## PROJECT INFORMATION

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|---|---|
| Project Director's Name* | Weihsueh Chiu |
| Organization* | Texas A&M University |
| Project Title* | Prioritizing Risks from Oil Spills: Supporting Decisions with Read-Across Using 21st Century Exposure and Toxicological Sciences |
| Reporting Period* | 6/15/2020-12/15/2020 |

**Note to Grantees: In sections 1 to 5, we ask you to highlight your accomplishments (including outputs and outcomes) through this grant award. These sections of the final grant report will be made available to the public.**

## 1. GOALS AND ACCOMPLISHMENTS

**1.1 Please restate the goals and objectives of your project.***

The project goal is to improve the risk-based decision-making framework for public health practitioners during oil spills by taking advantage of new technologies in exposure science and toxicology, two of the key areas identified in the 2017 National Academies report Using 21st Century Science to Improve Risk-Related Evaluations. Evaluation of public health impacts of oil spills has been largely based on information from a few specific chemical components ("known-knowns"). Approaches to examine the toxicity of the whole mixture (either "known-unknowns" or "unknown-unknowns") are lacking. This problem is exacerbated by the unknown and varying composition of crude oils and oil products, and additional complications of weathering, dispersants, additives, and proprietary blends. Moreover, individual targeted chemical analyses are time-consuming, and often infeasible during emergency response for all but a handful of substances. Clearly, the usual "bottom-up" approach of conducting risk evaluations based on adding up the toxicity of individual compounds is unlikely to be effective. As suggested in the 2017 National Academies report, our goal was to test whether new technologies to perform new "untargeted" exposomic analyses of chemical composition and human cell-based in vitro assays of bioactivity can substantially advance risk-based decision-making in the context of oil spills.

The project objectives were three-fold. First, we tested the hypothesis that rapid, high-dimensional/high content untargeted chemical characterization and in vitro biological activity profiling can prioritize the potential public health hazards of oil spill contaminated environmental samples. Second, we developed a framework for use of these new approaches for oil spill emergency response decision-making through a collaboration between researchers and practitioners. Third, researchers and practitioners worked together to develop several case studies to illustrate these applications.

**1.2 Describe the accomplishments of your project. You should include both the anticipated accomplishments that you outlined in your project proposal as well as any *unanticipated* accomplishments that have since occurred. Describe any activities you have conducted, programmatic progress made, or project benchmarks and milestones met.***

Our project's major accomplishments are as follows: (1) demonstrating the feasibility of rapid sample analysis using ion-mobility spectrometry/mass spectrometry (IMS-MS) to fingerprint as well as tentatively identify constituents in crude oils and refined petroleum products; (2) demonstrating the feasibility of human cell-based in vitro assays to screen and prioritize crude oil and refined petroleum products in terms of the biological activity; (3) engagement of stakeholders to develop and refine the data integration framework and its application to several case studies.

(1) IMS-MS for fingerprinting and constituent identification.

The complex chemical composition of crude oils presents many challenges for rapid chemical characterization in the case of a spill. A number of approaches are currently used to "fingerprint" petroleum-derived samples. Gas chromatography coupled with mass spectrometry (GC-MS) is the most common, albeit not very rapid, technique; however, with GC-MS alone, it is difficult to resolve the complex substances in crude oils. We demonstrated that IMS-MS, coupled with chem-informatic analyses, is an alternative high-throughput method for the chemical characterization of crude oils. Specifically, we analyzed 19 crude oil samples from on- and off-shore locations in the Gulf of Mexico region in the United States using both GC-MS (biomarkers, gasoline range hydrocarbons, and n-alkanes) and IMS-MS (untargeted analysis). Hierarchical clustering, principal component analysis, and nearest-neighbor-based classification were used to examine sample similarity and geographical groupings. We found that direct injection IMS-MS performed either equal or better than GC-MS in the classification of the origins of crude oils. In addition, IMS-MS greatly increased the sample analysis throughput (minutes versus hours per sample). Collectively, this study shows the utility of IMS-MS as a technique for rapid fingerprinting of complex samples and demonstrates its advantages over traditional GC-MS based analyses when used for decision-making in emergency situations. This work has been published in Environmental Toxicology and Chemistry (https://doi.org/10.1002/etc.4961).

