Quantifying the residence time and accumulation of PAHs in coastal Louisiana using natural radioisotope tracers

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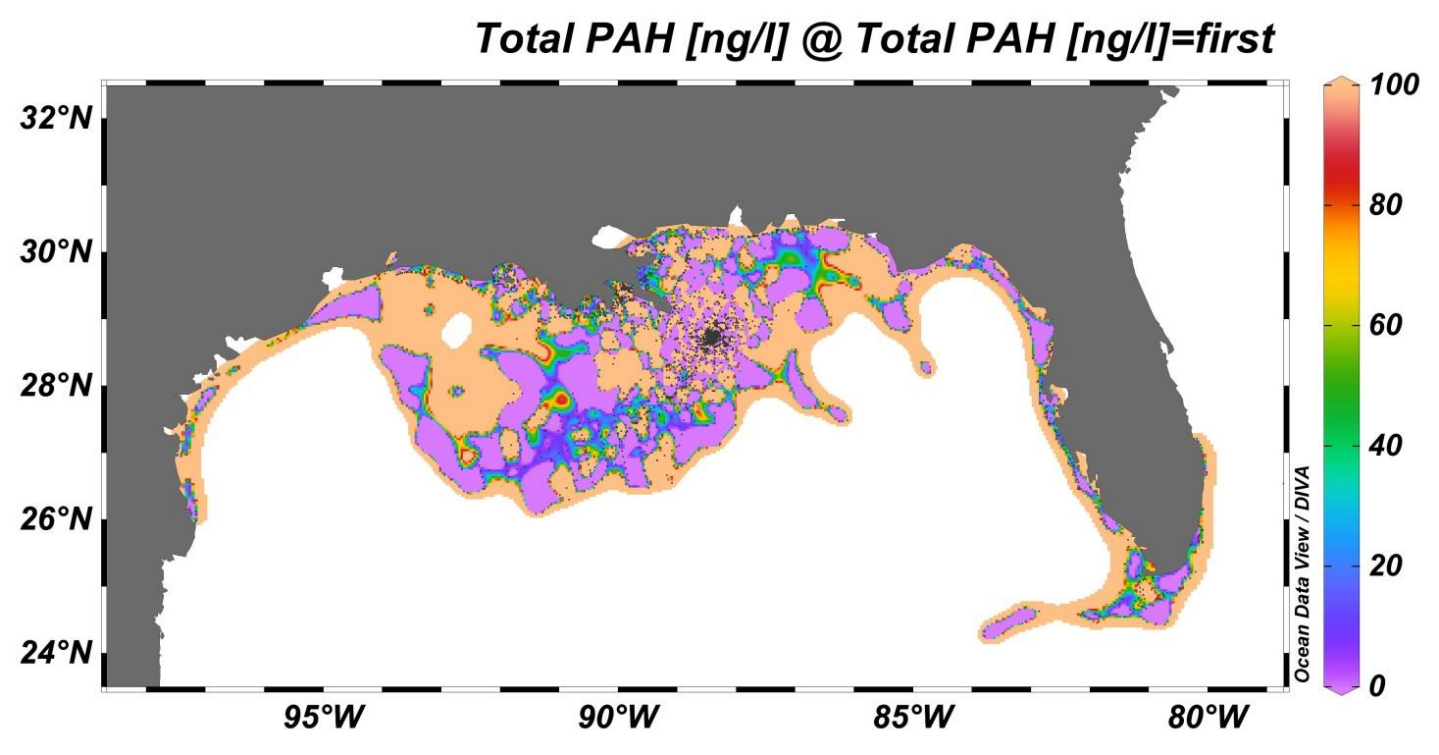
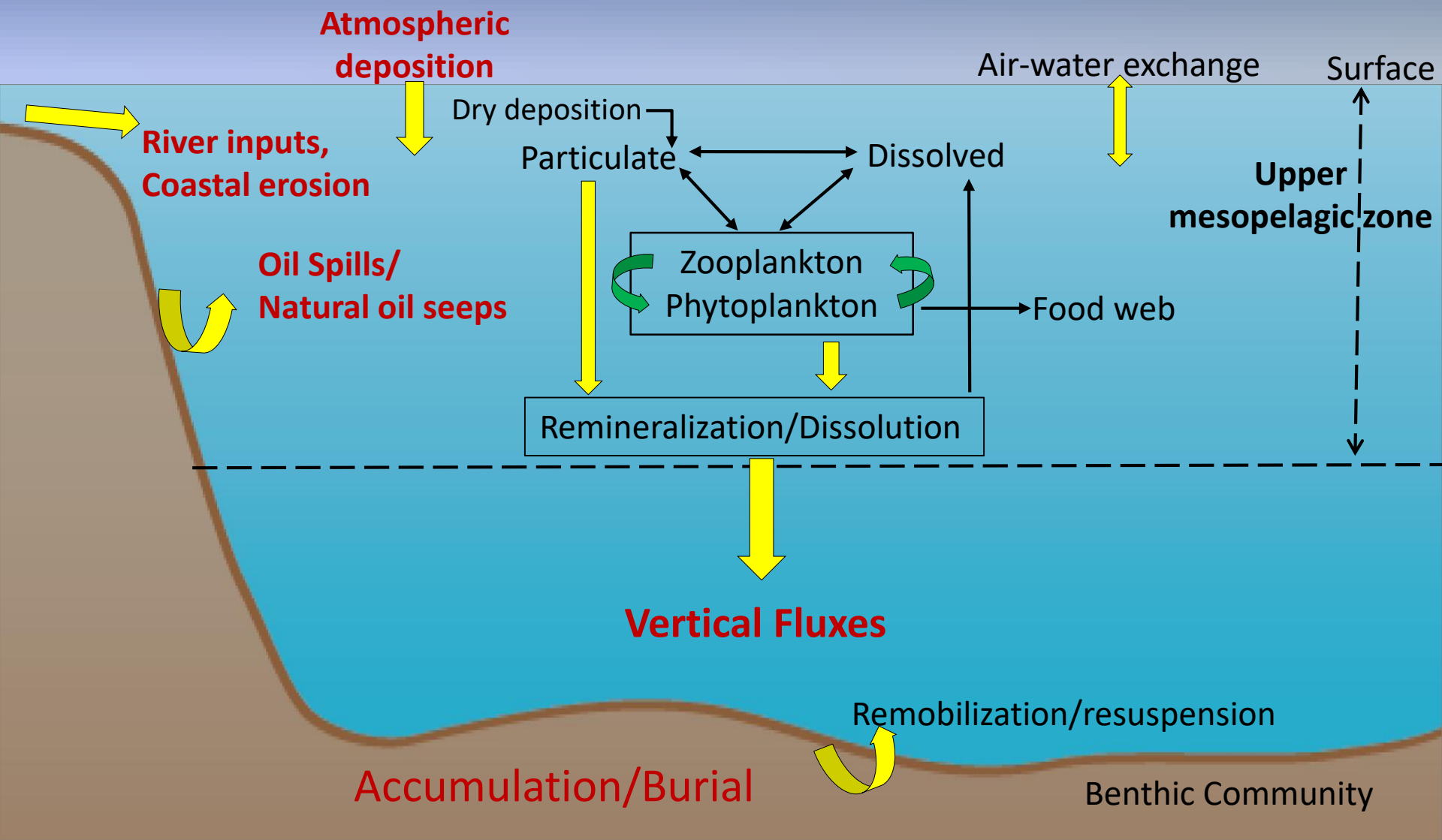
Bureau of Ocean Energy Management

Total PAH distribution in NGOM



To understand this distribution we need to understand the processes

Biogeochemical Cycling of PAHs in Marine Systems

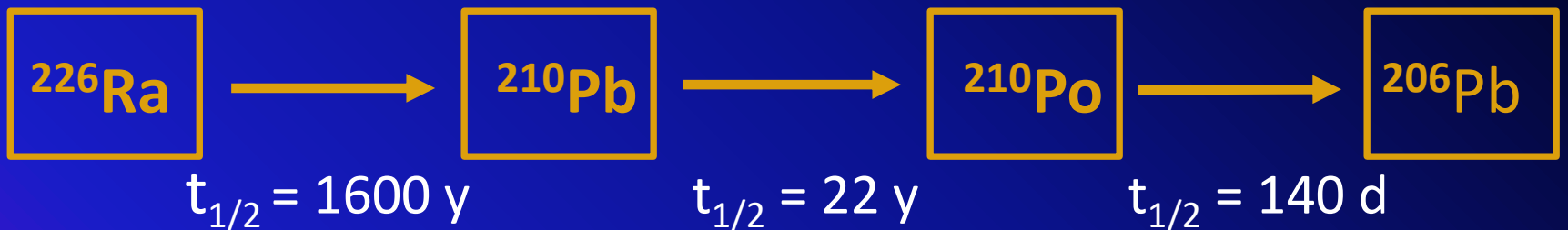


Sources of PAHs in the northern Gulf of Mexico

- Mississippi River, coastal erosion, atmospheric deposition, oil seeps, gas hydrates and oil spills.

