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RESEARCH NOTE

Field Trial Comparing Two Materials for Marine Oil Sheen Sampling

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The California Department of Fish and Wildlife (CDFW) uses fiberglass material for forensic analysis of oil sheens, while the United States Coast Guard (USCG) method uses a tetrafluoroetheylene-fluorocarbon (TFE-fluorocarbon) polymer net. We performed a field trial of these two materials by sampling natural oil seeps, two in Santa Monica Bay, and three sheen areas in the Santa Barbara Channel. Though the fiberglass material did collect less mass on some trials, the forensic chemistry results demonstrated that both materials were satisfactory for purposes of chemical forensic analysis as each pair of the sampling materials yielded results that were consistent with a common oil seep source.

Key words: fiberglass, fingerprint, oil, sheen, TFE-fluorocarbon polymer

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The current United States Coast Guard (USCG) method for the collection of petroleum sheens from a water surface utilizes a tetrafluoroetheylene-fluorocarbon (TFE-fluorocarbon polymer), also known as Teflon®, net (Greimann et al. 1995; Plourde et al. 1995). The TFE-fluorocarbon polymer net approach was published in 1995 by USCG staff who sought to improve upon the American Society for Testing and Materials (ASTM) standard practice for Sampling Waterborne Oils (ASTM method D4489) that uses the decanting method and the TFE-fluorocarbon polymer strip adsorption techniques. Their research determined that the TFE-fluorocarbon polymer net captured a greater mass of sheen material than the TFE-fluorocarbon strips. A greater mass of sheen helps improve analyte detection and the resolving power of the subsequent chemical analysis to fingerprint the source of petroleum hydrocarbons collected. They also compared nylon net to TFE-fluorocarbon polymer net and found that the TFE-fluorocarbon polymer net performed better by a factor of three in capturing sheen (Plourde et al. 1995; Greimann et al. 1995). At that time, the TFE-fluorocarbon polymer net cost $25; the current market price is $54.

The California Department of Fish and Wildlife (CDFW) Office of Spill Prevention and Response (OSPR) has, since the early 1990s, used a different but still non-reactive material to collect petroleum sheen samples from water. The kits supplied to CDFW law enforcement and field staff contain 3"x12" strips of fiberglass, with four strips per jar. The total material cost of these four strips of fiberglass is approximately $2.18, including the solvent rinse that is done on them in the laboratory prior to use. In the field, the strips are put into contact with the sheen to have it adsorb to the fiberglass material, and then the strips are packed into a certified pre-cleaned glass jar with a TFE-fluorocarbon-lined lid for shipment to the lab where they are analyzed.

In 2012 and 2015, CDFW-OSPR had opportunities to collect environmental samples near the Chevron El Segundo Refinery in a collaborative effort with Chevron staff. The Chevron refinery is located on the Santa Monica Bay in El Segundo, California. There are at least three known natural oil seeps in Santa Monica Bay that our team had interest in sampling for the purposes of a forensic fingerprint analysis, with two of these seeps being known to frequently emit oil. Seeps in Santa Monica Bay have been reported to emit an estimated 100 to 1000 tons (90,718 to 907,185 kg) of oil per year (Kvenvolden and Cooper 2003). In 2015, we added three additional sampling sites at known oil seeps near Santa Barbara California, to allow a more robust comparison of these two sheen sampling materials. Natural oil seeps are common in the Santa Barbara area (Hornafius et al. 1999; Kvenvolden and Cooper 2003; Lorenson et al. 2009). Our goal was to evaluate whether, under field test conditions, the material used to collect the oil sheen affected the results of the forensic analysis.

We obtained fiberglass materials from CDFW-OSPR (fiberglass strips and jar) supplies and purchased TFE-fluorocarbon polymer nets. On 24 April 2012 and 28 January 2015, we set out onto Santa Monica Bay aboard a Chevron owned vessel, and proceeded to Seep 1 where we encountered an oily sheen, and then to Seep 2 where we found another oily sheen (see Table 1 for location coordinates). At each of these seeps, the TFE-fluorocarbon polymer net was attached to a metal clip on the end of a wooden dowel rod approximately 1.2 m (4 ft) in length and swept through the sheen five times. Then the TFE-fluorocarbon polymer net, now containing the oil sheen, was removed from the hoop and packed into a glass jar with a TFE-fluorocarbon-lined lid. Similarly, the four fiberglass strips were attached to the wooden rod in a similar manner and swept through the sheen five times, then removed from the clip and packed into a glass jar with a TFE-fluorocarbon-lined lid. The sampling was performed using both a TFE net and the fiberglass strips at the same location to maximize the probability that the same area of sheen was being sampled with each material. The sheens observed and sampled were a mixture of rainbow-colored sheen and silvery sheen, indicating a variety of oil thicknesses present on the water surface. On 30 January 2015, we sampled the Santa Barbara seeps in the same manner as the Santa Monica Bay locations while onboard a CDFW patrol vessel. The Santa Barbara area locations are known as the Platform A, Coal Oil Point, and Summerland seeps. The sample types and locations are presented and described in Table 1.