In a second, we used samples of 6 petroleum refining-derived substances (US EPA High Production Volume (HPV) chemical categories of “Hydrocarbon solvents” (n=2) and “Lubricating oil basestocks” (n=4)). We obtained independent production batches of these samples to test the degree of variability within each substance, as well as the degree of sameness between substances that are currently classified into the same group (“Aromatic Hydrocarbons, Reformate-based” or “Base Oils (Paraffinic),” respectively) or HPV category. A total of 16 independent production run samples (2-3 per substance) were analyzed using direct injection IMS-MS (using varying ionization sources) to obtain their aliphatic and aromatic hydrocarbon chemical composition profile. Analytical features were filtered based on peak quality and abundance, and the individual features were then putatively identified using Kendrick mass defect analysis and collision cross section trends. Carbon number blocks and molecular classes of petroleum hydrocarbons and heteroatoms were also generated for each sample. These data were used to perform classification of the samples into groups. We found that, some compositional variability notwithstanding, production batch samples of the same substance were grouping together and substances from the same HPV category were also grouping together. These data demonstrate that despite chemical complexity of the petroleum substances, their “sameness” can be characterized using rapid chemical profiling enabled by IMS-MS. This work is being prepared for publication.

One unanticipated accomplishment of this project is the application of this technology to substances used to respond to oil spills. Specifically, when oil spills also involve fires, numerous fire suppression substances may be used that also can pose a risk to human health and the environment. Aqueous film-forming foams (AFFF) contain per- and polyfluoroalkyl substances (PFAS) - a class of compounds widely used as surfactants. PFAS are persistent organic pollutants that have been reported in waterways and drinking water systems across the United States. These substances are of interest to both regulatory agencies and the general public because of their persistence in the environment and association with adverse health effects. PFAS can be released in large quantities during industrial incidents because they are present in most firefighting foams used to suppress chemical fires, but AFFF composition is seldom disclosed, and their use elicits concerns from both regulatory agencies and the public because PFAS are persistent in the environment and potentially associated with adverse health effects. We demonstrated the use of coupled liquid chromatography, ion mobility spectrometry, and mass spectrometry (LC-IMS-MS) to rapidly characterize both known and unknown PFAS in AFFF. Ten AFFF formulations from seven brands were analyzed using LC-IMS-MS in both negative and positive ion modes. Untargeted analysis of the formulations was followed by feature identification of PFAS-like features utilizing database matching, mass defect and homologous series evaluation, and MS/MS fragmentation experiments. Across the tested AFFF formulations, we identified 33 homologous series; only ten of these homologous series have been previously reported. Among tested AFFF, the FireStopper (n = 85) contained the greatest number of PFAS-like features and Phos-Check contained zero. We therefore demonstrated that LC-IMS-MS-enabled untargeted analysis of complex formulations, followed by feature identification using data-processing algorithms, can be used for rapid exposure characterization of known and putative PFAS during fire suppression-related contamination events. This work has been published in Environmental Science and Technology (https://doi.org/10.1021/acs.est.0c04798).

(2) Use of human cell-based in vitro assays to screen and prioritize crude oil and refined petroleum products in terms of the biological activity.

One of the major challenges to using high throughput assays to test complex substances such as crude oil and petroleum products is determining bioavailable concentrations under in vitro conditions. Specifically, for in vitro testing, substances are commonly subjected to dimethyl sulfoxide (DMSO) extraction, and protein binding in cell culture media and dilution can all influence in vitro bioavailable concentrations. However, these in vitro factors have not been fully characterized. We therefore aimed to fill in these data gaps by characterizing the effects of these processes using both a defined mixture of analytical standards containing aliphatic and aromatic hydrocarbons, as well as 4 refined petroleum. Each substance was extracted with DMSO, and the protein binding in cell culture media was measured

by using solid-phase microextraction. Semiquantitative analysis for aliphatic and aromatic compounds was achieved via gas chromatography-mass spectrometry. Our results showed that DMSO selectively extracted polycyclic aromatic compounds (PACs) from test substances, and that chemical profiles of PACs across molecular classes remained consistent after extraction. With respect to protein binding, chemical profiles were retained at a lower dilution (higher concentration), but a greater dilution factor (i.e., lower concentration) resulted in higher protein binding in cell medium, which in turn altered the ultimate chemical profile of bioavailable PACs. Overall, we demonstrated that extraction procedures, protein binding in cell culture media, and dilution factors prior to in vitro testing can all contribute to determining the final bioavailable concentrations of bioactive constituents of petroleum substances in vitro. Thus, in vitro-to-in vivo extrapolation for such substances may require greater attention to the concentration-dependent and compound-specific differences in recovery and bioavailability. This work has been published in Toxicological Sciences (https://doi.org/10.1093/toxsci/kfaa007).