- Estimated 21,000 tons of PAHs was released during DWH
- 4-31% deposited on the seafloor within 50 km of wellhead.
- Ideal location to study long term fate and transport of PAHs with or without an oil spill.

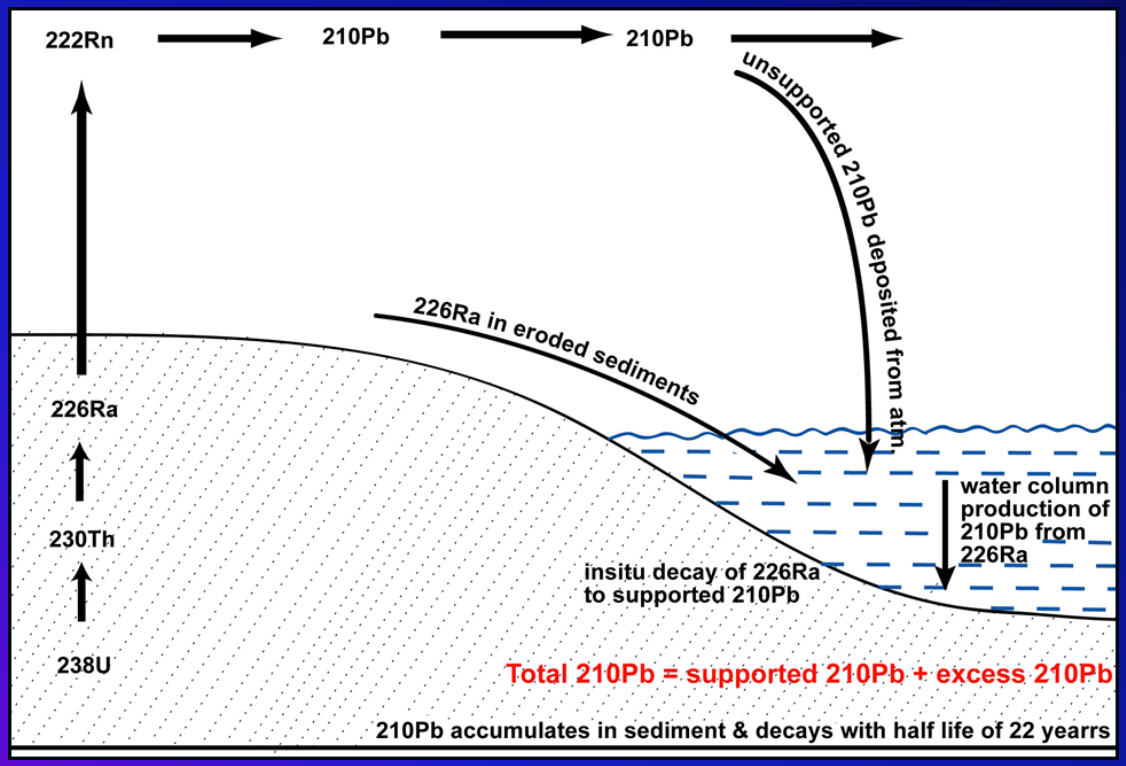
Radiotracers for Sedimentation rates and particle dynamics



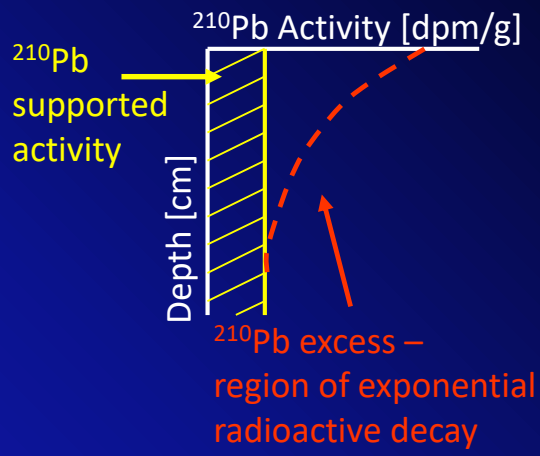
- ^{226}Ra is conservative and remains in dissolved phase.

- ^{210}Pb and ^{210}Po are both are highly particle reactive
  - ^{210}Pb analogous to lithogenic element
  - ^{210}Po bio-accumulative; more like biogenic element

