Are Our Beaches Safe? Using Solid-Phase Microextraction Gas Chromatography-Mass Spectrometry to Detect Hydrocarbons in Sand Post Huntington Beach Oil Spill

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KEY WORDS: oil spill, beach sand, solid-phase microextraction, gas chromatography, mass spectrometry

ABSTRACT

A pipeline between Long Beach, CA and the Elly drilling platform ruptured on October 2, 2021, allowing crude oil to reach the popular vacation destination of Huntington Beach, CA and resulting in beach closure. The public expressed skepticism and concern when city officials declared that no harmful substances were detected in the ocean water only ten days after the incident. Responding to community concerns, this project assessed how hydrocarbon compounds in the Huntington Beach sand changed over a year following the oil spill using a divinylbenzene/polydimethylsiloxane solid-phase microextraction (SPME) fiber and gas chromatography-mass spectrometry (GC-MS). An Agilent 59778 GC/MSD was used to separate and identify compounds in sand samples collected monthly. Preliminary data indicates the number of compounds varied throughout the year. Three months after the spill, notable hydrocarbons such as *n*-alkenes and *n*-alkanes were found. However, just weeks following the oil spill, biodegradation occurred, producing aldehydes and carboxylic acids.

METHODS

Sample Preparation. Sand samples were collected monthly (1 year) on both sides of the Huntington Beach pier, approximately 100 ft in front of the lifeguard stations. Two samples were taken from the surface and eight inches below the surface of the sand on each side of the pier. The samples were stored in tin-foil-sealed mason jars on ice until stored in a 1 °C refrigerator. Sand samples were transferred to Petri dishes and dehydrated for two days in a hood. The dried sand sample (2 g) was placed in a 20 mL headspace glass vial and incubated at 80 °C for 5 min.

Instrument Preparation. The column was cleaned at 250 °C for 10 min and a blank control was run before each set of sand samples. The SPME fiber was preconditioned and cleaned at 250 °C for 5 min in the GC-MS inlet. The fiber was transferred to the sample vial and sample extraction occurred for 10 min before the fiber was injected for 2 min into the GC inlet.

Chromatographic Conditions. GC-MS analysis of all samples was performed using an Agilent 5977B GC/MSD system (Agilent Technologies, Santa Clara, CA) equipped with a single quadrupole mass analyzer, L-PAL3 autosampler system (LECO Corporation, St. Joseph, MI), and electron ionization. The system was operated in scanned ion mode and used split injection (1:1) with an HP-5ms (Agilent Technologies, Santa Clara, CA) (5%-Phenyl)-methylpolysiloxane capillary GC column with 30 m length, 0.25 mm ID, and 0.25 μm film thickness. The GC oven temperature program was as follows: 40 °C hold 1 min, ramp to 300 °C, 20 °C/min. UHP Helium was used as the carrier gas and the flow rate was 1.2 mL/min. The inlet temperature was 250 °C and the transfer line temperature was held constant at 250 °C for each 14 min run.

Data Processing and Calculation. Samples were analyzed using full scan mode with a scanning range of 50-500 amu/sec at an electron voltage of 70 eV. Source and quad temperatures were 230 °C and 150 °C, respectively. Scanning occurred at 1.7 scans/sec. Following each run, a total ion chromatogram (TIC) was created using the Agilent MSD Productivity ChemStation software. The chromatogram was then integrated and the NIST 2020 library search results with a similarity index score threshold of >500 were used to identify compounds separated by retention time.

RESULTS AND DISCUSSION

Due to the NIST database indicating that certain *n*-alkanes had multiple retention times, *n*-alkane standards (C_5-C_{20}) were analyzed via GC-MS to confirm each retention time (Table 1).

Table 1. Retention times (RT) of C_5-C_{20} *n*-alkanes

***n*-alkane**	*n*-C_5	*n*-C_6	*n*-C_7	*n*-C_8	*n*-C_9	*n*-C_{10}	*n*-C_{11}	*n*-C_{12}
RT	2.619	2.669	3.945	4.226	5.109	6.013	6.817	7.580
***n*-alkane**	*n*-C_{13}	*n*-C_{14}	*n*-C_{15}	*n*-C_{16}	*n*-C_{17}	*n*-C_{18}	*n*-C_{19}	*n*-C_{20}
RT	8.303	8.976	9.619	10.222	10.804	11.357	11.919	12.462

Hydrocarbon and non-hydrocarbon compounds found in sand samples collected between October 2021 and September 2022 are shown in Tables 2 and 3, respectively. January 2022 displayed the highest hydrocarbon detection, ranging from C_{11} to C_{17}. The hydrocarbons detected in the first few months following the oil spill are predominantly *n*-alkanes, which are typically found in high concentrations in crude oils. This result demonstrates that we are in fact examining sand polluted by an oil spill.

