallel and ripple-cross lamination throughout, normally graded.	Formed by low-density turbidity currents; often triggered by river input, storms, or slides (Lowe, 1982; Ince, 1994).	Long chain PFAS are more likely to accumulate at the top of the bed or within fine-grained laminae, whereas short chain PFAS are more likely to continue migrating with pore water.
High-density turbidity current	High-density turbidite	Grain size: medium to very coarse and granular. Sedimentary structures: dominantly structureless.	Deposited from high-density turbidity currents, typically triggered by floods, earthquakes, delta collapse, or sudden sediment failure.	PFAS are concentrated at bed top and within mud-rich internal layers; this is typically observed in distal settings, where they are less susceptible to erosion.
Hybrid flow	Hybrid bed	Grain size: fine to medium sand. Sedimentary structures: banding, desegregating structures.	Deposition from flows with characteristics of both low- and high-density turbidity currents and debris flows (Houghton et al., 2003; Talling, 2004; Houghton et al., 2005).	PFAS are concentrated at bed top and within mud-rich internal layers; this is typically observed in distal settings, where they are less susceptible to erosion.
Debris flow	Debrisite	May include grains of all sizes. Sedimentary structures: chaotic, plastic deformation - fold and shear structures.	Deposition from debris flows where matrix strength is the main particle support (Lowe, 1982; Sohn, 1997).	Particles show little density stratification, and PFAS are randomly distributed within the muddy matrix, tending to accumulate in topographic lows.
Slump	Slump deposit	Structures: include evidence of plastic deformation, including folding and overturned beds.	Gravitational instability of unconsolidated sediments which move downslope for a limited distance and begin to disintegrate but retain original structures.	Slumping itself does not redistribute PFAS according to their chemical properties, although short-chain PFAS may be lost through pore-water exchange.
Slide	Slide deposit	Structures: include coherent bedding with thrust planes, sheared bedding (contracts, extensional and compressional features).	Gravitational instability of sediments which move downslope as a coherent mass and may retain internal structures.	Similar to slumps, their PFAS characteristics are mainly determined by the original sediment layers.

Locations



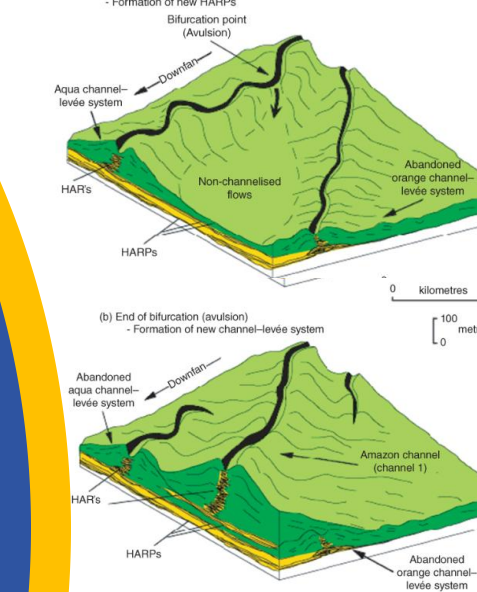
A. The environment and biological communities of the different environmental settings of submarine canyons.