Sediment Accumulation Rates



^{210}Pb profile



$$A = A_0 \exp\left[\frac{(S - \sqrt{S^2 + 4D_b\lambda})}{2D_b} z\right]$$

Assuming negligible mixing

$$A = A_0 \exp\left[-\frac{\lambda}{S} z\right]$$

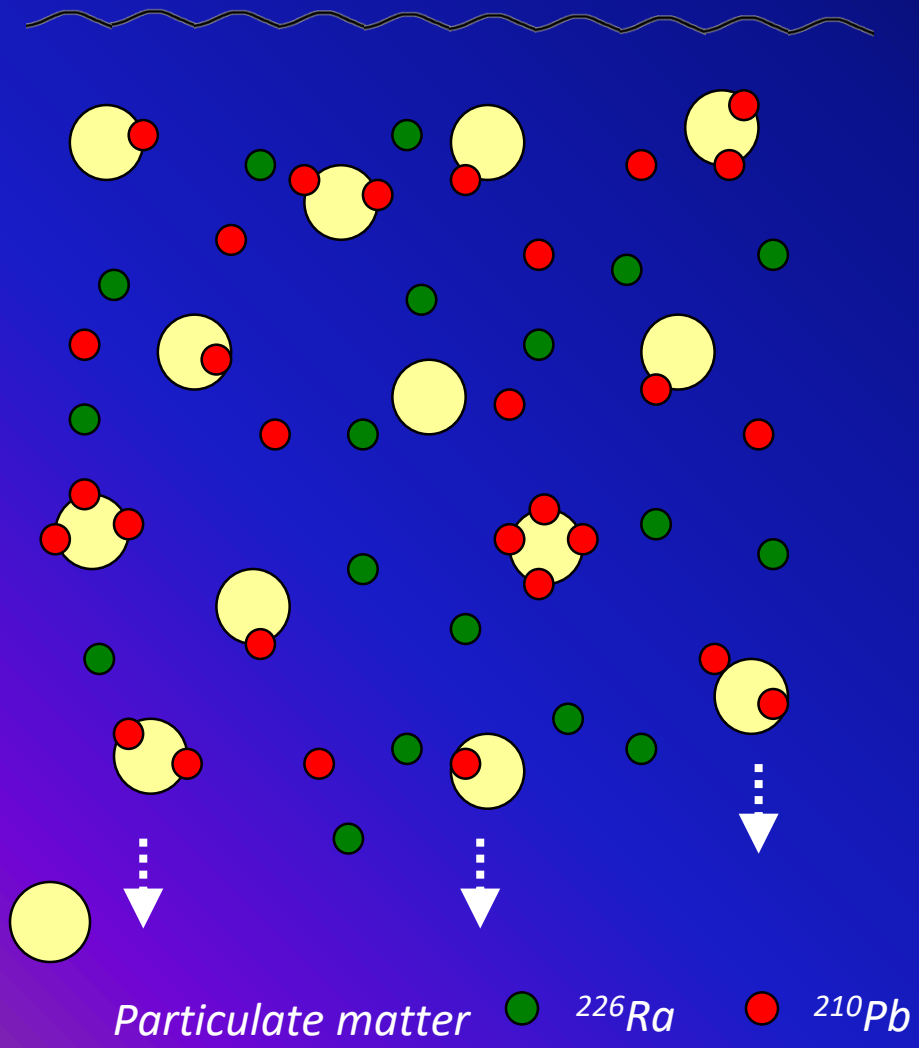
^{210}Pb-based PAHs Accumulation Rates

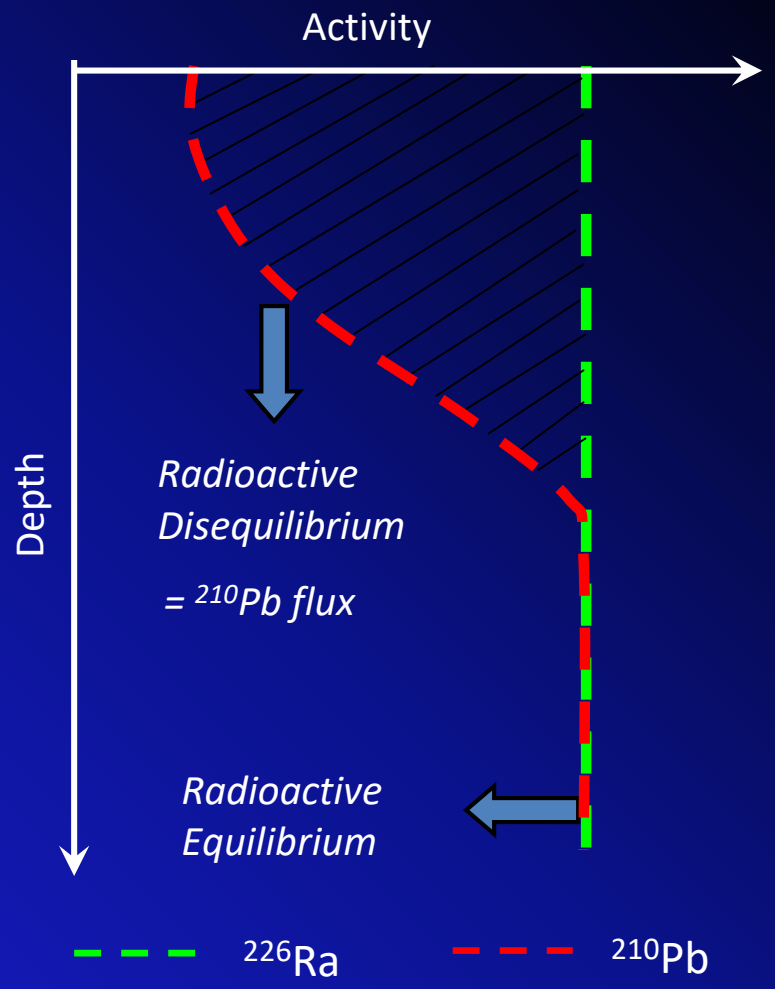
PAHs accumulation rates (ng cm^{-2} y^{-1}) = $C_i \times S_i$

C_i = concentration of $\sum PAH_{43}$ in each section of sediment core (ng/g).

S_i = ^{210}Pb-based sediment accumulation rate (g cm^{-2} y^{-1}).

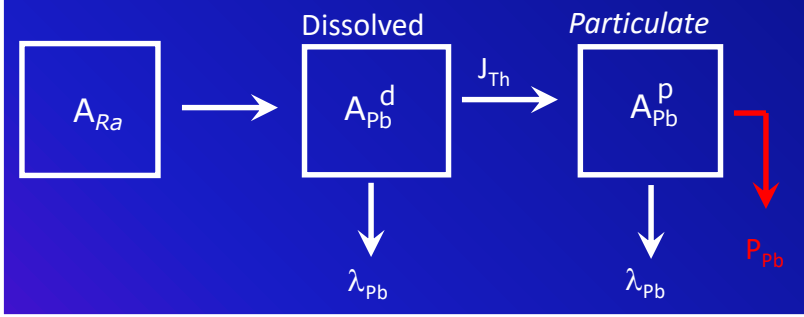
Water column processes





Scavenging Residence Time Calculation

Simple box-model for ^{210}Pb particle scavenging



Assumptions:

^{210}Pb scavenging is irreversible.

^{210}Pb is removed first by suspended particles and then via sinking particles.

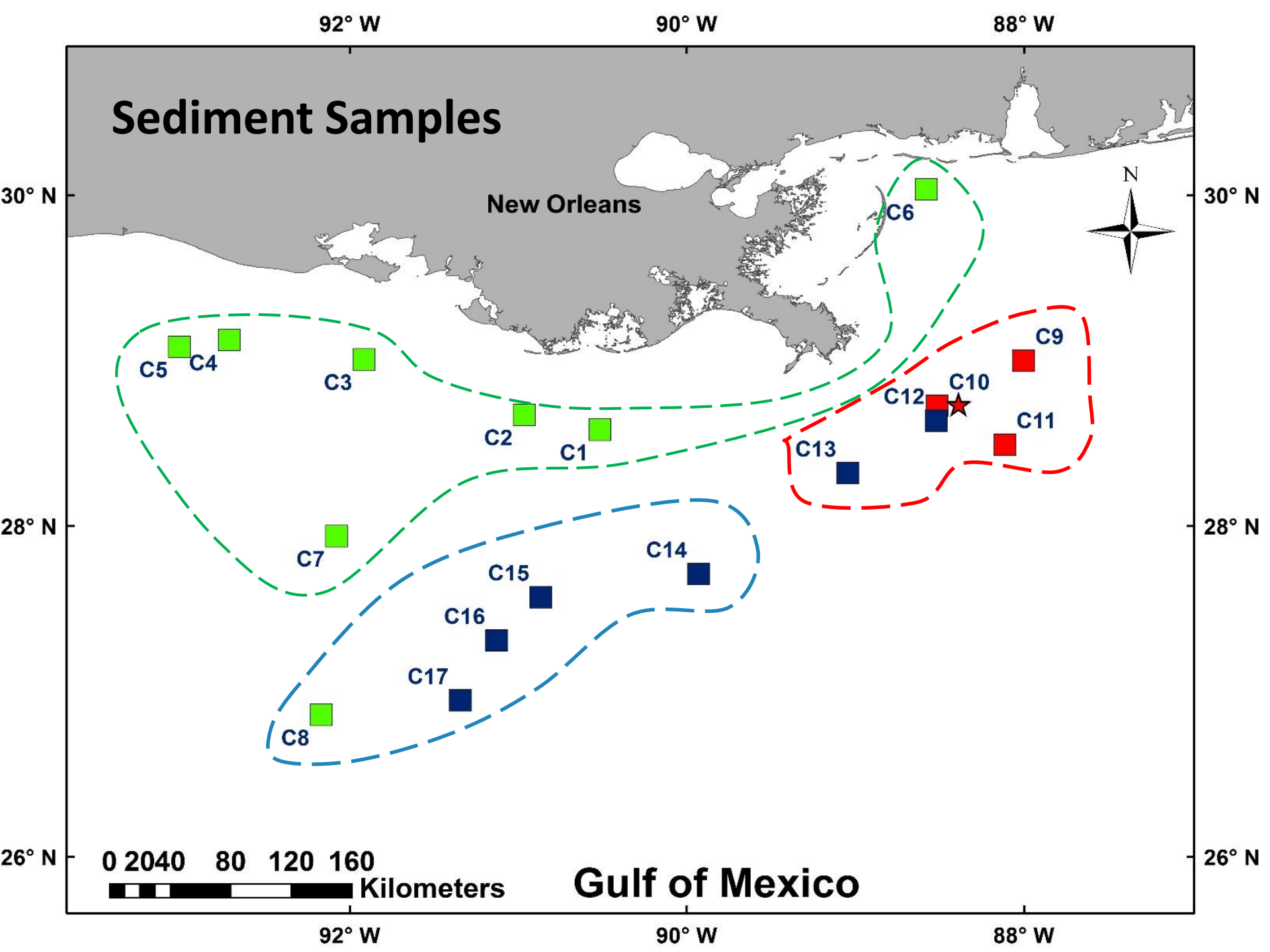
The assumption of steady state may not hold true in all cases

$$\partial A_{Pb}^{d}/\partial t = \lambda A_{Ra} - \lambda A_{Pb}^{d} - J_{Pb}$$

$$\partial A_{Pb}^{p}/\partial t = J_{Pb} - \lambda A_{Pb}^{d} - P_{Pb}$$

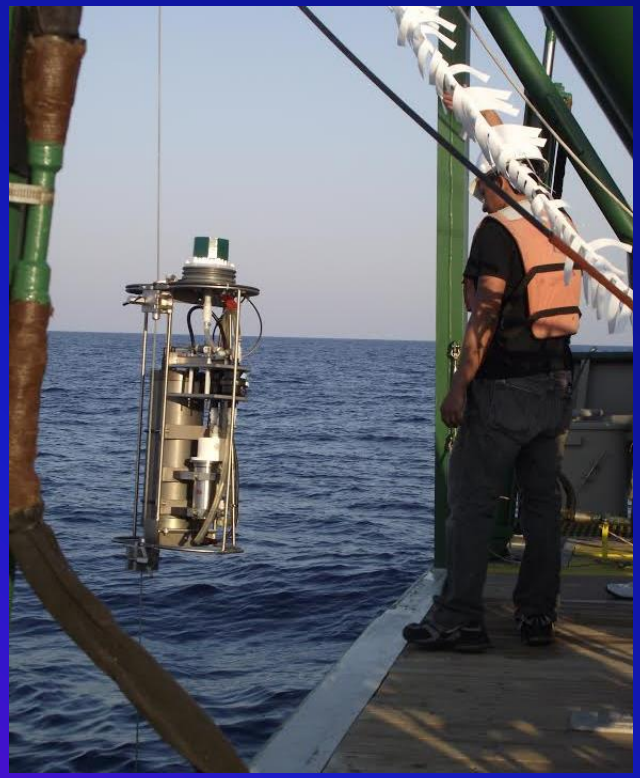
Residence Time :-

$$\tau = A_{Pb}^{p}/P_{Pb}$$


Sediment Samples
92° W
90° W
88° W
30° N
28° N
26° N
New Orleans
N
C1
C2
C3
C4
C5
C6
C7
C8
C9
C10
C11
C12
C13
C14
C15
C16
C17
0 2040 80 120 160
Kilometers
Gulf of Mexico

