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Tracking the Weathering of an Oil Spill with Comprehensive Two-Dimensional Gas Chromatography

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Comprehensive two-dimensional gas chromatography (GC × GC) was used to investigate the *Bouchard 120* oil spill. The latter occurred on April 25, 2003, when the barge *Bouchard 120* spilled ~375,000 liters of No. 6 fuel oil into Buzzards Bay, Massachusetts. In order to gain a better understanding of the natural processes affecting the fate of the spilled product, we collected and analyzed oil-covered rocks from Nyes Neck beach in North Falmouth, Massachusetts. Here we discuss the data from samples collected on May 9, 2003, and six months later, on November 23, 2003. Along with standard two-dimensional gas chromatographic analysis, we employed unique data-visualization techniques such as difference, ratio, and addition chromatograms to highlight how evaporation, water washing, and biodegradation weathered the spilled oil. These approaches provide a new perspective to studying oil spills and aid attempts to remediate them.

Keywords: comprehensive two-dimensional gas chromatography, GC × GC, difference chromatogram, oil spill, *Bouchard 120*, Buzzards Bay, Massachusetts, Bunker C, No. 6 fuel oil, petroleum weathering

Introduction

Comprehensive two-dimensional gas chromatography (GC × GC) is a promising new technology for analyzing petroleum hydrocarbons in environmental samples (Frysinger et al., 2002). GC × GC instruments produce high-resolution chromatographic separations because each petroleum compound is subjected to two different stationary phase selectivities. Most often, the first dimension separation uses a nonpolar phase to separate petroleum compounds by volatility differences, and the second dimension uses a more polar phase to separate first dimension coeluters by polarity differences. The resulting two-dimensional chromatogram can have thousands of resolved peaks sorted according to their volatility and polarity properties. A GC × GC chromatogram has compound peaks grouped by carbon number along the x-axis and by chemical class along the y-axis. For petroleum, this produces separated chemical classes such as alkanes, cycloalkanes, and one-, two-, and multi-ring aromatics, with additional groupings showing homologous series within each class (Phillips and Beens, 1999; van Deursen et al., 2000; Dimandja, 2004).

GC × GC has been used successfully to identify and quantify individual compounds and classes of compounds in crude oil and refined petroleum products. Gasoline was analyzed with GC × GC to quantify benzene and oxygenates individually, and total aromatics as a group (Frysinger et al., 1999; Frysinger and Gaines, 2000). GC × GC chromatograms of crude oil showed distinct groupings of alkylated polycyclic aromatic hydrocarbons (PAHs), sulfur-containing aromatic hydrocarbons (PASHs), and sterane and hopane biomarkers (Frysinger and Gaines, 2001). Once chemical class locations and patterns are known, the two-dimensional chromatogram can be rapidly inspected to detect variations in compound distribution and abundance. This procedure was used to fingerprint an oil spill sample and match it to a potential source (Gaines et al., 1999) and to characterize the chemical composition of a degraded No. 2 fuel oil in salt marsh sediments in West Falmouth, Massachusetts (Reddy et al., 2002). Determining the chemical composition of degraded petroleum is challenging because extensive degradation tends to remove abundant n-alkanes and aromatics, which often leaves an unresolved complex mixture (UCM) of petroleum hydrocarbons consisting of a large number of branched and cyclic alkanes. Using volatility-by-polarity or volatility-by-shape selectivity, GC × GC can resolve many of these saturated compounds and provide information previously unattainable with traditional gas chromatography or gas chromatography-mass spectrometry (GC-MS) methods. For example in a degraded fuel oil sample from West Falmouth, the n-alkanes were found to be completely degraded, but the isoprenoids (farnesane, pristane, and phytane)

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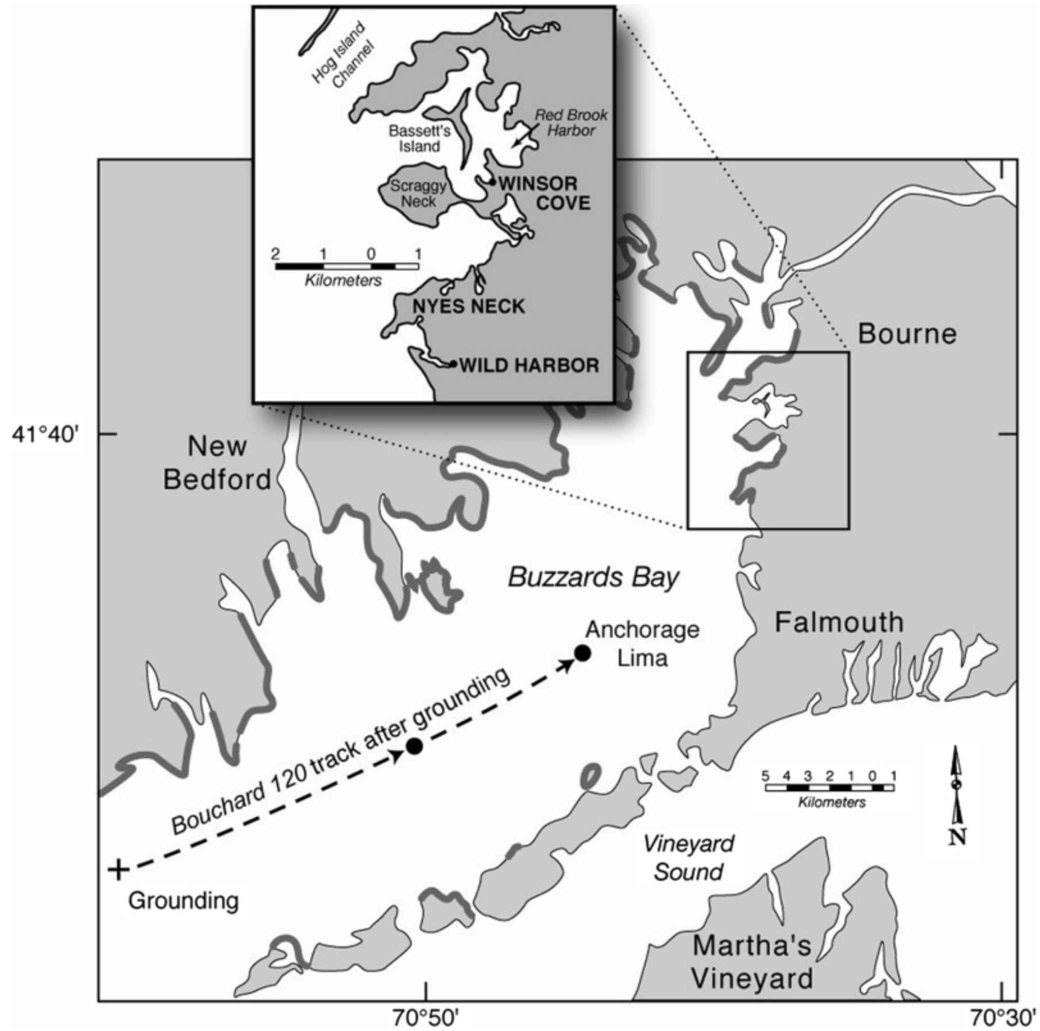