B. Sampling location: Three sites located at the head, axis, and outer levee of Nazaré Canyon.

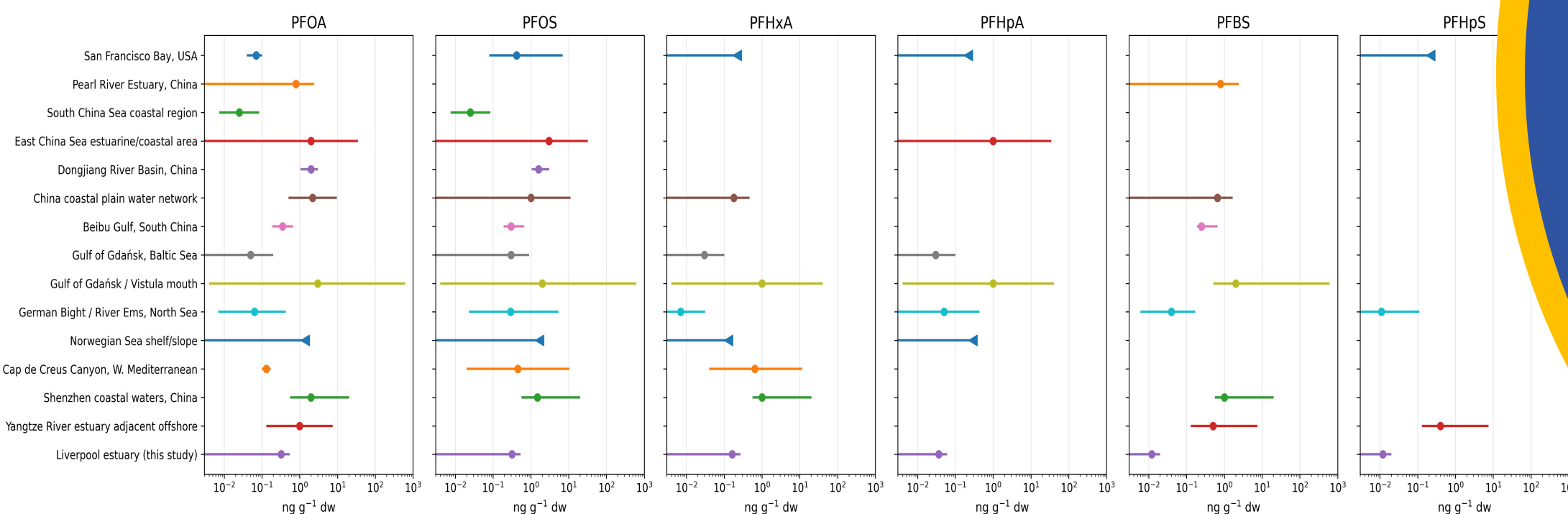
Deep-sea sedimentation mechanisms

Why the canyons?

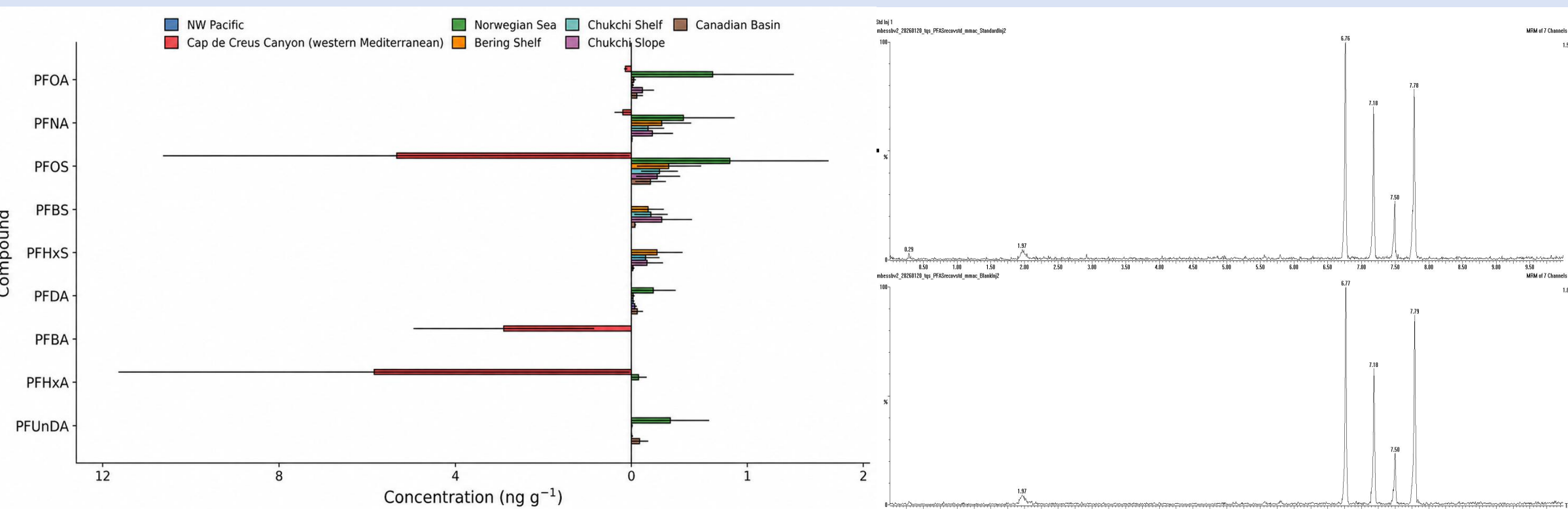
- Submarine canyons rapidly transport sediments, organic carbon, and PFAS to the deep sea.
- Potential role as long-term PFAS sinks remains unclear.
- PFAS accumulation may threaten biodiversity, seafood safety, and the blue economy.
- This study integrates sediment, water, organism, sedimentological, and mineralogical analyses to assess PFAS distribution and exposure.



Liverpool estuary samples



- Comparison of PFAS detected in Liverpool Bay sediments with globally reported levels. This experiment was mainly used to validate the LC-MS/MS method and provide a comparison with future deep-sea sediment samples. Freeze-dried sediments were extracted with acetonitrile/methanol, cleaned using ENVI-Carb, concentrated under N₂ at 40 °C, reconstituted in 100 µL acetonitrile, and analysed for PFAS by LC-MS/MS.
- Only six PFAS were detected in the sediment samples, all at low to moderate concentrations and dominated by short- to medium-chain compounds; long-chain PFAS and precursors were below the limit of quantification, possibly reflecting reduced local inputs following restrictions on legacy long-chain PFAS in the UK, although legacy compounds may persist and be preferentially transported offshore or retained in deeper depositional environments rather than degraded.



A. Globally reported PFAS levels in deep-sea sediments. Concentrations in submarine canyons are much higher than in other sedimentary environments.