Suspended Particulate Sample Collection (100-350m)

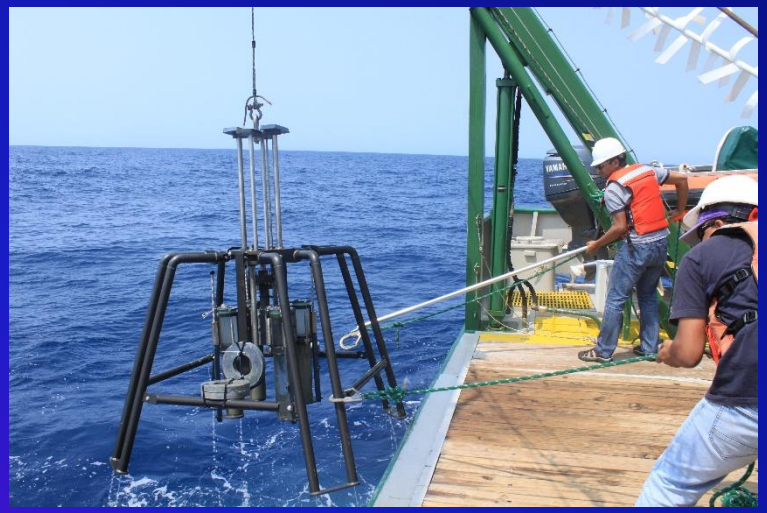
Large volume in situ pumps



- **~800 L** of water pumped and filtered at the rate of 4-6 L min^{-1}.
- Subsampled for particulate lead and rest for PAHs.

Sample Collection

Sediment cores: **Multi-corer**

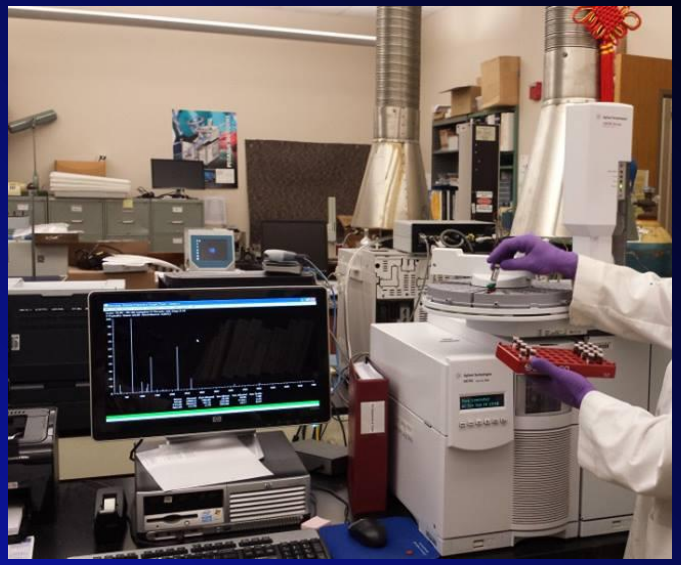


- Top 6 cm of first core, sliced and stored at -20^{o} C for PAHs.
- Whole second core, sliced and stored in a glass vial of known volume for ^{210}Pb dating.

Lab Analysis

PAHs Extraction and Analysis

- Extracted, analyzed using GC/MS and QC/QA following EPA SW-846 method 3540C.
- Forty-three individual PAHs were identified and quantified.
- Concentrations are represented as $\sum PAH_{43}$.



Lab Analysis

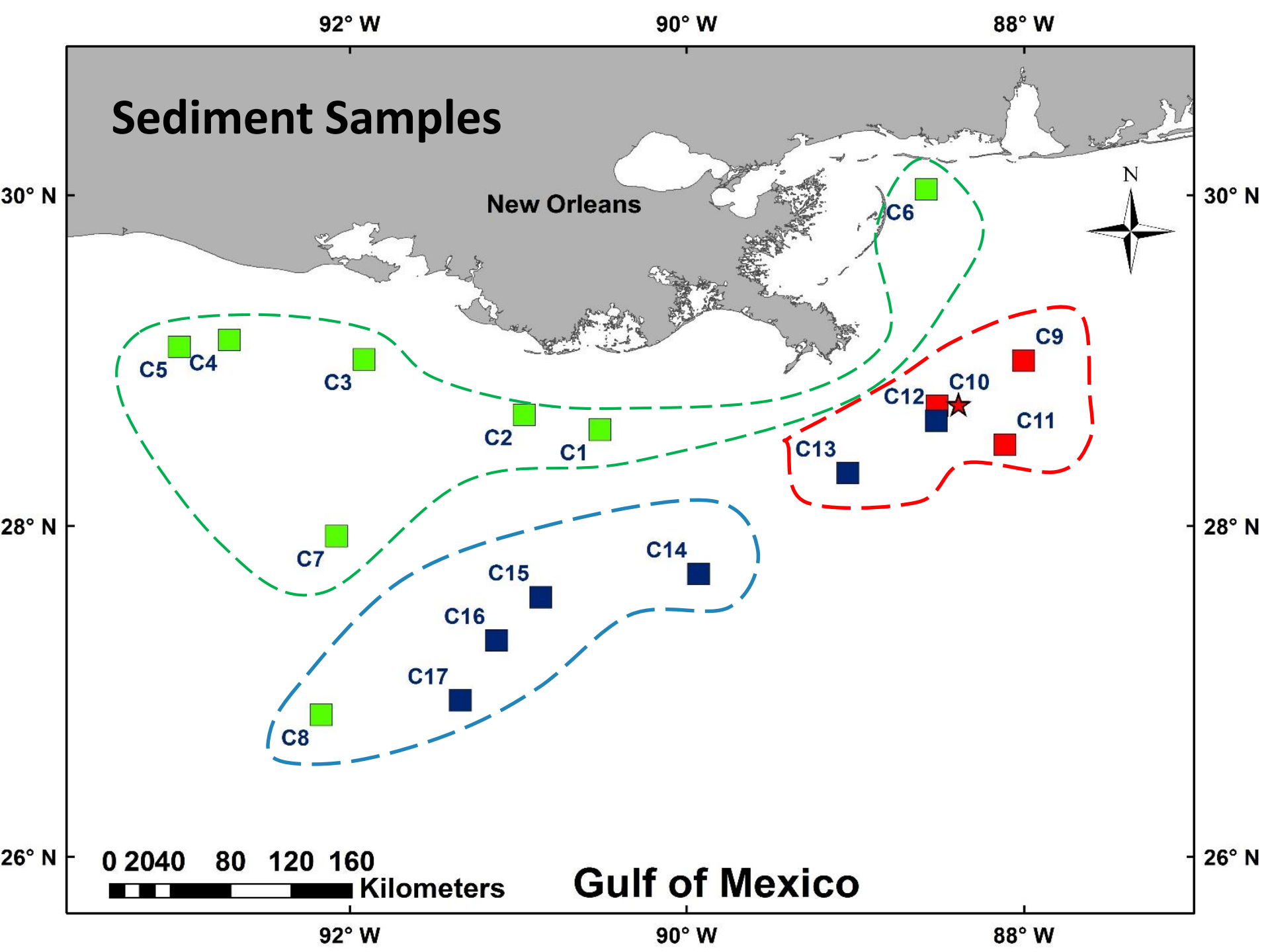
Sediment ^{210}Pb and ^{226}Ra activities

- Ground dry sediments were gamma counted for ^{210}Pb, ^{226}Ra and ^{214}Pb activities.
- High purity germanium well detectors *(Maiti et al., 2010).*
- $^{210}Pb_{excess} = {}^{210}Pb_{total} - {}^{214}Pb_{suported.}$
- The excess ^{210}Pb is used for sedimentation and accumulation rate estimation.