Figure 1. Map of Buzzards Bay, MA showing the track of the *Bouchard 120* barge on April 27, 2003. Oil-impacted beaches are highlighted in gray around the perimeter of the bay. The inset map indicates Nyes Neck where the samples used for this study were collected.

persisted after 30 years. In addition, GC × GC analysis provided a complete inventory of compounds remaining from the original No. 2 fuel oil that was used to help assess the dominant degradation mechanisms at that location (Frysinger et al., 2003).

In this study, we investigated the weathering of a No. 6 fuel oil spill that occurred on April 27, 2003, when the barge *Bouchard 120* struck a ledge at the entrance to Buzzards Bay, Massachusetts (Reddy, 2004; Figure 1). The single-hull barge was delivering fuel to a local power plant and released ~375,000 L of No. 6 fuel oil into Buzzards Bay. Oil was extracted from rocks collected after the spill. GC × GC analyses of the extracted samples were used to track the weathering progress. Three new GC × GC data visualization methods that employed difference, ratio, and addition chromatograms were used to identify weathering patterns. Second, GC × GC chromatogram peaks and regions were integrated to measure changes in individual compounds and chemical classes, respectively.

Methods

Sample Collection

Oil-coated rocks, mainly cobbles, were collected from Nyes Neck beach in North Falmouth, Massachusetts (Figure 1). This site was chosen primarily because wind, current, and tidal conditions combined to create a localized anomaly of excessive oil coverage on this stretch of beach in an otherwise lightly impacted area. Sampling began approximately two weeks after the spill and continued on a daily to monthly basis. Of the numerous samples collected, only samples collected on May 9 (day 12) and November 23, 2003 (day 179), were used in this effort. Each cobble was placed in a glass jar with a Teflon-lined cap. While in the field, approximately 40 mL of dichloromethane/methanol (90:10) was added to each jar or until the rock was completely submerged. Each jar was secured with Teflon tape, returned to the laboratory, and stored in darkness at room temperature until extraction.

Extraction and Sample Clean-Up

Each jar was sonicated for 20 minutes, and the solvent mixture was decanted into a separatory funnel. The sample was extracted two more times with 90/10 DCM/methanol, and the second and third extracts were combined with the original. Fifty milliliters of deionized water was added to the separatory funnel. The DCM fraction was collected, dried over activated sodium sulfate, and solvent exchanged into hexane while reducing the volume to ∼30 mL by rotary evaporation. The latter step caused the asphaltenes present in the samples to precipitate. To assure complete removal of the asphaltenes, each extract was eluted through a Pasteur pipette (14.5 cm long) packed with combusted glass wool and the pipette was then rinsed with hexane. The hexane extracts were reduced in volume to ∼10 mL and ∼10% of each sample was charged onto a solid-phase extraction (SPE) glass column with a Teflon frit containing 500 mg of Supelclean LC-NH_2 packing. To isolate the aliphatic and aromatic hydrocarbons, the SPE columns were eluted with 7.5 mL of hexane/DCM (90/10). The total volume of each sample was rotary evaporated to a final volume of 0.5 and 1.0 mL for the days 12 and 179 samples, respectively. Each extract was stored at room temperature until GC × GC analysis.

GC × GC Analysis

Each extract was analyzed on a GC × GC system that employed a loop-jet modulator (Zoex Corporation, Lincoln, NE) installed in an Agilent 6890 gas chromatograph (Agilent, Wilmington, DE) configured with a 7683 series split/splitless auto-injector, two capillary gas chromatography columns, and a flame ionization detector. The description and operation of this type of modulator has been described in detail (Gaines and Frysinger, 2004). Each extract was injected in splitless mode and the purge vent was opened at 0.5 minutes. The inlet temperature was 295°C. The first-dimension column and the loop jet modulator reside in the main oven of the Agilent 6890 gas chromatograph. The second-dimension column is housed in a separate oven installed within the main GC oven. With this configuration, the temperature profiles of the first-dimension column, thermal modulator, and the second-dimension column can be independently programmed. The first-dimension column was a nonpolar 100% dimethyl polysiloxane phase (Restek Rtx-1 Crossbond, 7 m length, 0.10 mm I.D., 0.4 μm film thickness) that was programmed to remain isothermal at 35°C for 10 minutes and then ramped from 35 to 320C at 2°C min^{-1}. The modulation loop was deactivated fused silica (0.8 m length, 0.10 mm I.D.). The modulator cold jet gas was dry N_2, chilled with liquid Ar, with a constant flow rate of 5.0 L min^{-1}. The modulator hot jet air was heated to 110°C above the temperature of the first column. The hot jet was pulsed for 300 ms every 20 s (0.05 Hz). Second-dimension separations were performed on a 50% phenyl polysilphenylene-siloxane column (SGE BPX50, 0.82 m length, 0.10 mm I.D., 0.1 μm film thickness) that was programmed to remain isothermal at 70°C for 10 minutes and then ramped from 70 to 340°C at 2°C min^{-1}. The carrier gas was H_2 at a constant flow rate of 1.7 mL min^{-1}. The FID signal was sampled at 100 Hz. Peaks were identified with commercially available standards from Aldrich, National Institute of Standards and Technology (NIST), and Chiron (Trondheim, Norway). To compare the separation achieved by GC × GC versus traditional GC, the samples were also run on the above system with the thermal modulator turned off and the second oven temperature programmed at 100°C above the main oven temperature. The data from the latter step is referred to in this work as a traditional one-dimensional GC chromatogram.