We transported the Santa Monica and Santa Barbara sheen samples to the CDFW-OSPR laboratory in Rancho Cordova, CA, for forensic analyses. All location names were removed from the sampling documentation that was delivered to the laboratory with the samples, obscuring the location-specific pairings of the fiberglass and TFE net samples to laboratory staff.

Forensic analysis was performed using methods described in ASTM D5739, Standard Practice for Oil Spill Source Identification by Gas Chromatography and Positive Ion Electron Impact Low Resolution Mass Spectrometry (ASTM, 2006). Samples were extracted and

Table 1. Sample collection types and locations of sheen samples that were collected, with result indicating if mass collected was sufficient for forensic chemical analysis.

Region	Site/Sample Name	Location Coordinates	Date	TFE-fc Net: sufficient mass[a]	Fiberglass: sufficient mass[a]
Santa Monica Bay	Seep 1	N 33.82961, W 118.42580	2012	Yes	Yes
Santa Monica Bay	Seep 2	N 33.86797, W 118.49289	2012	Yes	Yes
Santa Monica Bay	Seep 1	N 33.83033, W 118.42867	2015	Yes	No
Santa Monica Bay	Seep 2	N 33.86260, W 118.49017	2015	Yes	No
Santa Barbara Channel	Platform A	N 34.33144, W 119.61337	2015	Yes	Yes
Santa Barbara Channel	Coal Oil Point	N 34.38081, W 119.78531	2015	Yes	Yes
Santa Barbara Channel	Summerland	N 34.41485, W 119.59993	2015	Yes	Yes

[a] Determination of whether sufficient mass was collected was made by the analytical chemist, based upon whether there was enough sample, and therefore signal from the detector, present to allow for a forensic evaluation.

prepared with methylene chloride and the concentration determined. A portion of the extract was adjusted to 25 mg/mL and analyzed by Gas Chromatography/Mass Spectrometer (GC/MS, Agilent 6890/5973 gas chromatograph mass spectrometer equipped with a 30-m J & W DB-5MS chromatographic column) as a screening step.

Each of the whole extracts was screened by gas chromatography mass spectrometry and compared to the results from the other samples of the trial. Confirmation analysis was performed on samples identified as possible matches. The extracts were base-washed three times, and then the solvent was exchanged to hexane. The extracts were separated into aliphatic and aromatic fractions using a packed column of activated neutral alumina. Sample concentration for each fraction was adjusted to 20 mg/mL, spiked with appropriate internal standards, and then analyzed by GC/MS. No reference standards or standards from a library of existing potential source chromatograms were used in this work.

A Total Ion Chromatogram (TIC) and a series of Extracted Ion Chromatograms (EIC) were generated by the GC/MS for each fraction of the sample (aliphatic and aromatic). In addition to common petroleum hydrocarbon constituents, like paraffins, isoparaffins, naphthenes, isoprenoids, and others, over forty extracted ions including specific biomarkers found in petroleum hydrocarbons known to be more resistant to weathering were compared using visual overlay to the results from the other samples of the trial. Ion profiles of biomarkers such as hopanes and steranes, known to be more resistant to weathering, were also compared.

The TIC and generated extracted ion chromatograms were used to compare the sample to the results from the other samples of the trial. Where sample concentration permitted, characteristic ions for the various classes of compounds shown in Table 2 were extracted and compared for each sample. Final conclusions were presented as either consistent or not consistent with a common source, or inconclusive.

Table 2. Compound classes and retention time ranges, from chromatograms, used for forensic fingerprint analysis.

