Rapid Identification of *Deepwater Horizon* Oil Residues Using X-ray Fluorescence

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Ⓢ *Supporting Information*

ABSTRACT: Oil residues are found on Gulf of Mexico beaches due to the *Deepwater Horizon* (DWH) incident, alongside oil residues from natural seepage and other anthropogenic inputs. To identify the origin of oil residues found on beaches, especially after a spill, it is critical to have techniques that can be used in the field, can provide rapid identification, and can be used easily by response workers. Here we present the utility of a hand-held X-ray fluorescence (XRF) spectrometer to rapidly identify the origin of oil residues. When XRF data were coupled with a machine learning model, DWH samples could be distinguished from not-DWH samples with 95% accuracy. This approach enables the analysis of bulk samples without sample preparation, paving the way for utilizing XRF in the field for immediate oil residue source identification.
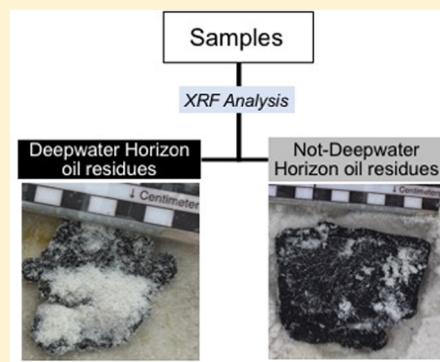
INTRODUCTION

The presence of oil residues in the marine environment is of both environmental and public concern.[1,2] Local communities, especially those with fishing-based or recreation-based economies, can experience significant financial losses as a result of oil contamination of public beaches, particularly in the aftermath of an oil spill.[3] Oil residues in the marine environment, however, can originate from a variety of different sources, including anthropogenic inputs, such as spills, as well as natural oil seeps.[4] Determining the origin of oil residues on beaches is fundamental to understanding the persistence of different types of oil in the coastal environment. Mixed inputs of oil from natural and anthropogenic origins are well-known, particularly in the Gulf of Mexico (GoM) following the *Deepwater Horizon* (DWH) incident,[5,6] as it is an area that has natural oil seeps[7,8] as well as anthropogenic inputs of oil.[9] It is also important to monitor persistent oil residues over time as they contain, among other chemicals, polycyclic aromatic hydrocarbons (PAHs), which can be toxic to humans and ecosystems.[10] Monitoring the persistence of a specific type of oil in the marine environment in the field can be challenging, although is a tractable problem once samples are collected and analyzed in the lab.

To determine the origin of oil in the marine environment, the chemical composition of oil, specifically the characterization of oil-derived hydrocarbon compounds known as biomarkers, is typically measured.[11,12] Well-defined methods of oil and biomarker analysis occur in specialized laboratories employing one-dimensional gas chromatography (GC) coupled to flame ionization detection (FID) or mass spectrometry (MS) as well as comprehensive two-dimensional

gas chromatography (GC×GC) coupled to either FID or time-of-flight MS (TOF-MS).[13] Bulk oil analysis methods such as Fourier transform infrared (FTIR) spectroscopy and thin layer chromatography with flame ionization detection (TLC-FID) are also employed to more generally characterize oil.[5,9,14] The aforementioned methods are robust in their applications but are both time and labor intensive, use harmful solvents, are destructive to the samples analyzed, and require the use of a specialized laboratory and a highly trained researcher. In contrast to lab-based approaches, field protocols based on physical and visual characteristics of oil residues have been developed.[15] While useful, these protocols rely on human interpretation and are not definitive in terms of distinguishing different inputs of oil. In this study, we sought to develop a rapid and portable approach that could be employed in the field to determine the origin of oil in different samples. A hand-held X-ray fluorescence (XRF) spectrometer was used to analyze samples for their elemental content.[16] A key benefit of this method is that it does not require time-consuming sample preparation steps, thus making it possible to analyze a large number of samples in a relatively short period of time. The method takes only minutes to complete from start to finish, whereas other analysis techniques can take hours. A second benefit is that this process is nondestructive, which allows for the preservation of samples.[17]

The XRF approach detailed here focuses on the analysis of elemental concentrations present in oil as a way to distinguish

Table 1. Rules and the Number of Each Sample Type Classified as either DWH or Non-DWH Oil by Each of These Rules

	rule[a]	classification	no. of DWH oil patties	no. of tar residues	no. of unknown oil residues	no. of non-oil samples[b]
rule 1	if Hg > 7 and Cu < 19[c]	not DWH		135	45	47
rule 2	if Ca > 2869, Zn < 31, and K < 245	DWH	276		1	
rule 3	if Sr < 189 and Ti < 729	not DWH			20	31
rule 4	if Cu < 19 and Fe < 15367	DWH	29			
rule 5	else	not DWH			4	7

[a]Individual rules have multiple clauses, and therefore, a single clause may be repeated between rules without redundancy or conflict. [b]Non-oil samples include samples that do not contain oil residues and are instead comprised of mud, peat, or wood. [c]Numbers represent concentrations of specific elements in ppm.