Table 2. Hydrocarbon compounds detected in sand from October 2021 to September 2022

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	-	-	-

Table 3. Non-hydrocarbon compounds detected in sand from October 2021 to September 2022

Month	Surface		8 inches below the 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
Sept.	*n*-Hexadecanoic acid	*n*-Hexadecanoic acid	*n*-Hexadecanoic acid	*n*-Hexadecanoic acid

In hydrocarbon-contaminated soils, biodegradation alters the molecular structure of hydrocarbons, often by oxidation. Although the compounds shown in Table 3 are not hydrocarbons, they are likely products of the biodegradation of *n*-alkanes and other hydrocarbons. Biodegradation products include oxygenated volatile organic compounds, including aldehyde, alcohol, ester, and carboxylic acid derivatives. The aldehydes (heptanal, nonanal, cinnamaldehyde, pentadecanal, and decanal) and carboxylic acids (*n*-octadecanoic, *n*-hexadecenoic, *n*-nonanoic, phthalic acid, and 2,5-dinitro-benzoic acid) shown in Table 3 are possible biodegradation products. Specifically, our data indicate that *n*-hexadecanoic acid (March to July) is the oxidation product of *n*-hexadecane (December and January); see Figure 1. It is important to emphasize that biodegradation is a naturally occurring process.

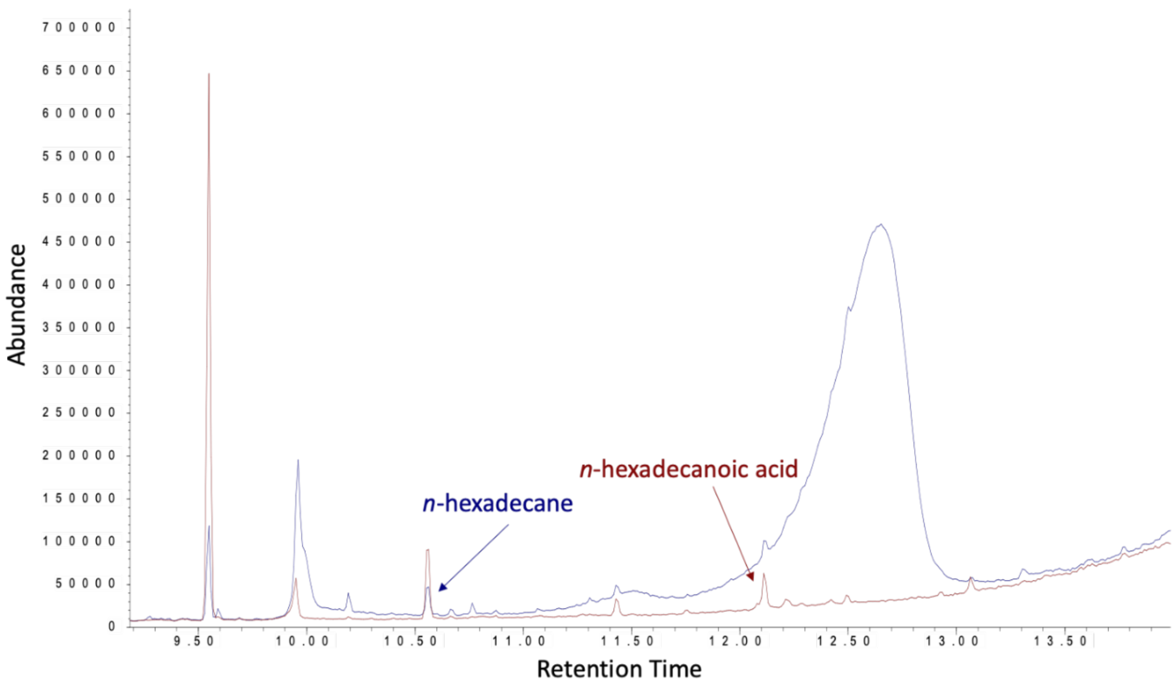

Figure 1. TIC (zoomed) showing the biodegradation of *n*-hexadecane (sample from January 2022) to *n*-hexadecanoic acid (sample from March 2022)

CONCLUSION

Following an oil spill that impacted Huntington Beach, California, in October 2021, we collected and analyzed sand samples every month for one year to detect the presence of dangerous compounds and observe the variation in concentrations of these substances. Using SPME-GC-MS, it was determined that the sand samples contained hydrocarbons, particularly *n*-alkenes and *n*-alkanes. The lack of harmful compounds, such as aromatic compounds like benzene or toluene, gives credibility to the city officials' statement that no dangerous compounds were discovered. Therefore, it is possible that the beach was safe to reopen following the 10-day closure. The subsequent discovery of biodegradation resulted in the production of aldehydes and carboxylic acids. Further study will be undertaken to analyze the change in concentrations of the identified compounds over the course of the year and conduct in-depth research on the biodegradation of the hydrocarbon compounds using GC-TOF/MS or GC×GC-TOF/MS. This work was supported by CSU Council on Ocean Affairs, Science & Technology (COAST) (award no. COAST-RR-2021-03).