Lab Analysis

Dissolved and particulate ^{210}Pb activities

- Electroplating and column chemistry with stable Pb recovery via ICP-OES
- Alpha counting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C11
C12
C13
C14
C15
C16
C17
0 2040 80 120 160
Kilometers
Gulf of Mexico

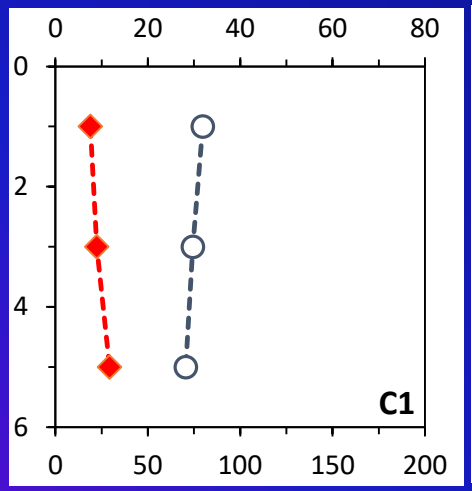
^{210}Pb-based Sediment Accumulation Rates

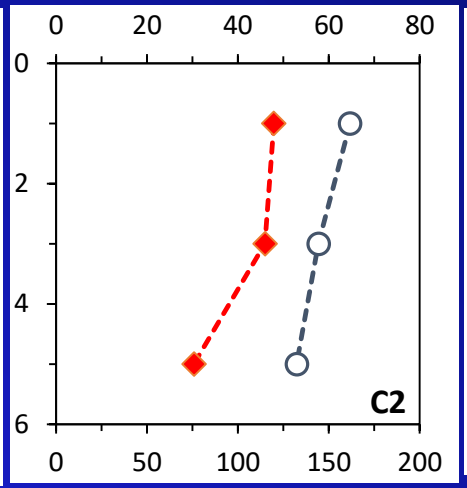
	CRS	CF:CS
Stations	($g\ cm^{-2}y^{-1}$)	($g\ cm^{-2}y^{-1}$)
C1	**0.09 - 0.17**	0.13±0.03
C2	**0.23 - 0.32**	0.21±0.04
C3	**0.19 - 0.58**	NA
C4	**0.20 - 0.30**	0.53±0.14
C5	**0.50 - 0.56**	0.50±0.14
C6	**0.26 - 0.32**	0.20±0.03
C7	**0.10 - 0.12**	0.11±0.01
C8	**0.05 - 0.21**	0.09±0.01
C9	**0.06 - 0.35**	0.56±0.06
C10	**0.06 - 0.42**	0.33±0.03
C11	**0.09 - 0.32**	0.13±0.02
C12	**0.10 - 0.34**	0.12±0.03
C13	**0.09 - 0.31**	NA
C14	**0.06 - 0.18**	0.16±0.03
C15	**0.07 - 0.11**	0.12±0.01
C16	**0.06 - 0.08**	0.08±0.005
C17	**0.04 - 0.25**	0.09±0.01

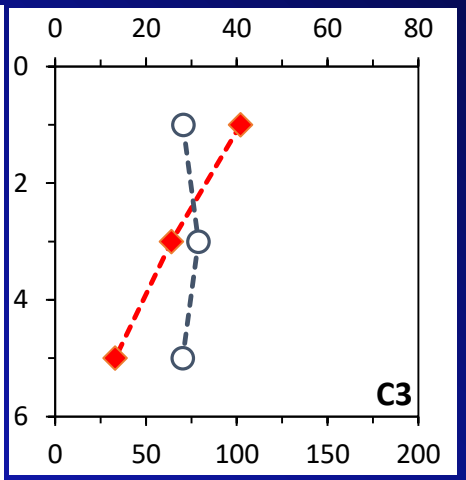
- Similar results from two different models
- CRS model used to calculate PAHs accumulation rates.

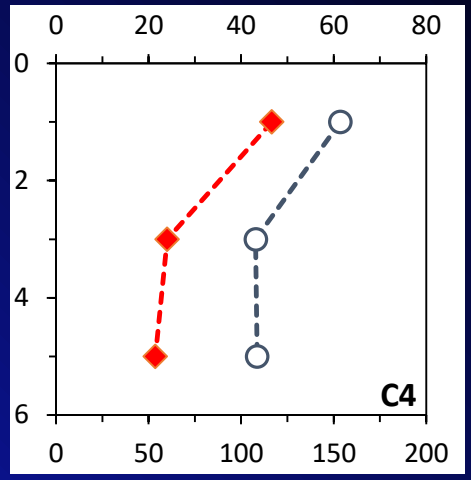
PAHs Concentration and Accumulation Rate in coastal sediments

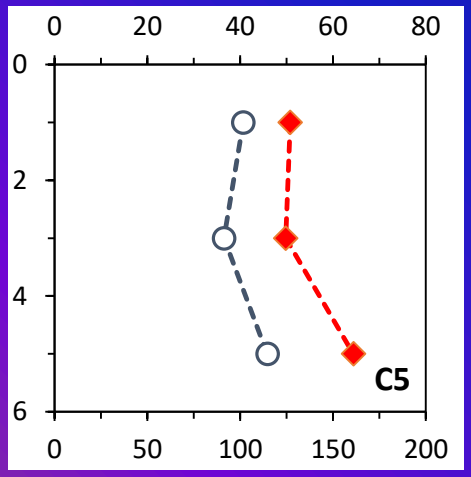
$\sum PAH_{43}$ Accumulation Rates (ng cm^{-2} y^{-1}) – *filled diamond*