Data Visualization

The GC × GC FID data was processed with GC Image software (GC Image, LLC, Lincoln NE; Reichenbach et al., 2003, 2004). Each GC × GC image was base-plane subtracted to remove the FID offset (Reichenbach et al., 2003). The intensity of each point in the GC × GC images was normalized to 17α(H)-21β(H)-hopane. This compound is often considered to be a conserved internal biomarker because it resists biodegradation on short time scales relevant to this study (Mills et al., 2003; Prince et al., 1994) and is not likely to biodegrade, evaporate, water wash, or photolytically degrade over extended time periods. Individual resolved peaks were automatically identified and integrated by the software. Chemical classes were identified by user-defined areas and collectively integrated as the sum of the individual peaks in the defined area. Sufficient first- and second-dimension retention time reproducibility from sample to sample allowed for direct point-by-point (810,000 points) mathematical operations (e.g., subtraction, division, or addition) between two chromatograms. GC × GC chromatograms shown in the figures were rotated to place *n*-alkane peaks at the bottom of the two-dimensional image.

Results and Discussion

Since there are no oil refineries in New England, a significant quantity of refined petroleum products travels via unmanned single-hulled barges along coastal water routes, where spills can and do occur. On April 27, 2003, while en route to the Mirant power plant on the Cape Cod Canal in Sandwich, Massachusetts, the barge *Bouchard 120* struck a submerged ledge at the entrance to Buzzards Bay, Massachusetts. The resulting oil spill released approximately 370,000 L of No. 6 fuel oil into Buzzards Bay (Figure 1). Within 24 hours, helicopter surveys showed a 20-km slick that eventually oiled ∼150 km of shoreline along the west and east coasts of Buzzards Bay. The cargo aboard the *Bouchard 120* was No. 6 fuel oil, sometimes called Bunker C. This type of oil is a residual fuel that is prepared from the remaining hydrocarbons once lighter constituents of crude oil have been removed at the refinery (Stout et al., 2002). The increasing demand for refined petroleum products has prompted oil companies to achieve higher refinery efficiencies, resulting in a higher density residual fuel at the end of the refining process. The viscosity

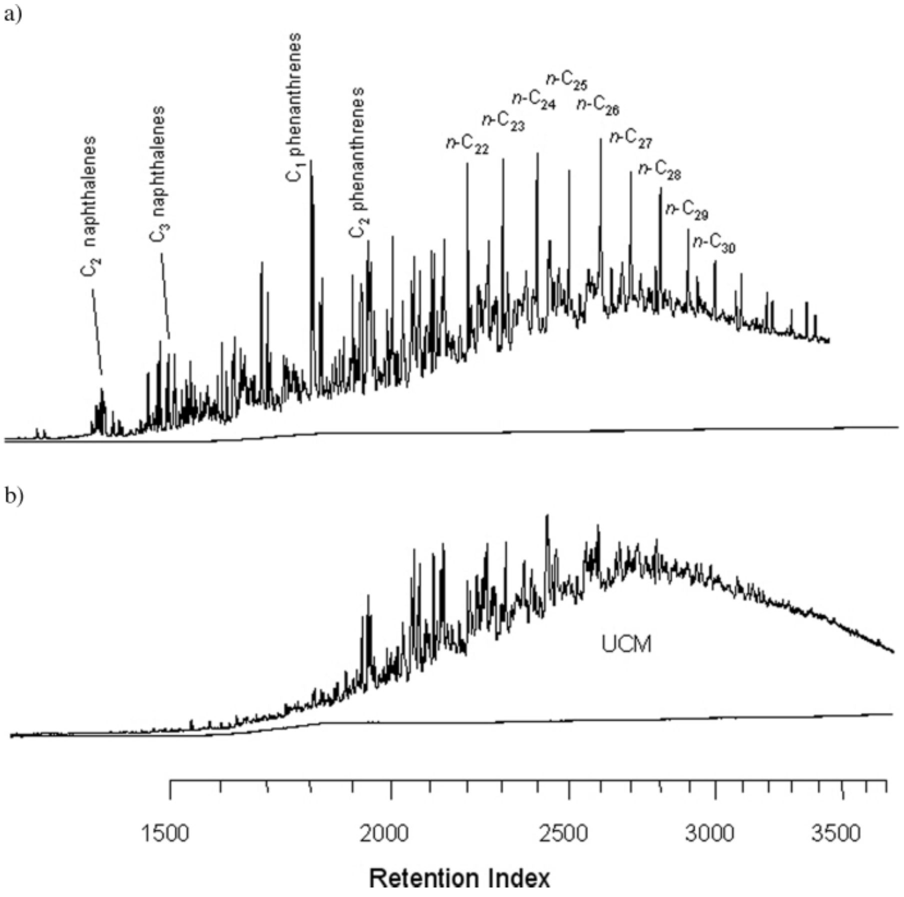

Figure 2. Traditional gas chromatograms of sample extracts from *Bouchard 120* oil-covered rocks collected (a) 12 days after the spill (May 9, 2003) and (b) 179 days after the spill (November 23, 2003). The retention index axis marks the n-C_{15} to n-C_{37} carbon number range. The retention index employed throughout this manuscript is the Kovats index (Kovats, 1965), which is useful for comparing compound retention between samples analyzed under varying temperature programs or between samples analyzed on different gas chromatographs.

of these fuels is such that they require pre-heating before use. They must also be mixed with more volatile and less viscous petroleum distillates (called cutting agents) to aid in transport, loading, and use in power generating engines. Because crude oils can differ and cutting agents vary, there is no standard No. 6 fuel oil (Stout et al., 2002). The *Bouchard 120* cargo includes compounds with an n-alkane range from n-C_{10} to greater than n-C_{45} with most of the GC-detectable mass residing in an elution window between n-C_{15} and n-C_{37}. The oil also contains abundant alkylated naphthalenes and phenanthrenes that most likely stem from the cutting agent.

Figures 2a and 2b show the traditional gas chromatograms of extracts from oil-covered rocks collected on May 9 and November 23, 2003, after 12 and 179 days of weathering, respectively. These dates span the temporal range of samples collected. Although there have been numerous petroleum spills in Buzzards Bay over the past 50 years, this study site (Nyes Neck beach) was chosen because it was directly impacted by this oil spill, it is a barrier beach in a relatively high energy environment, and it is easily accessible from our laboratory in Woods Hole, Massachusetts. Because of the completed beach clean-up efforts of the responsible party, it was difficult to acquire samples after day 179. The chromatograms reveal a complex mixture of hydrocarbons that elutes mainly between n-C_{15} to n-C_{37} alkanes (retention index 1500–3700). Significant differences in these chromatograms are apparent. For example, the n-alkane peaks, which were prominent in the day 12 chromatogram, are not discernable in the day 179 chromatogram. Also, most of the alkylated naphthalene and phenanthrene peaks eluting before n-C_{18} were also lost over this time interval. These changes are likely from the combined weathering effects of biodegradation, water washing, and evaporation. The end result of nearly six months of weathering is a mixture of petroleum hydrocarbons that appear as a UCM hump in the gas chromatogram.