In a second study, we examined the in vitro testing of petroleum products in the context of a hypothetical spill of an “oil blend” material with the following description of the components on the material safety data sheet: “lubricant base oil (petroleum, various CAS numbers), >70%; and additives (proprietary), <30%”. We posited that due to the cryptic description of the composition, first responders and local authorities may require additional information to inform the choice of the cleanup standard. Test material was investigated alongside two other petroleum refining products for comparison. These were testing via in vitro toxicological (bioactivity profiling in human iPSC-derived hepatocytes, neurons and cardiomyocytes) methods. Data from these methods were presented to a group of professionals knowledgeable about the oil spill response who represented a diverse set of stakeholders from the industry and state agencies. The participants agreed that the data rich bioactivity testing data allows for a more informed discussion of the potential hazards that may be present in the spilled product and provided for greater confidence in rapid decision making in this hypothetical case study. This work is being prepared for publication.

(3) Engagement of stakeholders to develop and refine the data integration framework and its application to several case studies.

We conducted three formal stakeholder meetings in addition to continued collaborative interactions with stakeholders that have enabled us to refine our experimental approaches, our data integration framework, and our case study exercise.

The first stakeholder meeting was held April 6, 2018 in College Station. This meeting included representatives from several oil companies, numerous Texas state agencies and local health districts, as

well U.S. EPA. The goals of this meeting were as follows:
(i) to introduce practitioners to the new technologies for chemical and biological profiling being developed by the TAMU and its partners;
(ii) solicit input from practitioners as to the types of scenarios and challenges to which these new technologies can be applied, and how they could be integrated into a framework to inform public health preparedness planning and decision-making; and
(iii) refine the project experimental and analysis plans based on practitioner-feedback
Stakeholders noted that this project will produce tools/methods that are likely to be most immediately useful for processes related to remediation and recovery, rather than in the emergency response phase of the first few days. Additionally, they noted that to the extent that faster and more accurate methods are being developed, they are always helpful and useful. However, they also cautioned that the manner in which the research is communicated to the public is very important, particularly with respect to in vitro studies, such as beating cardiomyocytes. As a result of this meeting, we refined our experimental approaches and finalized the case studies.

A second stakeholder meeting was held on October 9, 2019 in College Station. This meeting included representatives from oil companies and Texas state agencies, in particular emergency response experts from regulatory agencies and the oil industry. The main purpose of this meeting was to work through two case studies in a tabletop science-to-practice exercise.

The first case study simulated an oil pipeline burst, with the objective of identifying the origins of two “unknown” crude oil samples by comparison to a library of crude oils from known locations. The scenario was that after initial cleanup from the pipeline spill, further analysis may be needed to distinguish newly spilt oil from other oils that may have been transported by the pipeline in the past. Data from traditional analytical chemistry assays, as well as new analytical and bioactivity assays developed by TAMU, were presented for 19 samples from 6 on-/off-shore oil producing regions. Two samples were be “blinded” and the participants will attempt to identify their origin with the data provided. Participants were be divided into breakout groups and evaluated both “traditional” and “new” data packages. This activity showed that the stakeholders found the IMS-MS data to be highly informative for rapid chemical fingerprinting of complex substances in general, and specifically advantageous for accurate and confident source-grouping of crude oils. Thus, this exercise demonstrated the utility of IMS-MS as a technique for rapid fingerprinting of complex samples and demonstrates its advantages over traditional GC-MS based analyses when used for decision-making in emergency situations. Results of this case study have been published in Environmental Science and Technology (https://doi.org/10.1021/acs.est.0c04798).

The second case study simulated a spill of a refined product of unknown composition, with the objective

of assessing whether spills of proprietary blends require cleanup levels beyond that applied for crude oils, due to the presence of “unknown” additives/constituents. The scenario was that after initial cleanup of a spill of a refined petroleum product, concerns may be raised about how best to determine cleanup levels due to possible presence of additives in the product. Data from traditional analytical chemistry assays, as well as new analytical and in vitro bioactivity assays developed by TAMU, were presented for 7 samples of proprietary composition materials (6 “reference” and 1 “unknown”) and samples of crude oil. Determinations of the relative level of public health hazard of the “unknown” sample were made compared to “reference” products and crude oil. Participants were divided into breakout groups and evaluated both “traditional” and “new” data packages. This activity showed that the stakeholders found the in vitro data to be highly informative providing a basis to ask for additional hazard information on product constituents, particularly for products where Material Safety Data Sheets are missing important information and for companies that have poor product stewardship practices. They also noted that these data could be a “stop gap” for missing toxicity data, and is therefore useful in addressing “known unknown.” Thus, this exercise demonstrated the utility of high throughput in vitro assays as a technique for rapid hazard identification of complex samples when used for decision-making in emergency situations. A manuscript describing this case study is in preparation.