Class of compound	Carbon retention range (beginning)	Carbon retention range (end)
Alkanes	C8	C40
Isoparafins	C8	C28
Alkylcyclohexanes	C8	C28
Alkylbenzenes	C4	C4
Bicyclanes	C8	C20
Polycyclic Aromatic Hydrocarbons	C8	C40
Hopanes	C28	C34
Steranes	C20	C29
Monoaromatic Steranes	C21	C30
Triaromatic Steranes	C26	C30

The forensic chemists confirmed that significantly weathered petroleum hydrocarbons in the range of C14–C36 were present in all samples collected and were consistent with a common source in both 2012 paired samples and three of the five paired samples from the 2015 sampling effort. In the two cases where determinations could not be made for the paired samples, the comparisons were limited because insufficient mass of sample was collected on the fiberglass matrix. The mass extracted from the fiberglass strips was less than that extracted from the TFE-fluorocarbon polymer nets at seep 1 in 2012. In 2015, the mass of hydrocarbons extracted from the fiberglass-collected samples from both seeps 1 and 2 in Santa Monica Bay was insufficient to assess the attribution of their sources using forensic chemistry techniques. However, from the same sites, the mass of hydrocarbons extracted from both of the TFE-fluorocarbon nets was enough to identify that the samples originated from a common source, and neither of those samples needed their scale adjusted to produce usable overlays from the chromatograms that they produced. The paired TFE-fluorocarbon and fiberglass strip collected samples used at the three Santa Barbara area sites in 2015 all contained sufficient mass to allow the analysis and identification that those hydrocarbons were from a common source.

Forensic chemistry techniques, using chromatographic traces, produced evidence that both materials, fiberglass strips and TFE-fluorocarbon, collected samples that accurately identified each sheen as consistent with a common source, so long as enough mass was present to do so. Differences in the mass of hydrocarbons collected from each sheen source, as indicated primarily by the differences in detector response of the forensic chemist's instrumentation, were observed between fiberglass and the TFE-fluorocarbon materials, with the fiberglass material collecting less mass in three instances. For the Santa Barbara area samples, all three paired sets were correctly identified as originating from a common source, even though they were submitted 'blind' to the laboratory by the removal of source information in the accompanying documentation. This suggests that while the fiberglass strips were often less efficient than the TFE-fluorocarbon nets at collecting sheen mass in this field trial, they ultimately produced a forensic fingerprint result "consistent with a common source" when compared with the TFE-fluorocarbon polymer net sample results from the same seep. Samplers made efforts to collect from the same area of sheens with each of the paired TFE net and the fiberglass strip materials. However, because this was a field trial where precise sampling conditions were not controlled, including the proportions of each sheen encountered, the possibility remains that mass differences detected in the laboratory were affected by the sampling materials contacting different masses of sheen during the sampling process.

It is reasonable to expect that a chemically non-reactive substrate used to collect a sample of petroleum sheen would produce the same forensic result as another chemically non-reactive material. Barring evidence of some type of selective or biased adsorption or collection of hydrocarbons based on size ranges, or secondary or tertiary structures (i.e., aromatic rings, straight chain, or branched hydrocarbons), this result would be expected. However, since the literature is lacking in citations related to the use of fiberglass materials for this sampling purpose, this field trial is supportive evidence that this less expensive means of collecting sheen samples produces acceptable results once sufficient sample is adsorbed to the fiberglass. Further testing with more types of petroleum and distillate products and an increased number of replicates would be helpful in further evaluating this preliminary conclusion. Additionally, some form of sampling instructions or training materials for the samplers that is designed to aid them in obtaining a sufficient hydrocarbon mass when using the fiberglass material appears to be warranted.

It was evident that the on-water sampling of sheen using material attached to the end of a pole from a boat deck was simpler with TFE-fluorocarbon polymer nets than with the fiberglass strips. This was because the mechanics of collection were significantly easier with the net shape of the TFE-fluorocarbon polymer nets. The net was simple to maneuver through the sheen, while the fiberglass strips flexed and bent with each sweeping motion, making the strips less effective at collecting sheen material off the water surface. In fact, two samples taken using fiberglass at the Santa Monica area seeps in 2015 contained such a low mass of sheen material that they were not able to be successfully analyzed using forensic chemistry techniques. Nevertheless, considering the cost of the nets is greater than 20 times that of the four fiberglass strips, the comparability of the results suggest that the decision by CDFW to continue to use the fiberglass material is acceptable as long as sufficient mass of the sheen is collected. CDFW uses the fiberglass strips in routine evidence collection activities related to petroleum spill cases or forensic investigations such as when seabirds are found oiled near natural oil seeps. CDFW provides hundreds of oil sheen sampling kits to staff all over the State of California that contain the fiberglass strips, making the cost savings over TFE-fluorocarbon polymer nets significant at this scale of utilization.

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