GC × GC chromatograms of the slightly weathered day 12 sample are shown in Figures 3a and 3b, in which select peaks are annotated in the former (Table 1) and distinct chemical classes in the latter. The data are displayed as color-contour plots, with blue representing low signal, white representing medium signal, and red representing a high signal. In order to visualize the minor peaks, the dynamic range that is plotted is often less than the total dynamic range of the sample. This result often "chops-off" the

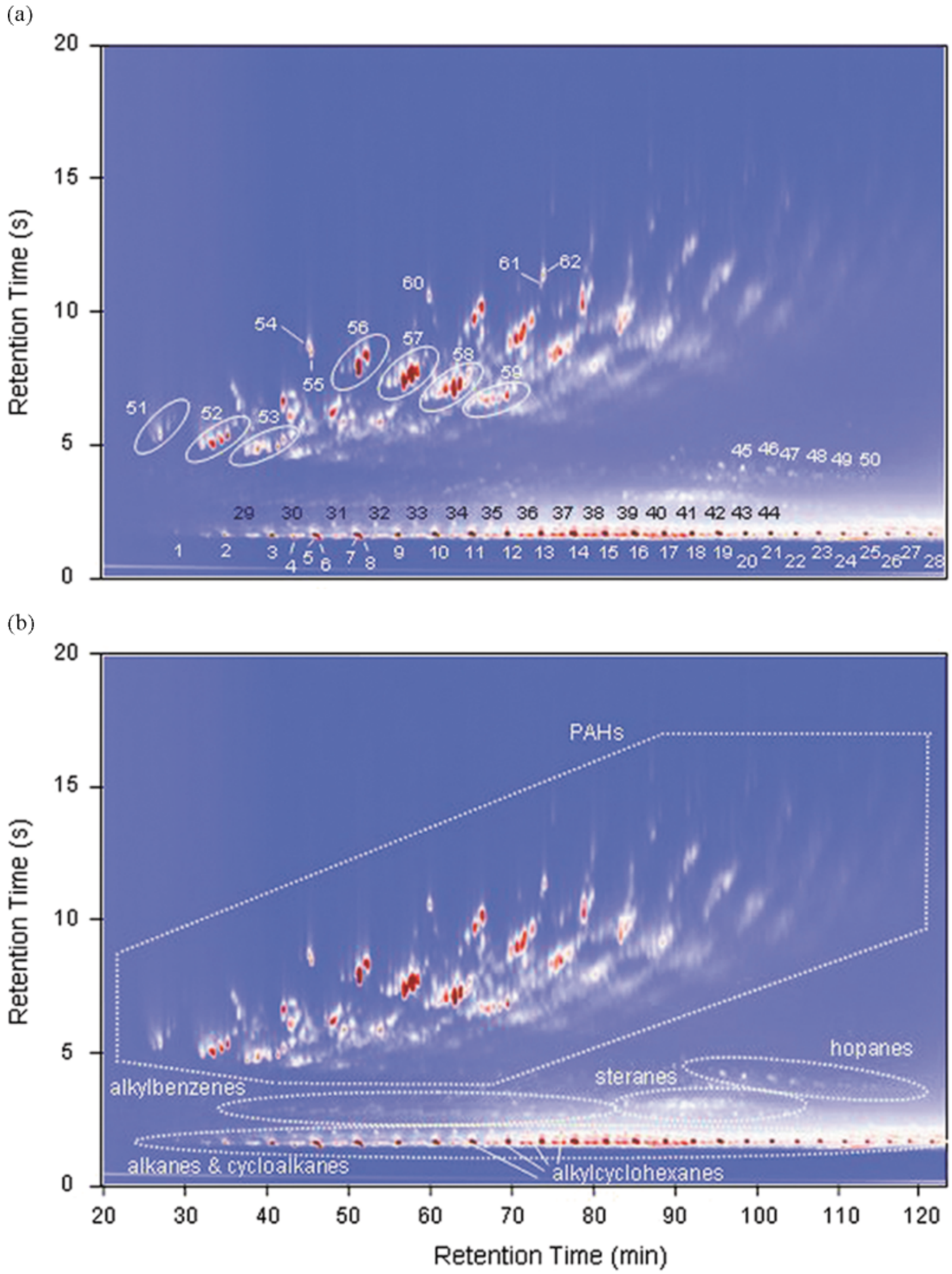

Figure 3. GC × GC color contour chromatograms of day 12 (May 9, 2003) sample with (a) individual compounds identified (Table 1) and (b) chemical classes annotated.

tops of the tallest peaks and produces a larger red area with white at the center of large peaks. A volatility-based separation with a nonpolar polydimethylsiloxane column produced essentially a boiling point separation along the x-axis. A polarity-based separation with a 50% phenyl-substituted polydimethylsiloxane column yielded chemical class-type separation along the y-axis. In the second dimension, the least polar petroleum classes observed in this sample, the branched and normal alkanes, have the least retention on the second column and are located at the bottom of the chromatogram. The most polar classes, multi-ring PAHs, have the greatest retention on the second column and are located near the top of the chromatogram. The cycloalkanes appear in bands just above the branched alkanes. The first of the cyclohexane bands contain the numerous one-ring alkylcycloalkanes, including the alkylcyclohexanes and alkylcyclopentanes. Other petroleum components of interest shown in Figure 3a are the

Table 1. Peak number and identification table for compounds numbered in Figure 3a