Plans for a third in person stakeholder meeting were derailed by the COVID-19 pandemic. However, we did hold a virtual stakeholder seminar on June 17, 2020 that focused on an update to the use of IMS-MS for chemical fingerprinting and characterization. In particular, we summarized findings of the published studies as well as presenting preliminary data looking at petroleum product variability, using of the IMS-MS library for chemical identification, and application of Kendrick Mass Analysis to characterize hydrocarbon series. A summary of the conclusions are as follows: (i) IMS-MS offers orders of magnitude greater throughput (e.g., 15 min. vs. 3 days) as compared to GC-MS; (ii) IMS-MS achieves similar accuracy in terms of chemical similarity and grouping as compared to GC-MS; (iii) additional CCS separation enables IMS-MS to resolve the “UCM hump”; (iv) IMS-MS Library is portable because CCS values are reproducible across labs and instruments; and (v) in applying Kendrick Mass analysis, CCS values allow IMS/MS to assign molecular formulas with greater confidence that High Resolution MS alone.

We plan on continuing to engage with stakeholders as we complete the remaining manuscripts for publication.

## 2. Outputs

Before the form is completed, you may click "Save & Continue Editing" at the bottom of the page at any time to save your work or "Next" to move onto the next page of this form.

When the form is completed, you may click "Mark as Complete" at the bottom of the page to save your work and return to the dashboard.

** denotes required fields*

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## 2. OUTPUTS

**Outputs** are tangible or measurable deliverables, products, data, or publications produced during the project period.

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### 2.1. Please indicate the number of students (K-12, undergraduate, or graduate), postdoctoral scholars, citizen scientists, or other trainees involved in the project. *

Please enter 0 if none were involved.

| | |
|---|---|
| K-12 students | 0 |
| Undergraduate students | 2 |
| Graduate students | 3 |
| Postdoctoral scholars | 1 |
| Citizen Scientists | 0 |
| Other Trainees | 0 |

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**2.2. Has your project generated any data and/or information products?** *

Generation of data includes transformations of existing data sets and generation of data from existing resources (e.g., maps and images). Information products include publications, models, software, code, curricula, and digital resources.

(Check all that apply.)

## Responses Selected:

| |
|---|
| Data |
| Information Products |

**2.3. Briefly describe how you fulfilled the approved Data Management Plan and, if applicable, any changes from the approved plan.** *

As described in the data management plan, all electronic data such as manuscripts, presentations, software, computational results, raw data, and case studies are archived on network file-servers in order to ensure preservation for future reference and dissemination. As results are published, we release data as supplementary materials or via upload to public repositories. All results published in peer reviewed journals are uploaded to PubMed Central. Our modes of dissemination include the scientific literature and scientific conferences.

During this grant period, we also created an IMS-MS library containing molecular properties for >3,000 chemicals with ~1200 being classified as hazardous substances. To translate these values to the scientific community, a website listing the IMS collision cross section (CCS) values and specific molecular information for each molecule assessed such as CAS, m/z ratio, ion type, and charge state was created (https://brcwebportal.cos.ncsu.edu/baker/). For the library formation, we utilized commercially available standards for both endogenous and exogenous analytes. Additionally, each molecule was assessed in both positive and negative ion modes and had low error (<1%) in the triplicate runs.

