Detecting Hydrocarbons in Sand after Huntington Beach Oil Spill Using Solid-Phase Microextraction Gas Chromatography-Mass Spectrometry (SPME-GC-MS)

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Project supported by CSU Council on Ocean Affairs, Science & Technology (COAST), Award #: COAST-RR-2021-03

Background: Huntington Beach Oil Spill

- Pipeline connecting Long Beach and Elly drilling platform burst
- Ten day beach closure post oil spill
  - City officials stated that toxic compounds were not detected in sand and ocean water
- Skepticism throughout the public

Figure 1. Image taken after oil spill. Adapted from "2021 Orange County Oil Spill Response", 2021.

Goal: Determine how hydrocarbon compounds in the Huntington Beach sand change monthly for a year using solid-phase microextraction (SPME) with a combination of gas chromatography-mass spectrometry (GC-MS)

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Conditions

- Sample Collection
  - Once a month: right and left side of HB pier
  - 100 ft in front of closest lifeguard stands
  - Eight Samples: 4 - surface level; 4 - 8 in below surface
- Sample Preparation
  - Desiccated; 2 g in 20 mL headspace glass vial
  - Incubate: 5 mins at 80 °C
- SPME fiber
  - Divinylbenzene/Polydimethylsiloxane fiber
  - Precondition: 5 mins at 250 °C
  - Sample Extraction: 10 mins in incubator

Figure 2. Image of DVB/PDS fiber taken from "PAL SYSTEM: Ingenious Sampling Handling", 2020.

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GC-MS

- GC: HP-5ms GC column
  - Sample Injection: 2 mins
  - Oven Temperature: 40 °C to 300 °C at a ramp of 20 °C min^{-1}
  - Helium Flow: 1.3 mL min^{-1}
- MS: Agilent 5977B
  - Transfer Line: 250 °C
  - Scanning Range: 50-500 amu sec^{-1}; full scan mode
  - Electron Voltage: 70 eV
  - Source and Quad Temperatures: 230 °C and 150 °C, respectively
  - Scanning: 1.7 scans sec^{-1}
- Agilent MSD Productivity ChemStation for GC and GC/MS System
  - Using the NIST 2020 Mass Spectral Library Database with a Match Factor (Similarity Index scores) threshold of 500

Figure 3. Image of fiber injection in GC inlet.

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Hydrocarbon Detection

Month	Surface		8 inches below the surface	
-	Right	Left	Right	Left
Oct.	-	2-Methylindene	-	-
Dec.	Heptadecane Octadecane	-	-	Hexadecane Heptadecane
Jan.	-	-	Dodecane Tetradecane Hexadecane	Dodecane Tetradecane Pentadecane Hexadecane Heptadecane
June	9-Octadecene	-	-	-

- *n*-alkenes and *n*-alkanes detected in early months of the year
- no toxic hydrocarbons detected

Biodegradation

- Degradation of hydrocarbons occurs through oxidation
- Algae in water assists with oxidation
- Rapid biodegradation
- **Next:** Further analyze biodegradation and concentrations of hydrocarbons as the year progresses

Month	Surface		8 inches below surface	
-	Right	Left	Right	Left
Oct.	-	-	Nonanal	-
Nov.	Phthalic acid, isobutyl 2-methylpent-3-yl ester	Phthalic acid, hex-3-yl isobutyl ester	-	Phthalic acid, isobutyl 2-methylpent-3-yl ester
Dec.	Heptanal Nonanal Cinnamaldehyde Nonanoic acid Pentadecanal	Nonanal	Nonanal	-
Jan.	Heptanal Nonanal	Heptanal Nonanal Benzoic acid, 2,5-dinitro-	Heptanal Nonanal	Heptanal Nonanal Decanal Nonanoic acid
Mar.	Cinnamaldehyde	Nonanal *n*-Hexadecanoic acid	*n*-Hexadecanoic acid	-
Apr.	-	-	-	Nonanal *n*-Hexadecanoic acid
May	Nonanal *n*-Hexadecanoic acid	Nonanal *n*-Hexadecanoic acid	Nonanal *n*-Hexadecanoic acid	Nonanal *n*-Hexadecanoic acid
June	Nonanal Nonanoic acid *n*-Hexadecanoic acid Octadecanoic acid	Heptanal Nonanal *n*-Hexadecanoic acid	Heptanal Nonanal Nonanaoic acid n-Hexadecanoic acid	*n*-Hexadecanoic acid
July	Hexathiane *n*-Hexadecanoic acid	Hexathiane *n*-Hexadecanoic acid	Hexathiane *n*-Hexadecanoic acid	-
Aug.	Heptanal Nonanal	-	-	Nonanal

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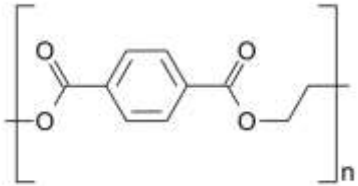
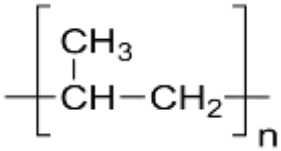
Organic Compounds Adsorbed on Microplastics (MPs)

Polyethylene terephthalate (PET)



MPs standards

Polypropylene (PP)



GCxGC-FID

GC-TOFMS

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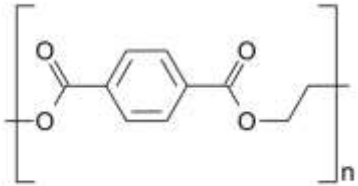

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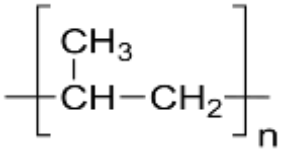

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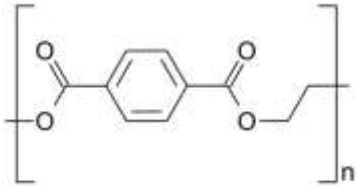

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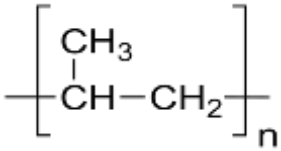

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