Peak no.	Compound name	Peak no.	Compound name
1	n-C_{14}	32	n-dodecylcyclohexane
2	n-C_{15}	33	n-tridecylcyclohexane
3	n-C_{16}	34	n-tetradecylcyclohexane
4	Norpristane	35	n-pentadecylcyclohexane
5	n-C_{17}	36	n-hexadecylcyclohexane
6	Pristane	37	n-heptadecylcyclohexane
7	n-C_{18}	38	n-octadecylcyclohexane
8	Phytane	39	n-nonadecylcyclohexane
9	n-C_{19}	40	n-eicosylcyclohexane
10	n-C_{20}	41	n-heneicosylcyclohexane
11	n-C_{21}	42	n-docosylcyclohexane
12	n-C_{22}	43	n-tricosylcyclohexane
13	n-C_{23}	44	n-tetracosylcyclohexane
14	n-C_{24}	45	$17\alpha(H),21\beta(H)$-hopane
15	n-C_{25}	46	Homohopane S&R epimers
16	n-C_{26}	47	Bishomohopane S&R epimers
17	n-C_{27}	48	Trishomohopane S&R epimers
18	n-C_{28}	49	Tetrahomohopane S&R epimers
19	n-C_{29}	50	Petakishomohopane S&R epimers
20	n-C_{30}	51	C_2-naphthalenes
21	n-C_{31}	52	C_3-naphthalenes
22	n-C_{32}	53	C_4-naphthalenes
23	n-C_{33}	54	Phenanthrene
24	n-C_{34}	55	Anthracene
25	n-C_{35}	56	C_1-phenanthrenes
26	n-C_{36}	57	C_2-phenanthrenes
27	n-C_{37}	58	C_3-phenanthrenes
28	n-C_{38}	59	C_4-phenanthrenes
29	n-nonylcyclohexane	60	Pyrene
30	n-decylcyclohexane	61	Benz[*a*]anthracene
31	n-undecylcyclohexane	62	Chrysene

sterane and hopane biomarkers. Chemical class regions were drawn and identified in Figure 3b so that one could rapidly determine changes from weathering in these regions.

Qualitative Analysis of Oil Spill Weathering with GC × GC Chromatogram Comparisons

To identify the compositional changes of the oil during weathering, GC × GC chromatograms are shown for day 12 (Figures 4a and 5a) and day 179 (Figures 4b and 5b). Each chromatogram is normalized and scaled to the conserved biomarker $17\alpha(H)$-$21\beta(H)$-hopane (marked with star) (Prince et al., 1994). In Figures 4a and 4b, the data are viewed as color-contour plots. Alternatively, GC × GC data can be viewed as three-dimensional images or mountain plots such as those shown in Figures 5a and 5b. These views are ideal for displaying relative differences between different components in the samples from varying viewpoints and aspect ratios. Extreme differences in the hydrocarbon composition of the two samples are readily apparent in both views.

Difference, ratio, and addition chromatograms are more advanced image processing techniques that can be used to identify weathering progress between standard GC × GC chromatograms. In each case, the GC × GC data from the chromatograms for both the slightly weathered sample (day 12) and the heavily weathered sample (day 179) were either point-by-point subtracted, divided, or added respectively. To produce robust results, compound peaks in both chromatograms must have the same first- and second-dimension retention times. Table 2 lists

Table 2. A data registration comparison of two-dimensional GC × GC peak apex retention times for select compounds for the day 12 and 179 samples

	Day 12 9-May-2003		Day 179 23-Nov-2003	
Component	1st Dimension modulation #	2nd Dimension elution time (s)	1st Dimension modulation #	2nd Dimension elution time (s)
n-C_{24}	227	1.62	227	1.62
n-C_{34}	323	1.63	323	1.63
C_4-phenanthrene isomer	181	7.05	181	7.06
$17\alpha(H),21\beta(H)$-hopane	287	4.12	287	4.12

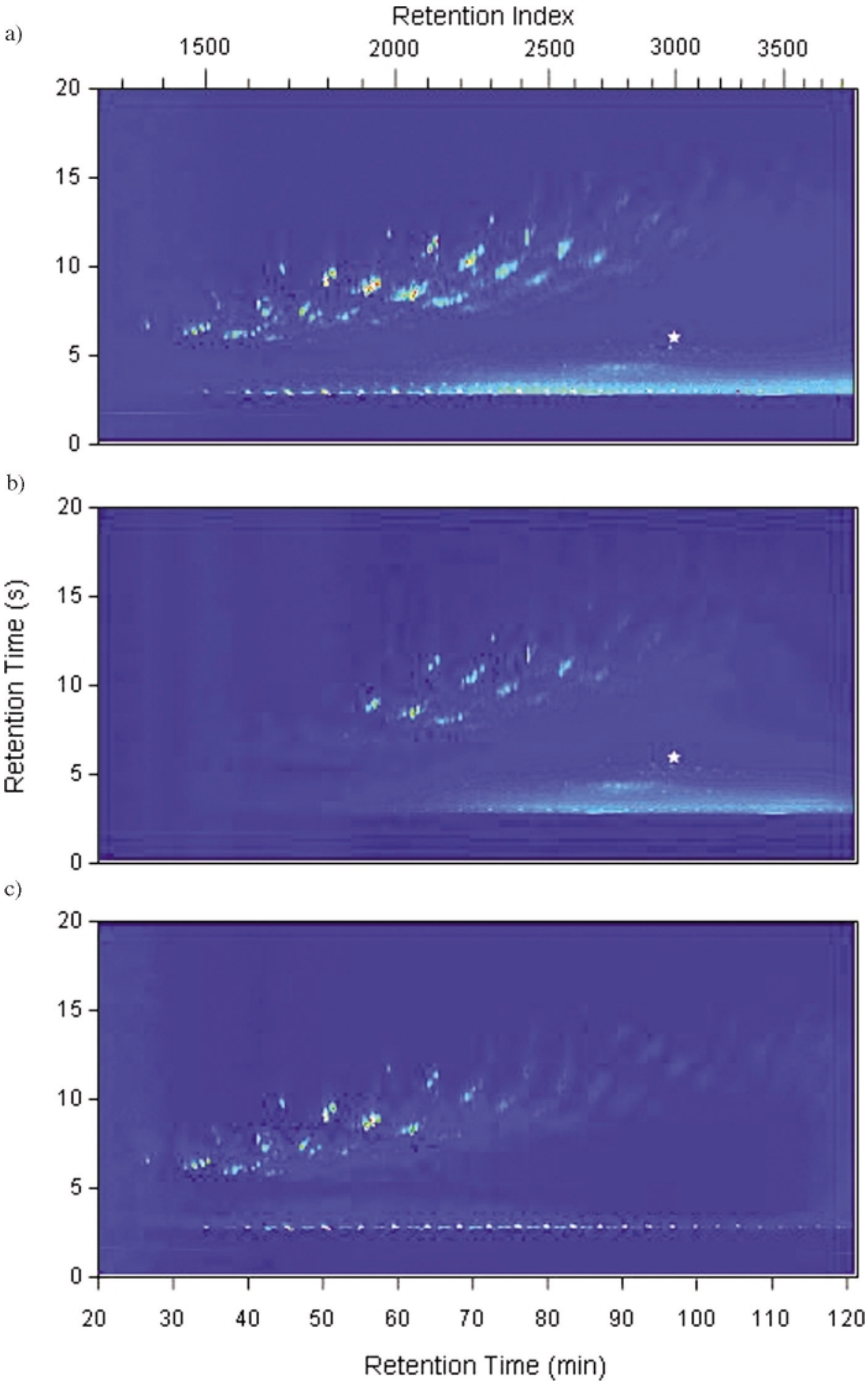

Figure 4. GC × GC color contour chromatograms of sample extracts from *Bouchard 120* oil-covered rocks collected (a) 12 days after the spill (May 9, 2003), and (b) 179 days after the spill (November 23, 2003). The conserved standard 17α(H)-21β(H)-hopane is marked with a star. The difference chromatogram produced by the subtraction of Figure 4b from Figure 4a is shown in Figure 4c.