different inputs of oil. Specific metals, primarily nickel and vanadium, have previously been used to characterize oils from different sources.[18−20] This approach is successful in part because nickel and vanadium are two of the most abundant elements in oil. However, a variety of other metals are also consistently found in oil samples,[19] but their utility with respect to determining the source of the oil has not been extensively explored. Typically, a broad range of metals beyond nickel and vanadium are examined with the intent of understanding the toxicity of oil as well as how the concentrations of these elements may be altered as oil is weathered in the environment.[21,22] In studies related to the DWH incident, for example, chromium, aluminum, iron, magnesium, nickel, lead, thallium, vanadium, cobalt, zinc, copper, and mercury have all been examined.[21,23] Other studies have also measured the abundance of calcium, titanium, and strontium in crude oils.[24,25]

For the development of this XRF analytical approach, samples that had been collected from GoM beaches in Florida, Alabama, Mississippi, and Louisiana between 2012 and 2017 were utilized. Samples were analyzed in the laboratory to develop the XRF approach, but because the XRF spectrometer used is a hand-held system, the same approach could be utilized directly in the field. The samples analyzed included oil residues that originated from the 2010 DWH incident as well as oil from natural seeps, other anthropogenic spills, road asphalt, and samples that visually resembled oil but did not contain oil-derived hydrocarbons. Subsequent analysis of the element content data by machine learning approaches was then used to distinguish DWH oil residues from other inputs of oil and non-oil samples. The machine learning approaches employed included a rule-based classifier, which uses IF-THEN rules for its predictions, as well as a decision tree classifier, which is structurally organized as a flowchart-like structure. These two approaches were chosen on the basis of their interpretability, which, unlike traditional statistical approaches, produce outcomes in the form of element content data that can be directly deployed in the field for the interpretation of environmental samples.

EXPERIMENTAL SECTION

Sample Collection. Between June 2012 and June 2017, 119 individual oil residue samples were collected from GoM beaches as previously described.[9,14] This sample set includes oil patties originating from the DWH incident (62 samples), tar residues originating from natural seepage offshore (27 samples), unknown oil residues (13 samples, six of which also contain sand), and non-oil samples that have the appearance of oil but do not contain any oil residues (17 samples). All samples were collected in precombusted glass jars (450 °C, 8

h), shipped to Haverford College, and kept frozen until further analysis. The classification of these samples as DWH oil patties, tar residues, unknown oil residues, and non-oil samples was previously described (see refs 9 and 14).

X-ray Fluorescence of Samples. XRF spectroscopy was performed using an Oxford Instruments X-MET 7500 X-ray fluorescence spectrometer, a portable, hand-held device with detection limits on the scale of 1 ppm.[16] No extraction steps were performed on the samples prior to analysis. The minimum size of samples analyzed was approximately 2 cm × 3 cm × 1 cm. To consistently analyze the interior of each sample, sand patties and oil residues were sliced in half with a solvent-rinsed razor blade prior to analysis. Samples were placed on a Mylar circular window film (6 μm thick, 64 mm diameter) on the XRF X-ray detection site. The XRF standard "soil" method was used, with a 60 s detection time.[26] To capture the variation within individual samples, five data points were taken per sample, each the average of three measurements. Each of the five data points was taken sequentially from a different location on the inside of the sample, with a distance of approximately 2−5 mm between each data point. Element concentration data were therefore collected in triplicate for a total of 595 subsamples, representing 119 individual samples, each measured in five places. To evaluate the heterogeneity of the samples further, eight samples representing different GoM coastal beaches were solvent-extracted according to previously described methods (see ref 14), so that the resulting oil residue extracts and remaining unextractable materials (primarily sand and shells) could be analyzed separately from one another.[14] The extracts and unextracted residues were then dried overnight at room temperature prior to XRF analysis.

Machine Learning Analysis. The 595 XRF samples from 119 unique samples were used to train interpretable machine learning models to infer the presence or absence of DWH oil from XRF data. The element concentration data have been deposited with Figshare (DOI 10.6084/m9.figshare.7272644). All element concentrations were used as trainable features, with a binary class variable (origin of oil is DWH or not-DWH). The training set used to construct the model was comprised of a random selection of 66% of the samples (393 subsamples, 79 unique samples). The remaining 33% of the samples were held out as a test set (202 subsamples, 40 unique samples) so that the accuracy of the model with respect to unseen data could be determined. Subsamples from the same patty were grouped together into the training set or test set to ensure the model did not have prior exposure to samples similar to those in the test set. The PART rule-based classifier[27] and C4.5 decision tree classifier[28,29] were used for the binary classification task of determining if a sample contained oil residues from the DWH oil spill.

■ RESULTS AND DISCUSSION

Elements Detected by X-ray Fluorescence. A total of 25 elements were detected across the range of samples. In order of typical average abundance across all samples collected, the elements are calcium (Ca), iron (Fe), potassium (K), titanium (Ti), zirconium (Zr), strontium (Sr), manganese (Mn), vanadium (V), molybdenum (Mo), thorium (Th), barium (Ba), rubidium (Rb), nickel (Ni), cadmium (Cd), zinc (Zn), copper (Cu), lead (Pb), cobalt (Co), chromium (Cr), mercury (Hg), thallium (Tl), antimony (Sb), tantalum (Ta), selenium (Se), and gold (Au). The minimum, median, maximum, and first and third quartile concentrations of these elements for each sample type are provided (Table S1) along with the concentrations of all 25 elements for each sample category (Figures S1−S4). Variations in element concentrations are observed within and between the extracted oil residues and sand matrix when they are separated from one another (Table S5).