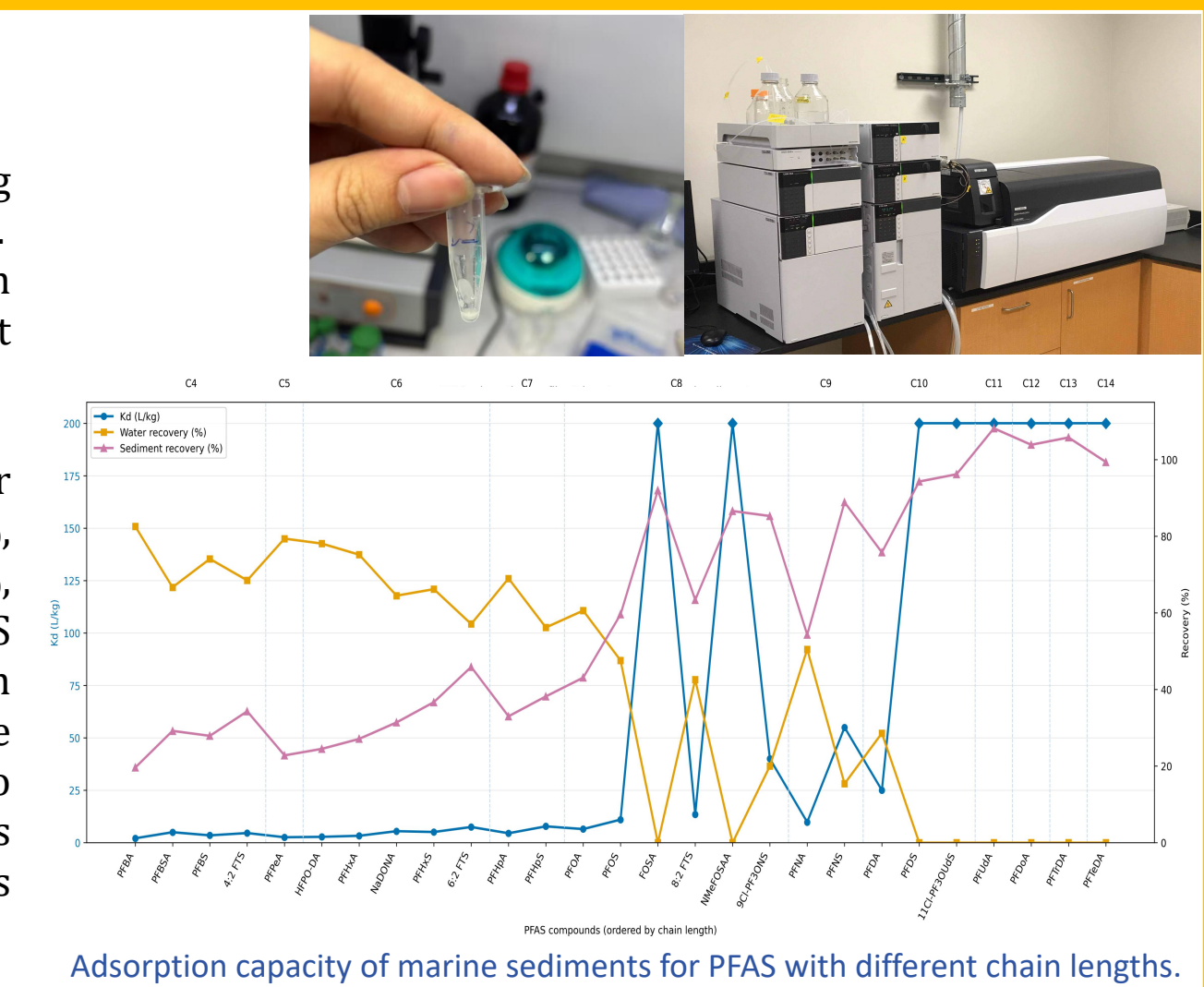
B. PFAS target compounds detected by high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS).



PFAS adsorption by sediments

Method A 1-day batch adsorption test used 1.0 g sediment with 10 mL of 20.0 ng/mL 27-PFAS standard. Water and sediment fractions were extracted with MeOH/ACN and analysed by LC-MS/MS; sediment recovery was based on a 200.0 ng/g spike.

Results & Discussion PFAS partitioning in sediments showed clear structure dependence: short-chain PFCAs had low recoveries (PFBA 19.6%, PFHxA 27.1%), increasing with chain length (PFOA 43.1%, PFNA 54.3%, PFDA 75.8%). PFSAs and FTSs showed stronger sediment affinity, e.g. PFOS 59.6% > PFOA 43.1% and 8:2 FTS 63.4% > 4:2 FTS 34.3%. This agrees with PFAS sorption theory, where longer chains and sulfonate groups enhance solid-phase partitioning. Water and sediment recoveries need not sum to 100% due to extraction losses or sediment background PFAS. These results suggest that the lack of long-chain PFAS in Liverpool sediments reflects limited source input rather than weak sediment sorption capacity.



Adsorption capacity of marine sediments for PFAS with different chain lengths.

Future direction

- Analyse PFAS levels in Nazaré Canyon by LC-MS/MS and compare spatial differences.
- Analyse PFAS levels in Messina and Whittard canyons and compare them with Nazaré Canyon.
- Conduct further adsorption experiments to assess how deep-sea sediment composition affects PFAS sorption.
- Identify a bivalve species as a biological indicator of seabed PFAS.