**If your project has generated data, please download the Excel worksheet entitled GRP Data Management Reporting. Use the "Data Report" tab in the worksheet to create an inventory of data sets that you produced and to verify deposit in a curation facility. Upon completion, please upload the worksheet to your task list. If you need guidance on how to complete the Data Report, please e-mail gulfgrants@nas.edu. A member of GRP's data management staff will reach out to you.**

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**If your project has produced publications, websites or data portals, GIS applications, models or simulations, software packages or digital tools, code, curricula, or other interactive media, please download the Excel worksheet entitled GRP Information Management Reporting. Use the "Information Products Report" tab in the worksheet to create an inventory of these products and to verify deposit in a curation facility. Upon completion, please upload the worksheet to your task list. If you need guidance on how to complete the Information Products Report, please e-mail gulfgrants@nas.edu. A member of GRP's data management staff will reach out to you.**

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**2.4. Aside from data and information products, what other tangible or measurable deliverables or products (e.g., workshops, trainings, and outreach events) were produced during the project period?** *

**Upon completion of this form, you may upload supplemental material that represent the tangible or measurable deliverables or products to complement this narrative report.**

We conducted three stakeholder meetings (described above) that represent measurable deliverables. The presentations from these workshops are uploaded as supplemental materials.

## 3. Data Management

Before the form is completed, you may click "Save & Continue Editing" at the bottom of the page at any time to save your work or "Next" to move onto the next page of this form.

When the form is completed, you may click "Mark as Complete" at the bottom of the page to save your work and return to the dashboard.

** denotes required fields*

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**3. DATA MANAGEMENT**

In this section, please provide a response to each question to complement the **Data Report** in the GRP Data Reporting Excel worksheet.

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**3.1 If you listed multiple data sets in the data reporting table, please briefly describe how these data sets relate to one another.** *

N/A

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**3.2. Please provide a list of additional documentation to describe the data listed in the reporting table (e.g., code books, lab manuals, workflow procedures). Enter none if you did not produce any additional documentation to describe the data.** *

Additional documentation is contained in published manuscripts.

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**3.3. Beyond depositing data and metadata in a repository, what other activities have you undertaken or will undertake to ensure that others (e.g., researchers, decision makers, and the public) can easily discover project data? What other activities have you undertaken to ensure that others can access and re-use these data in the future?** *

As results are published, we release data as supplementary materials or via upload to public repositories. All results published in peer reviewed journals are uploaded to PubMed Central. We will also continue to maintain our relationships with stakeholders both formally and informally. In several cases, collaborative research projects have grown out of these relationships.

**3.4. Are any data products you produced sensitive, confidential, and/or proprietary?** *

No

# 4. Information Products

Before the form is completed, you may click "Save & Continue Editing" at the bottom of the page at any time to save your work or "Next" to move onto the next page of this form.

When the form is completed, you may click "Mark as Complete" at the bottom of the page to save your work and return to the dashboard.

* *denotes required fields*

**4. INFORMATION PRODUCTS**

In this section, please provide a response to each question to complement the **Information Products Report** in the **GRP Information Products Management** Excel worksheet.

**4.1. Please select the type(s) of information products that your project produced.** *

## Responses Selected:

| |
|---|
| 1. Scholarly publications, reports or monographs, workshop summaries, or conference proceedings |
| 2. Websites or data portals |

**Scholarly publications, reports or monographs, workshop summaries, or conference proceedings** *

Please provide a list of citations for project publication, reports and monographs, workshop summaries, and conference proceedings.

Published manuscripts:

1. Aly NA, Luo YS, Liu Y, Casillas G, McDonald TJ, Kaihatu JM, Jun M, Ellis N, Gossett S, Dodds JN, Baker ES, Bhandari S, Chiu WA, Rusyn I. Temporal and spatial analysis of per and polyfluoroalkyl substances in surface waters of Houston ship channel following a large-scale industrial fire incident. Environmental pollution (Barking, Essex : 1987). 2020;265(Pt B):115009. Epub 2020/06/24. doi: 10.1016/j.envpol.2020.115009. PubMed PMID: 32574947; PMCID: PMC7857671.

2. Luo YS, Aly NA, McCord J, Strynar MJ, Chiu WA, Dodds JN, Baker ES, Rusyn I. Rapid Characterization of Emerging Per- and Polyfluoroalkyl Substances in Aqueous Film-Forming Foams Using Ion Mobility Spectrometry-Mass Spectrometry. Environmental science & technology. 2020;54(23):15024-34. Epub 2020/11/12. doi: 10.1021/acs.est.0c04798. PubMed PMID: 33176098; PMCID: PMC7719402.

3. Luo YS, Ferguson KC, Rusyn I, Chiu WA. In Vitro Bioavailability of the Hydrocarbon Fractions of Dimethyl Sulfoxide Extracts of Petroleum Substances. Toxicological sciences : an official journal of the Society of Toxicology. 2020;174(2):168-77. Epub 2020/02/11. doi: 10.1093/toxsci/kfaa007. PubMed PMID: 32040194; PMCID: PMC7098373.