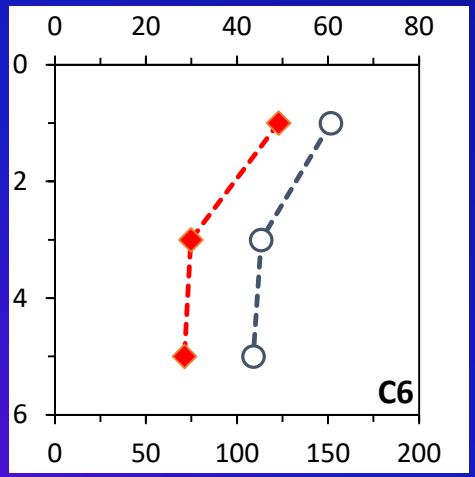


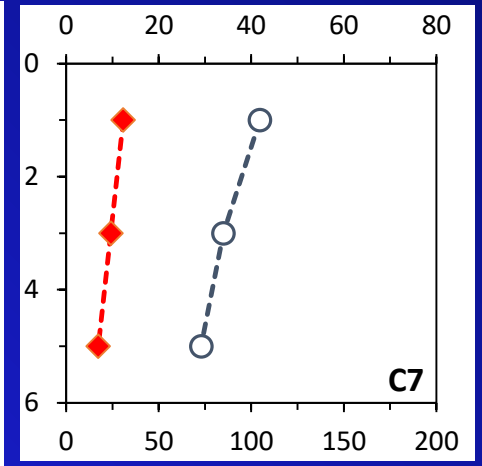










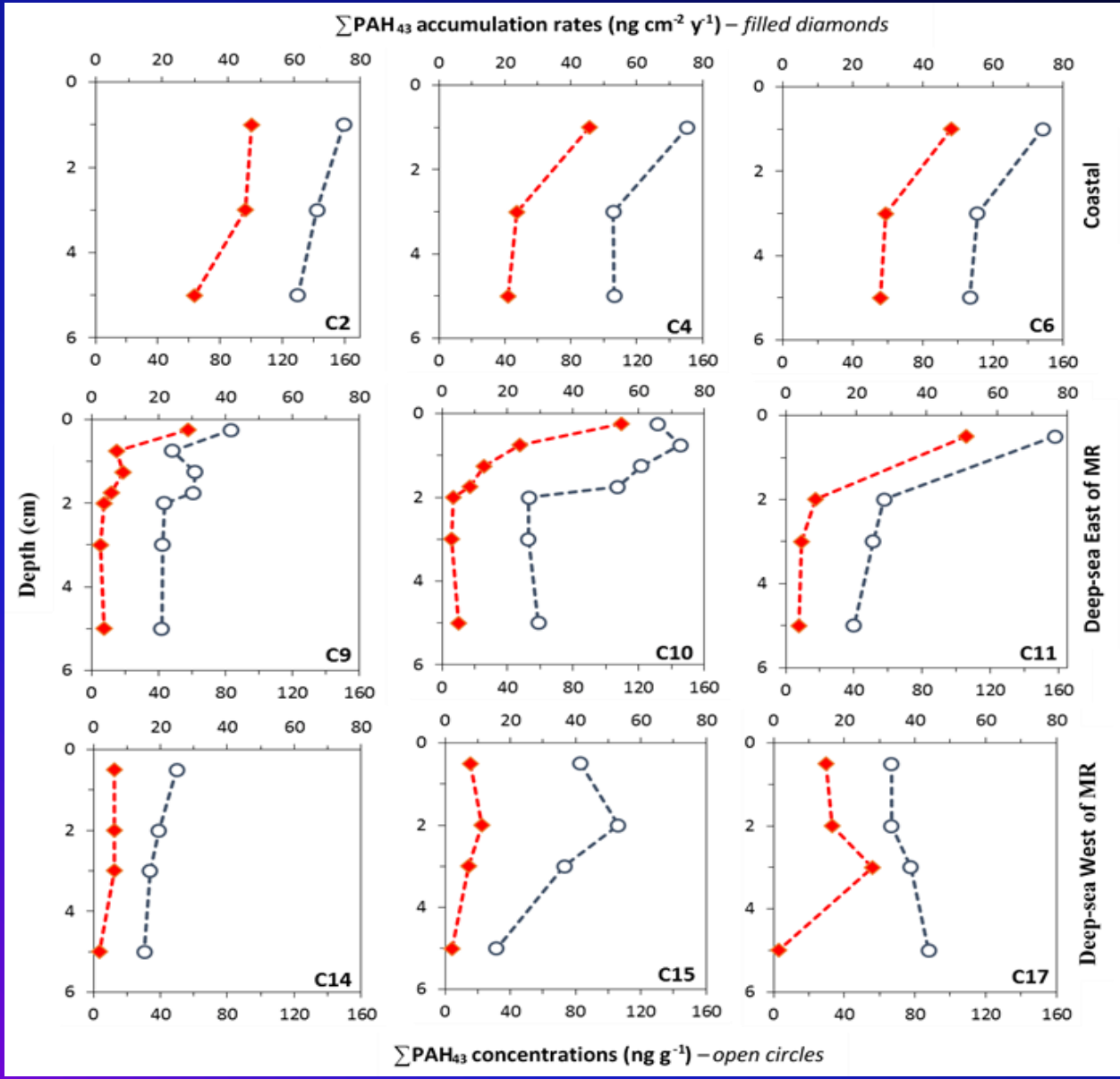


Concentrations
70 -160 ng g^{-1}

Accumulation rates
25 -65 ng cm^{-2} y^{-1}

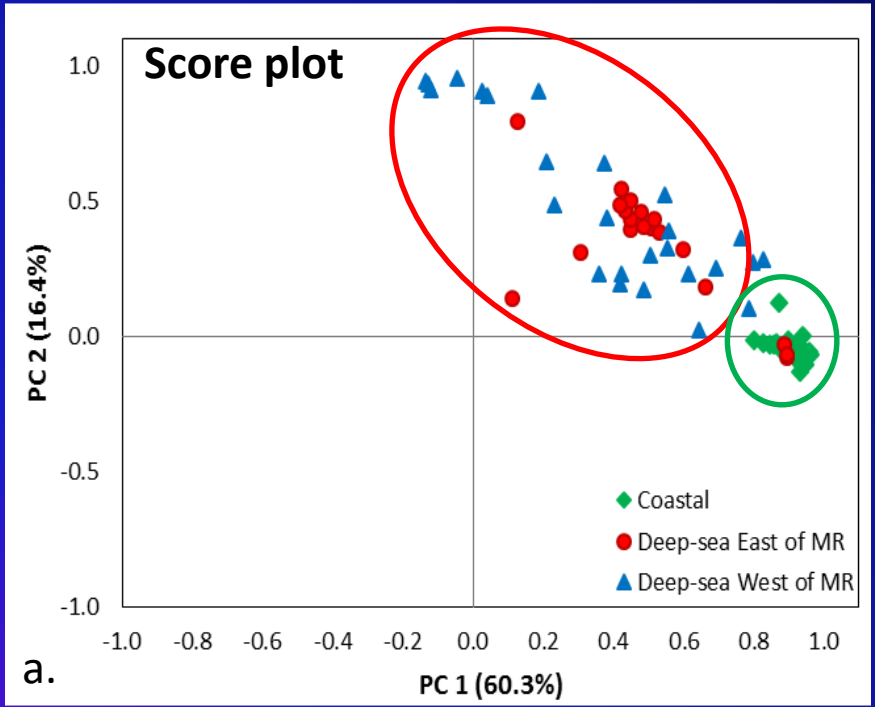
$\sum PAH_{43}$ Concentrations (ng g^{-1}) – *open circles*