the modulation number (a measure of first-dimension retention time) and second-dimension retention time for the peak apex for n-C$_{24}$, n-C$_{34}$, a C$_4$-phenanthrene isomer, and 17α(H)-21β(H)-hopane. The results show reproducible data registration between both samples.

The difference chromatogram generated by subtracting the heavily weathered sample (day 179) from the slightly weathered sample (day 12) is shown in Figures 4c and 5c as color contour and mountain plots, respectively. The difference chromatograms provide a way to identify peaks that have changed in volume

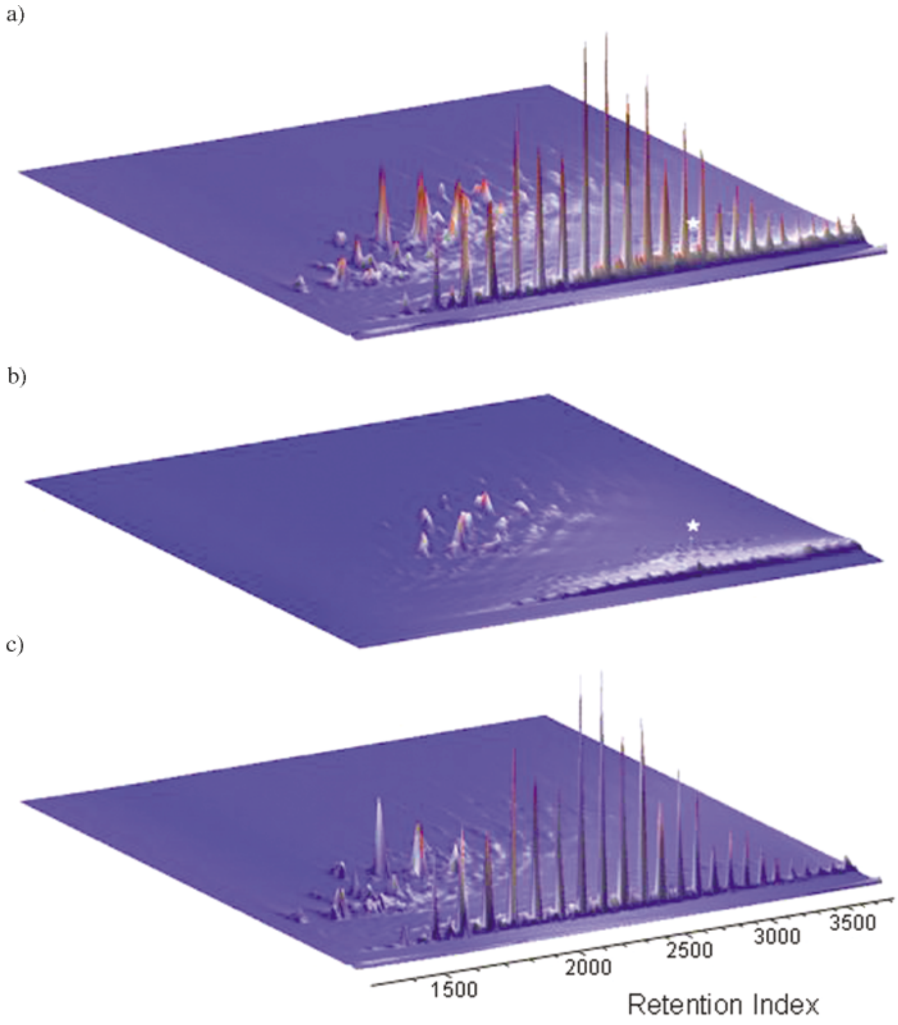

Figure 5. GC × GC mountain plot chromatogram of sample extracts from *Bouchard 120* oil-covered rocks collected (a) 12 days after the spill (May 9, 2003), and (b) 179 days after the spill (November 23, 2003). The conserved standard 17α(H)-21β(H)-hopane is marked with a star. The difference chromatogram produced by the subtraction of Figure 4b from Figure 4a is shown in Figure 4c.

relative to 17α(H)-21β(H)-hopane over this six-month weathering time frame. Compounds that have not changed in relative peak volume over this period appear to vanish from the chromatogram (subtracting a data value from itself yields zero). The peaks appearing in the GC × GC difference chromatogram are those that have changed in intensity value over time, which translates to those peaks that were lost through weathering. The *n*-alkane peaks were lost (presumably to biodegradation and evaporation) over time and therefore are prominent in the difference chromatogram. The peaks interdispersed between the *n*-alkanes are the branched alkanes. These peaks were minimally degraded and so are less prominent in the difference chromatogram. The lower molecular weight PAHs, specifically alkylated naphthalenes, appear as large peaks in the difference chromatogram at less than retention index 2100, most likely due to the combined weathering effects of evaporation, water washing, and possibly biodegradation. The sterane and hopane peaks are relatively recalcitrant to weathering over this six-month period so these peaks appear to vanish in the difference chromatogram. An enlargement of the n-C_{15} and n-C_{25}region of the difference chromatogram is shown in Figure 6a.

GC × GC ratio chromatograms are another way to identify compositional changes during weathering. Figure 6b is a difference plot resulting from the division of the slightly weathered sample (day 12) by the heavily weathered sample (day 179). Peaks colored red are for those compounds that exhibited the largest relative loss from weathering. Peaks colored white showed only a modest relative loss, and peaks colored blue (i.e., not visible) showed little or no loss. The transition for compounds lost in day 12 relative to day 179 to those nearly conserved begins at about n-C_{19}. Two exceptions to this trend are the PAHs, which have second-dimension retention times greater than 4 s, and continue to show losses until around n-C_{21}. The other exception is the *n*-alkanes with loss of signal through n-C_{25}. This image shows that alkanes and aromatics in the n-C_{19} to n-C_{25} range are more likely to be weathered than one- and two-ring cyclolkanes and alkylbenzenes.