4. Roman-Hubers AT, McDonald TJ, Baker ES, Chiu WA, Rusyn I. A comparative analysis of analytical techniques for rapid oil spill identification. Environmental toxicology and chemistry. 2020. Epub 2020/12/15. doi: 10.1002/etc.4961. PubMed PMID: 33315271.

5. Dodds, JN, Hopkins, ZR, Knappe, DRU, Baker, ES. Rapid Characterization of Per- and Polyfluoroalkyl Substances (PFAS) by Ion Mobility Spectrometry-Mass Spectrometry (IMS-MS). Anal. Chem. 2020; 92(6), 4427-4435. Epub 2020/02/24. doi: 10.1021/acs.analchem.9b05364. PubMed PMID: 32011866; PMCID: PMC7173758.

6. Dodds, JN, Alexander, NLM, Kirkwood, KI, Foster, MR, Hopkins, ZR, Knappe, DRU, Baker, ES. From Pesticides to PFAS: An Evaluation of Recent Targeted and Untargeted Mass Spectrometry Methods for

Xenobiotics. accepted in Anal. Chem. Epub 2020/11/02. doi: 10.1021/acs.analchem.0c04359. PubMed PMID: 33136371; PMCID: PMC7855838.

Posters:

1. Roman-Hubers, A., Cordova, A., Rhode, A., Baker, E., McDonald, T., Chiu, W. and Rusyn, I. Evaluation of the Sameness of Production Batches of Petroleum Refining Products with Ion Mobility Spectrometry-Mass Spectrometry (IMS-MS). SETAC North America. Fort Worth, TX. 2020.
2. Aly, N., Luo, Y.S., Roman-Hubers, A. T., Liu, Y., Baker, E.S., Chiu, W.A. and Rusyn, I. Creating an Ion Mobility Collision Cross Section Library for the ToxCast Chemicals and Utilizing it for Rapid Exposure Assessment. ASMS Conference on Mass Spectrometry and Allied Topics. Houston, TX. 2020.
3. Luo, Y.-S., Aly, N.A., Dodds, J., Foster, M., Baker, E.S., Chiu, W.A., and Rusyn, I. Rapid Characterization of Emerging Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous Film Forming Foams (AFFF) Using Ion Mobility Mass Spectrometry. SETAC North America Focused Topic Meeting: Nontarget Analysis for Environmental Risk Assessment. Durham, NC. 2020.
4. Roman-Hubers, A., Wade, T., Baker, E., McDonald, T., Chiu, W., and Rusyn, I. Forensic fingerprinting of petroleum: Comparative analysis of analytical techniques for rapid identification of oil spills. 9th Young Environmental Scientists (YES) of the Society of Environmental Toxicology and Analytical Chemistry meeting, Waco, TX. 2020.
5. Roman-Hubers, A., Chen, Z., McDonald, T., Tuttle, K., Chiu, W., and Rusyn, I. Rapid hazard identification using innovative high throughput bioactivity and chemical profiling assays: A case study of a hypothetical spill of a complex substance. Society of Toxicology Annual Meeting, Anaheim, CA. 2020.
6. Roman-Hubers, A. Chen, Z., Liu, Y., McDonald, T., Wade, T., Lyon, D., Chiu, W., and Rusyn, I. Passive dosing methods for in vitro testing of UVCB substances. SRP Annual Meeting, Seattle, WA. 2019.
7. Aly, N., Luo, Y.S., Liu, Y., Casillas, G., McDonald, T., Kaihatu, J., Jun, M., Ellis, N., Gossett, S., Dodds, J., Baker, E.S., Chiu, W.A. and Rusyn, I. Temporal and Spatial Analysis of Poly/perfluoroalkyl Substances in Houston Ship Channel Following Firefighting Foam Deployment at the Intercontinental Terminal Company Fire. SRP Annual Meeting, Seattle, WA. 2019.
8. Aly, N.A., Luo, Y.S., Roman-Hubers, A.T., Liu, Y., Zheng, X., Baker, E.S., Chiu, W.A. and Rusyn, I. Reproducibility of collision cross section measurements with ion mobility mass spectrometry-mass spectrometry. International Congress of Toxicology, Honolulu, HI. 2019.
9. Aly, N.A., Luo, Y.S., Roman-Hubers, A.T., Liu, Y., Zhang, X., Baker, E.S., Chiu, W.A. and Rusyn, I. A library of 4,000+ Environmental chemicals for high throughput exposomic measurements. Superfund Research Program Annual Meeting, Sacramento, CA. 2018.
10. Roman-Hubers, A., Aly, N., Sweet, S., Wade, T., Bushang, S., Baker, E., Chiu, W., and Rusyn, I. The application of Ion Mobility-Mass Spectrometry technique as a rapid analytical method for identification of the origin of oil spills. Lone Star SOT Annual Meeting, Austin, TX. 2018.