The Element Content Can Predict the Presence of DWH Oil. The rule-based and decision tree models yielded 96% and 95% classification accuracy, respectively (detailed in Figure S6). The two models made decisions based on very similar features, primarily considering Hg, Cu, Ca, Zn, K, Sr, Zr, and Fe (Table 1). The concentrations of these eight elements for all DWH and not-DWH samples are shown in Figure 1.
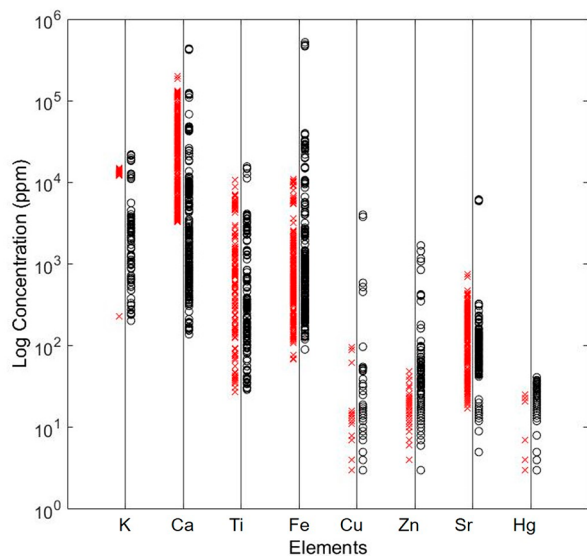

Figure 1. Concentrations of the eight elements used in the rule-based model shown for all samples. Black circles represent those classified as not-DWH samples, and red crosses represent those classified as DWH samples. Concentrations are on a logarithmic scale, and zero values are not shown.

Model Interpretation. Analysis of the model provides insight into the sample composition that enables the identification at 95−96% accuracy. Mixtures with sand play a key role in the identification parameters. For example, from the XRF analysis, we find that mercury is present in oil but is not sand (Figure S5), but DWH samples are identified by lower mercury contents (rule 1) because the presence of sand dilutes the mercury concentration present in the oil. Calcium is found at high levels in both extracted sand and extracted DWH oil (Figure S5), allowing DWH samples to be distinguished from all other samples (Table S1) that contain neither sand nor

DWH oil. Compared to the non-oil samples, the DWH patties have lower concentrations of Sr, Ti, and Cu (Table S1), allowing some of the samples in these categories to be separated from one another.

Implications. This study successfully utilizes bulk elemental analysis as determined by XRF coupled with machine learning analysis with decision tree and rule-based models to distinguish DWH from not-DWH oil residues with 95−96% accuracy. Each of the models trained can be easily simulated by humans and requires <10 basic comparisons to evaluate. These results allow for the potential of new samples to be directly analyzed in the field with a hand-held XRF spectrometer, with confirmation of oil origin using rules from the machine learning algorithm taking only a few minutes for each sample analyzed. For applications requiring rapid sample identification in the field, the method developed could provide direct and clear information to first responders and researchers, without the need for expensive, time-consuming, and environmentally unfriendly methods.

It is important to recognize that the rule-based models described here apply specifically to oil residues and non-oil samples that are collected from GoM beaches. To explore the broad applicability of this research, more samples containing different oil residues from a variety of environments would need to be examined. Other important considerations include developing a better understanding of the role of the oil-derived elements versus non-oil-derived elements in the model. The rules in the model described in this study include a mixture of elements originating from both the oil residues and other non-oil inputs, including those that are natural (e.g., sand, mud, and peat) and those that are anthropogenic (e.g., storage vessels and industrial inputs). To ground truth this approach and explore its broad applicability, chemical analysis of different oil samples of different types and from different reservoirs would be required with subsequent statistical analysis to determine whether there is significant variation in the elemental composition of oil alone. If the elemental compositions of different oils are statistically distinguishable from one another, then this approach could likely be widely applied to different oils spilled in different locations and combined with a variety of environmental matrices. While outside of the context of this current GoM-specific study, these analyses would be an important next step. Ultimately, testing this approach on samples collected from other locations contaminated with different oil residues will confirm the broader utility of this protocol and its potential to introduce a novel rapid analysis technique to the standard methods of oil spill identification. This method could support more direct and efficient communication between researchers and spill responders and increase the accessibility of information for the general public. The overall goal is to develop this method to a point where it can be adapted and utilized by other researchers and applied to oil residues analyses at any site where oil contamination is found.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.8b00589.

> Additional experimental data of the elemental content for each sample, including data for the separate analysis

of extracted oil and sand, and the decision tree developed for sample classification (PDF)

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Notes
The authors declare no competing financial interest.

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