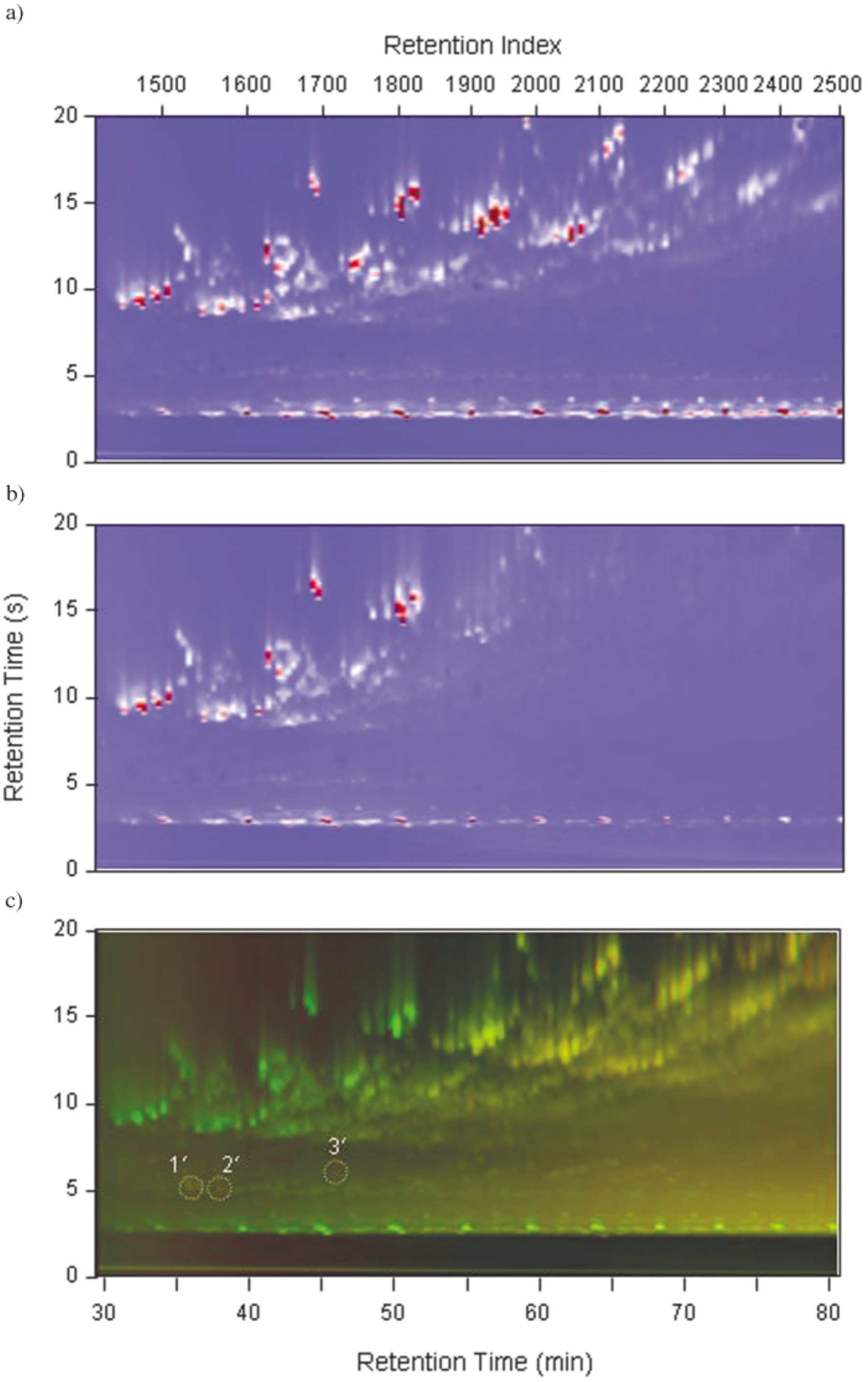

Figure 6. Enlarged GC × GC color contour (a) difference chromatogram, (b) ratio chromatogram, and (c) addition chromatogram. The addition chromatogram was produced using both color and intensity values for each chromatogram. All the peaks in the day 12 (May 9, 2003) chromatogram were assigned the color green, while all the peaks from the day 179 (November 23, 2003) chromatogram were assigned the color red. Compounds that are present in one chromatogram but are absent in the other appear either green or red. However, compounds that are present in both chromatograms appear yellow. Red peaks at the left of the chromatogram (labeled 1′, 2′, and 3′ in Figure 6c) indicate either that these compounds were not present in any appreciable amount in the day 12 chromatogram or that these compounds are preferentially conserved while proximal compounds are lost during oil weathering.

A third way to visualize compositional changes with weathering is a GC × GC addition chromatogram shown in Figure 6c. This data visualization method discriminates peaks using both a color and a color intensity value to distinguish between day 12 and 179 data samples. In this figure, the colors green and red were assigned to each pixel from the GC × GC chromatograms of days 12 and 179, respectively, and then the images were added together. If a pixel has a large intensity value in one image but not the other, it will be bright green or red, signifying a high value for a given sample. If it has a large intensity value in both, the red plus green pixels yield yellow, which signifies a high value for both samples. If a pixel has a small color intensity value, it will remain colored but will not appear bright. Figure 6c shows the loss of compounds eluting before n-C_{19} as peaks are colored bright green on the left of the chromatogram. A left-to-right transition from bright green to bright yellow is consistent with evaporative weathering processes. However, green regions also extend farther at the top of the chromatogram, indicating a preferential loss of aromatics. This loss of more polar (water soluble) PAHs again reveals a water washing component to the weathering. The n-alkane homologous series across the bottom of the chromatogram is green throughout the chromatogram, indicating that high-molecular-weight n-alkanes are removed while other compounds with equal carbon number are not. This also indicates that biodegradation is contributing to the weathering of the No. 6 fuel oil at that site. Red peaks at the left of the chromatogram (labeled 1′, 2′, and 3′ in Figure 6c) mean either that these compounds were not present in any appreciable amount in the day 12 sample or that these compounds are preferentially conserved when proximal compounds are lost. These compounds have second-dimension retention times consistent with either multi-ring cycloalkanes or alklybenzenes.