11. Aly, N., Luo, Y.S., Roman-Hubers, A., Liu, Y., Zhang, X., Baker, E., Chiu, W., and Rusyn, I. Enabling high-throughput Exposomics by developing a library of 4,000+ environmental chemicals for solid phase extraction-ion mobility spectrometry-mass spectrometry. Lone Star SOT Annual Meeting, Austin, TX. 2018.

**Websites or data portals** *

Please provide a list of project websites and data portals (including the website URL).

During this grant period, we also created an IMS-MS library containing molecular properties for >3,000 chemicals with ~1200 being classified as hazardous substances. To translate these values to the scientific community, a website listing the IMS collision cross section (CCS) values and specific molecular information for each molecule assessed such as CAS, m/z ratio, ion type, and charge state was created: https://brcwebportal.cos.ncsu.edu/baker/. For the library formation, we utilized commercially available standards for both endogenous and exogenous analytes. Additionally, each molecule was assessed in both positive and negative ion modes and had low error (<1%) in the triplicate runs.

**How long beyond the grant period will you maintain the project website/data portal and its contents? Please describe plans to archive the website/data portal and its contents after regular maintenance concludes.***

We plan to keep this open for the extended future with Dr. Baker's group maintaining it as it is a great resource for the scientific community.

**4.2. Beyond depositing information products in a repository, what other activities have you undertaken or will undertake to ensure that others (e.g., researchers, decision makers, and the public) can easily discover and access the listed information products?** *

All new data will be added to the website and it will be cited in each corresponding paper (in preparation).

**4.3. Are any of the information products you produced confidential, proprietary, or subject to special license agreements?** *

No

# 5. Project Outcomes

Before the form is completed, you may click "Save & Continue Editing" at the bottom of the page at any time to save your work or "Next" to move onto the next page of this form.

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* *denotes required fields*

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**5. PROJECT OUTCOMES**

**Outcomes** refer to the **impact(s), consequence(s), result(s), or effect(s)** that occur from carrying out the activities or outputs of the project. Outcomes may be environmental, behavioral, health-related, or programmatic. Example outcomes include, but are not limited to: increased learning, knowledge, skills, and motivation; policy changes; actions taken by a group as a result of information generated by your project.

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**5.1. Please describe the outcomes achieved during your project and how they were assessed. For this question, we are interested in learning about the immediate short-term outcomes that have already occurred during or as a result of your project. Do not include long-term outcomes you foresee your work contributing to beyond the end of the project.** *

This project has increased learning, knowledge, and skills among researchers, trainees, and practitioners with respect to using IMS-MS and high throughput in vitro assays to characterize crude oils and petroleum substances. The second stakeholder meeting was particularly instrumental in this outcome, as it involved case study exercises among all three groups. Additionally, additional research collaborations have result from this project, which will continue to increase the learning, knowledge, and skills of those involved.

**5.2. We're interested in hearing not just the results of your project but what are their implications for or contributions to:**

- **offshore energy system safety,**
- **environmental protection and stewardship, and/or**
- **health and community resilience**

**Please describe what you consider to be the most remarkable accomplishment or finding of your project. What can others learn from your accomplishment and finding? How do you see it fitting in with your greater field of study or community of practice?** *

The most important finding of this project is that IMS-MS has the potential to substantially increase the speed and accuracy of oil spill fingerprinting. Moreover, this approach will be able to identify "unknown unknowns" that warrant additional investigation. These approaches will improve environmental protection and stewardship as well as health and community resilience by enabling much more comprehensive characterization and analysis of contamination after oil spills. The higher throughput will enable many more samples to be analyzed, as well as enable the testing of replicates that will increase confidence and accuracy. Furthermore, the use of this "untargeted" technique in combination of computationally-enable data analysis will provide greater confidence that samples that may contain potentially harmful substances are identified for further characterization.

## 6. Communication

Before the form is completed, you may click "Save & Continue Editing" at the bottom of the page at any time to save your work or "Next" to move onto the next page of this form.