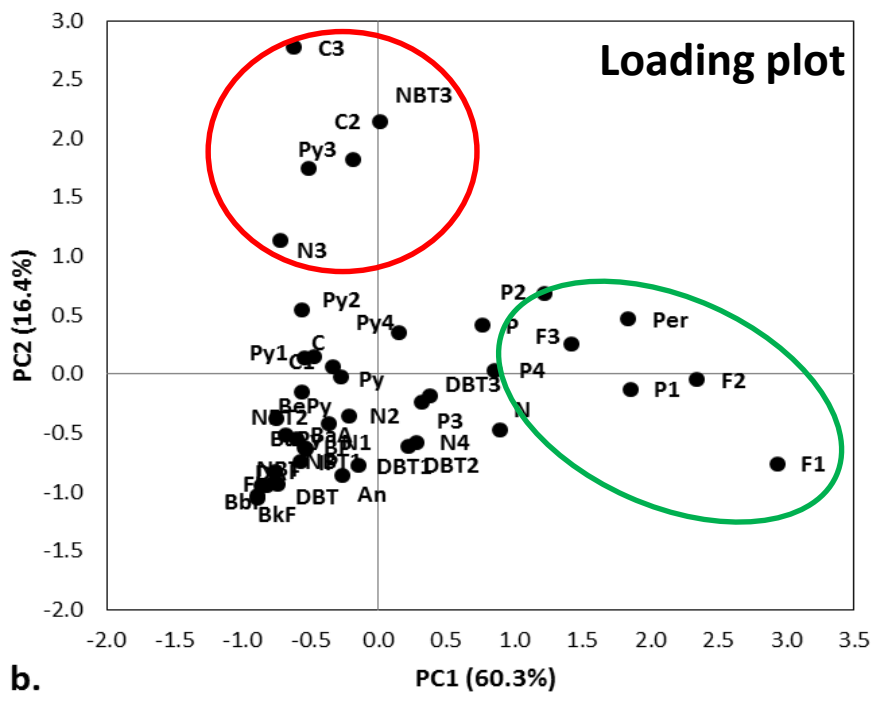
Comparison with deep ocean sediments



Adhikari & Maiti 2016

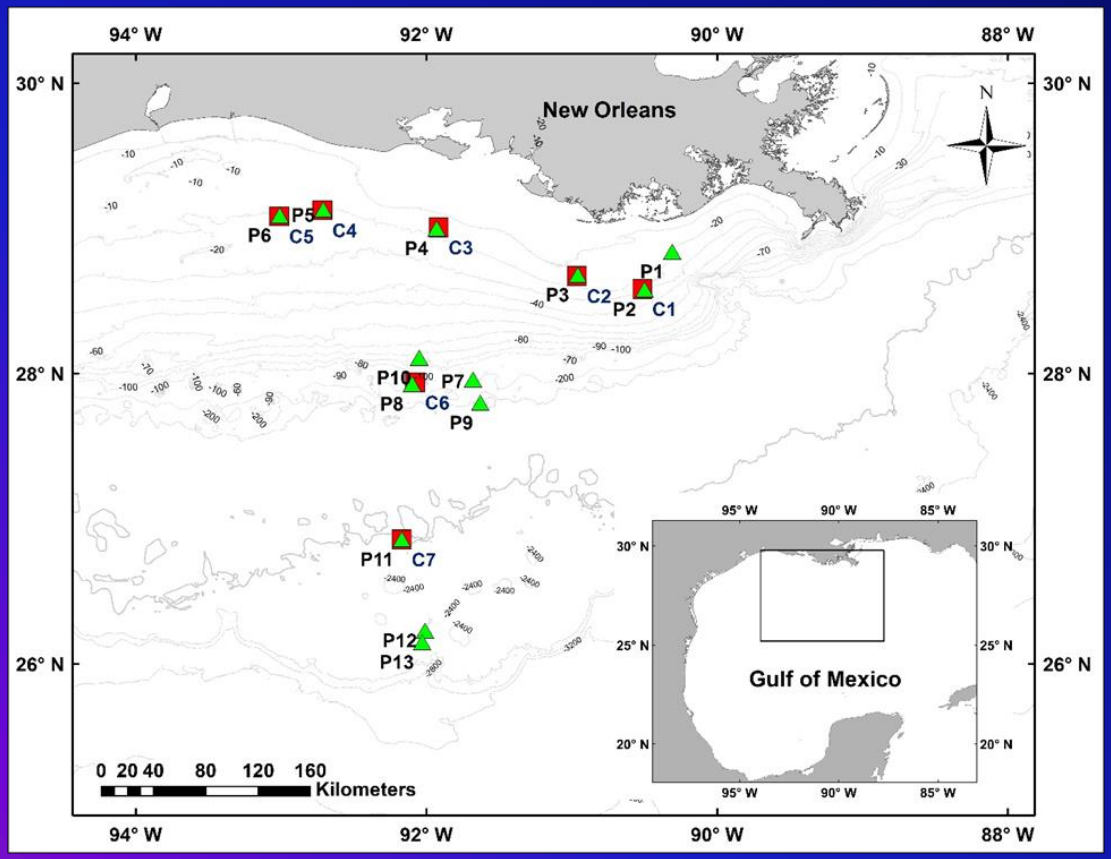
Principal Component Analysis

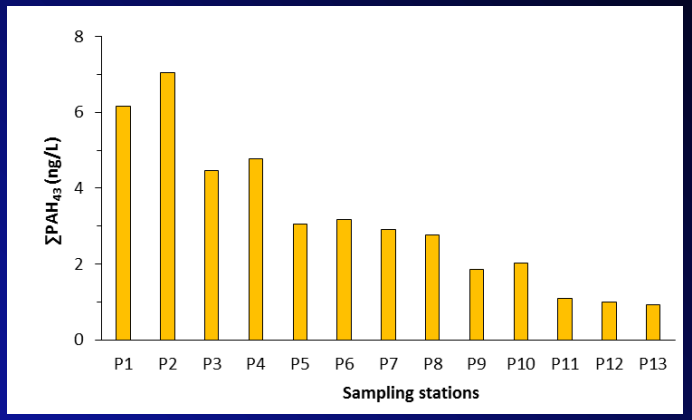


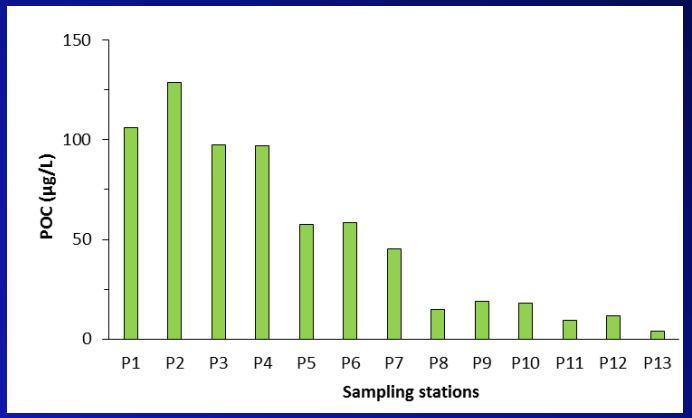


- PC1 and PC2 explain ~77% of the variability in PAHs composition.
- Coastal and deep-sea stations clearly separated.
- Coastal sediments have higher percentages of LMW-PAHs (83 ± 4%) than the deep-sea sediments (53 ± 15%).
- Deep-sea sediments have higher MMW-PAHs (41 ± 14%) than the coastal sediments(12 ± 3%).

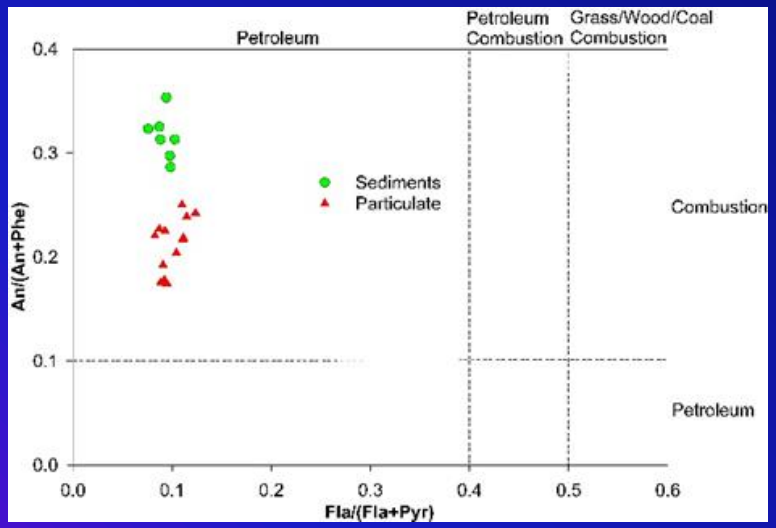
Suspended particulate PAH concentration in coastal waters

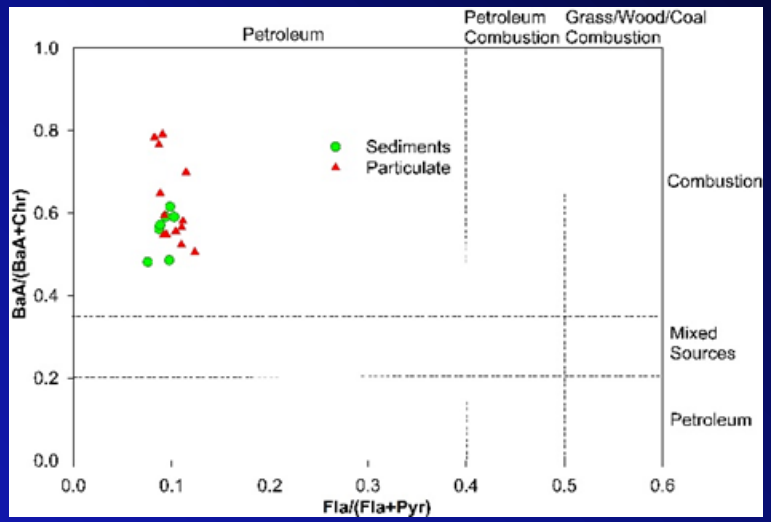


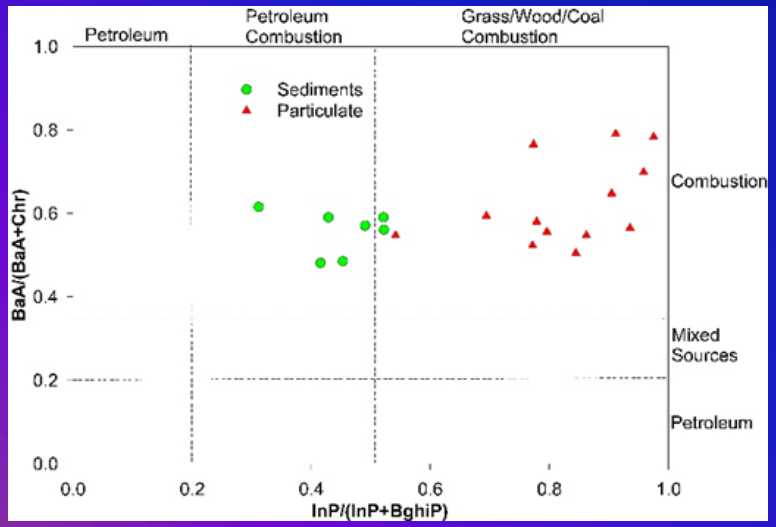




Suspended particles versus sediments





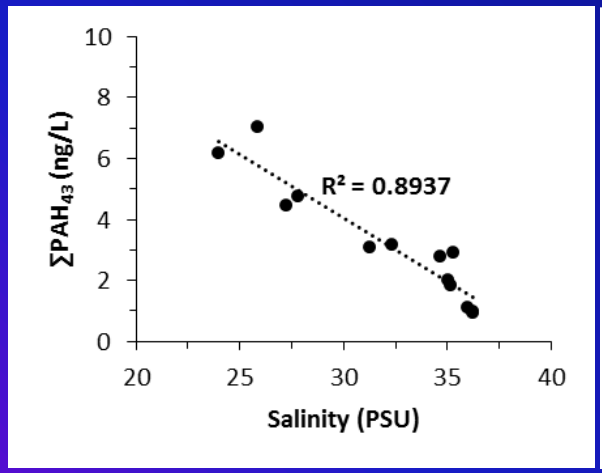


Particulate samples were dominated by LMW-PAHs (89±1.7%) while MMW-PAHs contributed ~10 ± 1.4% which is similar to seafloor sediment distribution.

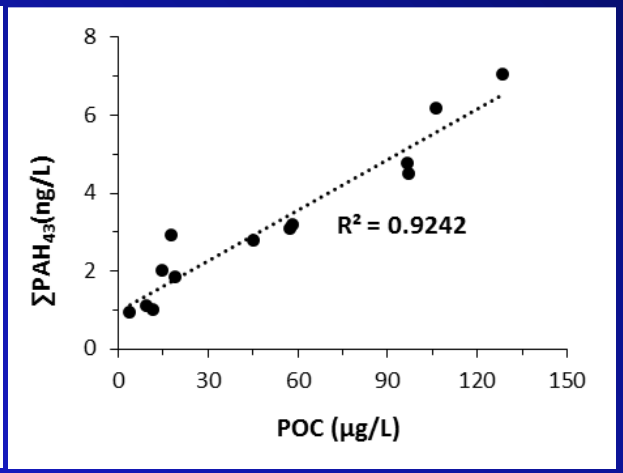
88% of particulate PAHs and 74% of sediment PAHS comprised of alkylated homologs.