Quantitative Analysis of Oil Spill Weathering

One of the benefits of using a flame ionization detector with GC × GC is that the detector response does not vary widely for different compounds. Given this advantage, a single GC × GC-FID analysis can provide a complete and quantitative inventory of petroleum hydrocarbon classes present in a sample extract. As mentioned previously, each chromatogram was normalized and scaled to the conserved biomarker $17\alpha(H)$-$21\beta(H)$-hopane (Prince et al., 1994) prior to peak integration. This approach assumes that this hopane is recalcitrant to the weathering processes of evaporation, water washing, biodegradation, and photolysis. Hence, the resulting data comparisons are of absolute compositional changes over this six month time frame.

The five chemical classes identified in Figure 3b, 1) alkanes and cycloalkanes (normal, branched, and monocyclic), 2) alkylbenzenes, 3) hopanes, 4) steranes, and 5) PAHs, were integrated. The integration results are presented in terms of percent composition (Table 3). Peaks not specifically included in one of those five chemical classes (Figure 3b) are classified as Other. The regions labeled as alkanes, alkylbenzenes, and PAHs all decreased in relative amount over the six-month weathering period (Table 3). There were significant losses of n-alkanes, presumably from evaporation and biodegradation, but the relative losses of the alkane group nearly matched the losses of the PAHs. The loss of PAHs was mainly due to the relatively lighter naphthalenes evaporating and water washing from the spilled product. Conversely, the sterane and hopane biomarkers as well as other unclassified compounds (Other) increased their relative amount, revealing their environmental recalcitrance when compared with the alkanes and PAHs. These results indicate that the UCM in traditional gas chromatograms (e.g., Figure 2b) for the day 179 sample is nearly half PAHs and the remainder is mainly steranes, hopanes, and unresolved saturated compounds.

Figure 7 is a comparison of the relative percent loss for a homologous series of n-alkanes, n-alkylcyclohexanes, and some isoprenoid branched alkanes (norpristane, pristane, and

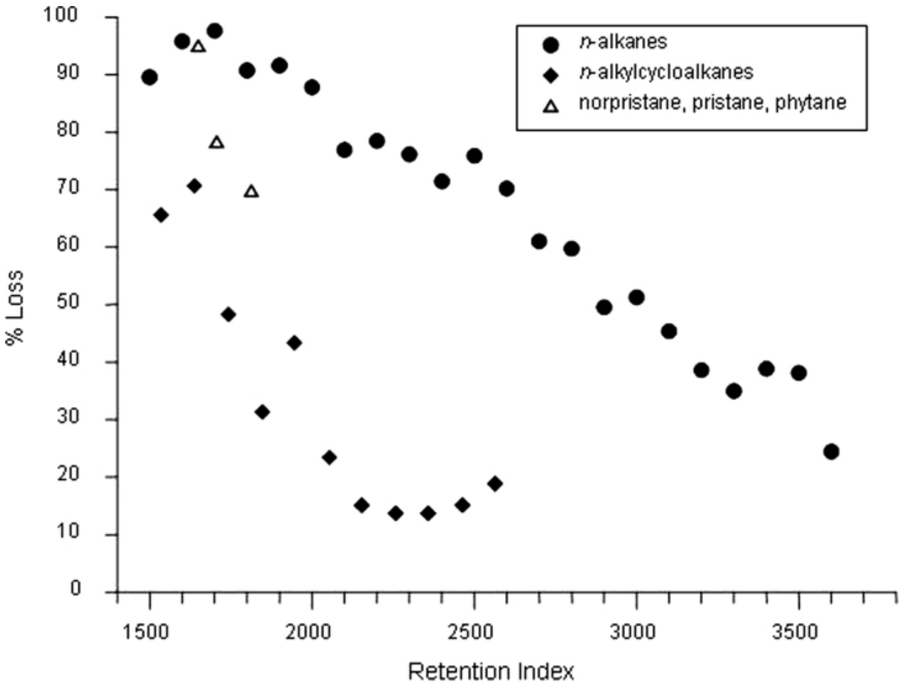

Figure 7. Percent losses of select hydrocarbons from *Bouchard 120* oil-covered rocks collected at Nyes Neck after six months of weathering.

Table 3. *The distribution of chemical classes at Nyes Neck beach after day 12 and 179 following the* Bouchard 120 *oil spill (see Figure 3b for key)*

Compound class	Day 12 9-May-2003 % of total	Day 179 23-November-2003 % of total	% change from day 12 to day 179[a]
alkanes and cycloalkanes	35.9	34.5	−3.9
alkylbenzenes	4.4	4.2	−4.5
PAHs	52.1	46.5	−10.7
steranes	2.3	4.1	+78
hopanes	1.4	2.5	+79
Other Compounds	3.9	8.3	+113

[a] $\% \text{ Change} = \frac{(\text{volume Day 179} - \text{volume Day 12})}{(\text{volume Day 12})} \times 100.$

phytane). The data are presented by retention index because compounds that have similar retention indices are assumed to have similar tendencies to evaporate. Since these saturates have very low water solubilities (Eastcott et al., 1988), they all should be affected by water washing in a similar manner. (We recognize that this is a simplistic approach, and efforts to use more highly refined models are underway; Arey et al., 2005.) Due to the minimal water partitioning properties of the saturated compounds, it is likely that the dominant removal modes of the low-molecular-weight saturates of this No. 6 fuel oil are evaporation and biodegradation. The *n*-alkanes show a near constant loss of 90 to 100% oil for retention indices of 1500 to 2000 and then an ordered drop-off to only 20% loss at retention index of 3600. The *n*-alkylcyclohexanes only have 30 to 60% loss in the retention indices of 1500 to 2000 and a nearly constant loss of 15% from 2100 to 2600. The differences in weathering loss between these compounds with similar tendencies to evaporate and water wash highlight ways to discriminate weathering patterns. In this case, these results show how susceptible *n*-alkanes are to biodegradation relative to *n*-alkylcyclohexanes once the evaporation component is removed.

Summary

GC × GC analysis of samples from the *Bouchard 120* oil spill have documented a transition in resolved hydrocarbons from *n*-alkane to PAH-dominated chromatograms. In the course of six months, 20 to 100% of the *n*-alkanes were removed, while steranes and hopanes have changed very little. Difference chromatograms and other image-based techniques readily showed major trends in weathering patterns and should facilitate future studies involving GC × GC analysis of petroleum hydrocarbons in the environment. These tools will be useful in source identification and monitoring natural and enhanced bioremediation of petroleum hydrocarbons (Swannell et al., 1996).

Future efforts, which will include many more samples collected over the course of this spill event, will focus on modeling the overall contributions of biodegradation, evaporation, and water washing during the first six months after the spill (Arey et al., 2005).

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