Particulate PAH to other parameters

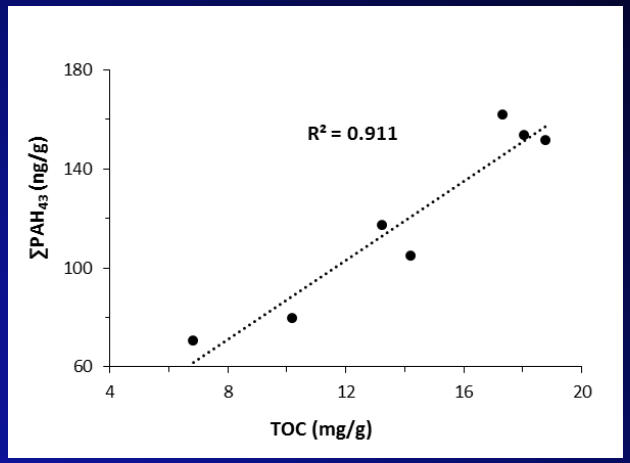
Water column



Water column



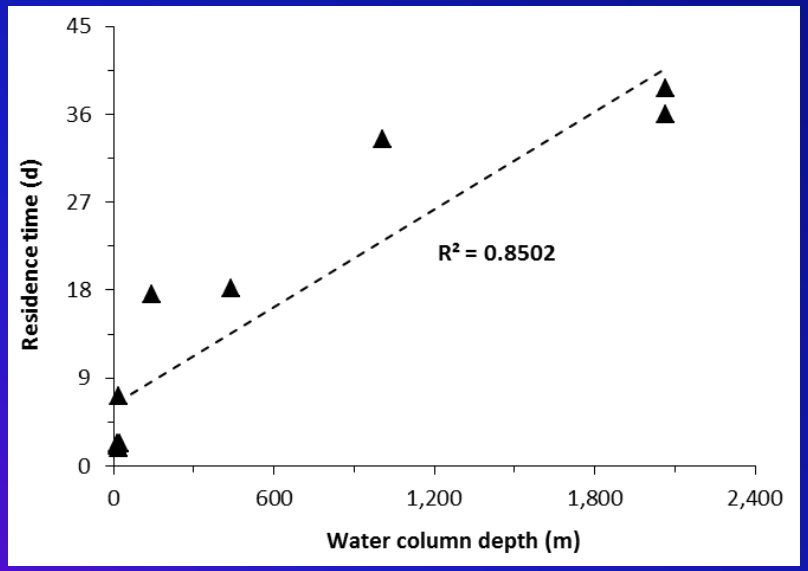
Sediment

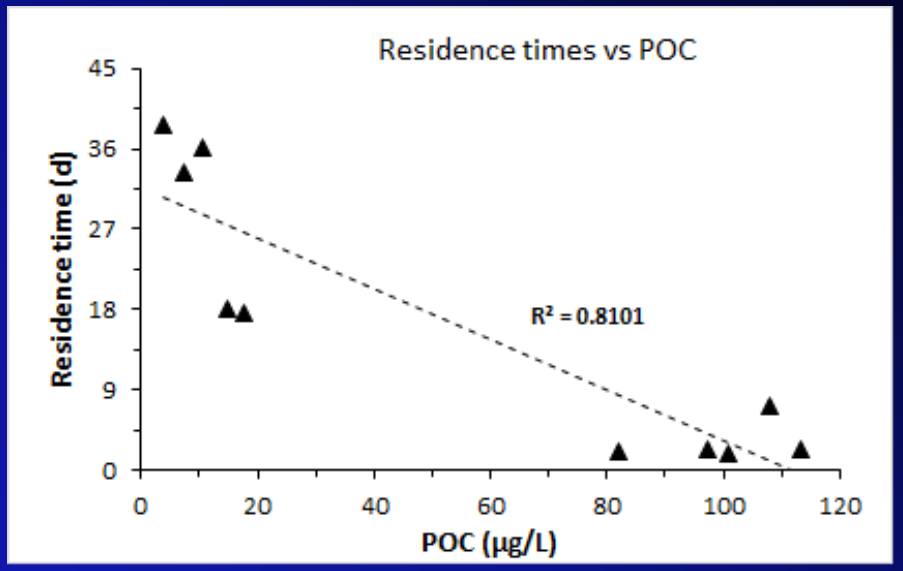


Well correlated with salinity and POC indicating river plume as a possible important source.

Cannot rule out atmospheric deposition.

^{210}Pb based Particulate Residence Time





Removed from the water column within a week for shallow coastal ocean; about a month for deep ocean.

How to translate calculated residence time of particulate ^{210}Pb (τ_{Pb}) to particulate PAH ???

$K_d = [A_{part}/A_{diss}] \times TSM$

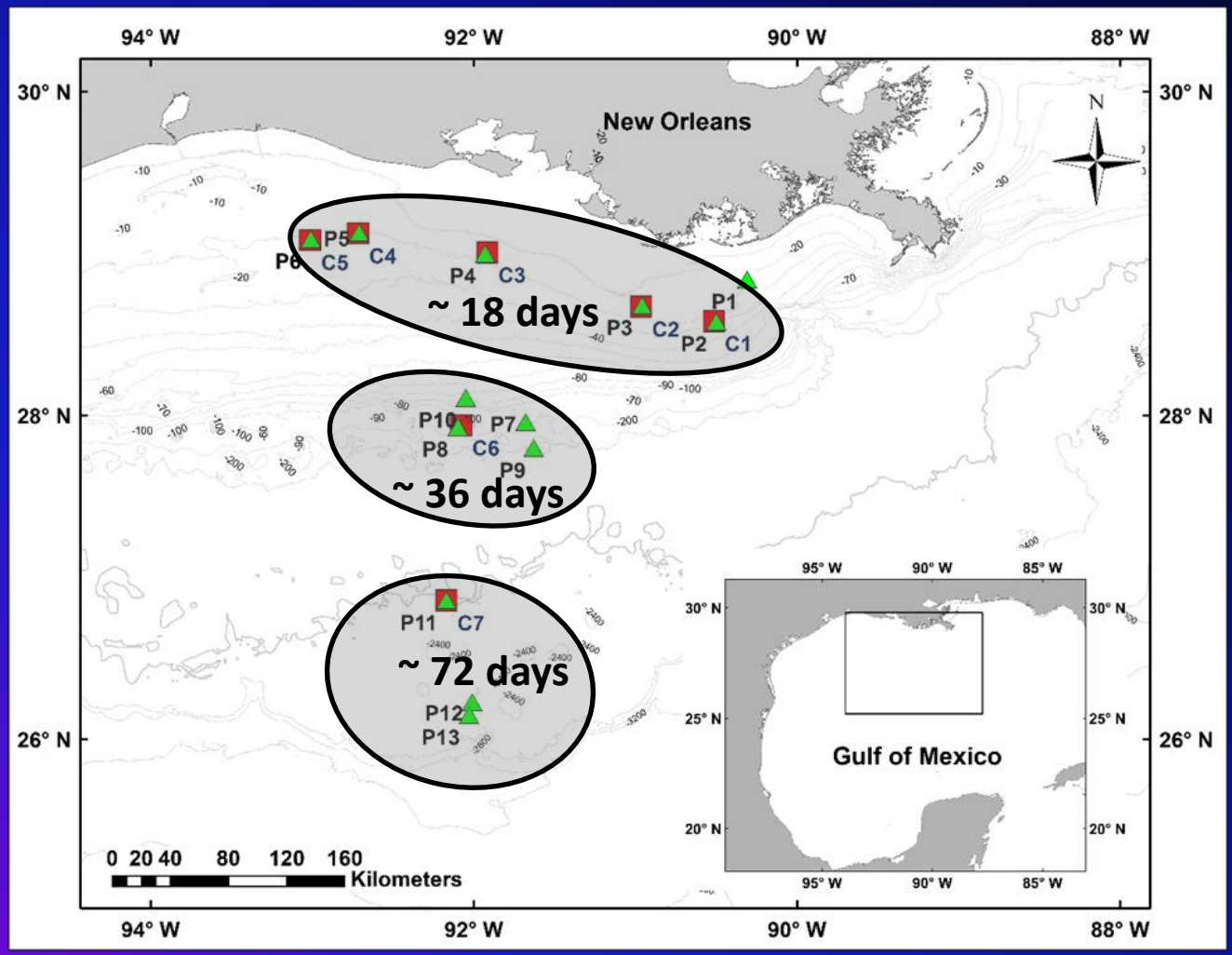
Fractionation Factor (FF) = $[K_d]_{210Pb} / [K_d]_{PAH}$

$\approx 2.1 \pm 0.8$ for this study

Residence Time of particulate PAH (τ_{PAH}) = τ_{Pb} x FF

- Assumes negligible loss of particulate PAH due to other processes like photo degradation.
- Individual PAH compound has different K_d which means different FF.

Residence time of particulate PAHs (preliminary estimates)



Adhikari & Maiti in prep.

Conclusions

- Low to moderate levels of PAHs pollution in the northern GOM sediments below ERL (effective range-low) toxic levels.
- PAH accumulation rates in coastal Louisiana sediments range between 25 -65 ng cm^{-2} y^{-1}.
- LMW-PAHs more dominant in coastal sediments.
- Residence time of particle reactive contaminants in coastal Louisiana are about two weeks before they are removed from the water column via scavenging.
- Water column particulate PAHs are found to be significantly correlated with POC concentration.

Acknowledgement

- The captain and crew of the *R/V Endeavor*, *R/V Walton Smith* and the *R/V Pelican* for their help in sample collection.
- Thanks to Chris DuFore for project oversee and helpful discussions.
- Funding provided by Bureau of Ocean Energy Management

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