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**Note to Grantees: In Section 6, we seek input from you to help us evaluate the Gulf Research Program's funding strategy. This section will not be made available to the public.**

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**6. Information to Inform GRP Evaluations**

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**6.1. Sharing the difficulties you encountered helps us learn from your experience. Describe any challenges you encountered in your project and how you addressed or overcame them. Challenges are inherent to conducting any complex project. These may include (but are not limited to): unexpected staffing changes, changes in the community you are working in, appearance of a new technology or dataset in the field you are working in, challenges accessing a field site, policy or regulatory changes that affect the issue you are addressing, low recruitment rates, delays in setting up services, or other problems in implementing and conducting your project.** *

It was originally anticipated that the partnership with CTEH would enable the project to obtain fresh crude oil samples from oil spills. However, it turned out the companies were generally unwilling to provide samples from “actual” spills, or even from their own production cycles. Thus, a general challenge in this field is the sensitive nature of oil spills from an industry perspective.

Additionally, two personnel changed institutions during the first year of the grant. Dr. Horney moved to University of Delaware, and was unable to continue as part of the project. Additionally, Dr. Baker moved to North Carolina State University (NCSU). Dr. Baker will continue her involvement in the project, but there was a gap of several months due to the need to transfer the subcontract from Pacific Northwest National Labs to NCSU. Thus, in general, personnel changes, though inevitable as part of academic careers, can be disruptive.

Additionally, we initially had challenges in terms of staff to administer and coordinate activities for this grant. It was no until Year 2 that we had a stable, highly competent staff member to perform these activities. A further challenge was the starting of the grant in December, which made it difficult to recruit new graduate students to work on this research until they began their studies 8 months later in August.

**6.2. We like to hear about what you learned from your work and how you feel it affects future work or the work of others. Think back on your project strategies, methods, and activities, what worked and what did not? Is there anything you would do differently in the future? If so, tell us what and why.** *

The main challenge in this area is that there is substantial inertia in the methods used for addressing oil spills, and there is a wariness in making changes to approaches that have “worked” in the past. Thus, stakeholder engagement, particularly in table-top exercises, is probably the only way to move the field forward.

**6.3. What are the next steps for this work, either for you and your project team or other researchers? Has this project led to other opportunities to work in this area?** *

We will continue to finish manuscripts based on this project. This work has led to additional opportunities with respect to petroleum products through new collaborations/partnerships (see next question). More generally, the approaches described here are not unique to oil spills, and are applicable more broadly to emergency response / disasters, so we anticipate continuing to apply these in broader contexts as well.

**6.4. Have you developed new collaborations or partnerships (formal or informal) as a result of this work? If yes, please describe the new collaborations or partnerships.** *

We have developed a new partnership with Exxon in which they are sending TAMU water and oil samples from one of their weathering experiments for testing in our laboratory.

**6.5. What, if any, positive changes in policy or practice do you foresee as a result of your work?** *

With continued partnerships, particularly with Agilent, we foresee that IMS-MS will come a more routine practice when it is taken up by commercial analytical laboratories. Additionally, in vitro toxicology continues to be very important in the field, and we anticipate increased use of high throughput assays such as the ones we have developed in the field of petroleum research.

**6.6. If you could make one recommendation to the Gulf Research Program for how best to build on the work you conducted in this project, what would it be?** *

We found that engagement with oil spill practitioners, particularly in industry, is challenging, and that it is difficult to convince them to change methods they have been using for many years. Is there any way the GRP can facilitate engagement, perhaps through convening meetings that include multiple stakeholders? The only meeting that was held was mostly other researchers in the GRP, so bringing in stakeholder groups may be an effective way to disseminate GRP supported research to those in industry and non-governmental organizations.

## 7. Communication and Dissemination

Before the form is completed, you may click "Save & Continue Editing" at the bottom of the page at any time to save your work or "Next" to move onto the next page of this form.

When the form is completed, you may click "Mark as Complete" at the bottom of the page to save your work and return to the dashboard.

* *denotes required fields*

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**Note to Grantees: In Section 7, we ask you to help us communicate the importance, progress, and accomplishments of your work. Information provided in this section will be used by the Gulf Research Program to highlight its funded projects in print and electronic informational and promotional materials. The intended audience for the information provided in this section is different and should be thought of as a general audience. When you return to the dashboard, you may upload images that represent and illustrate the work of your project.**

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**7.1. Please describe the most exciting or surprising thing you have learned while working on this project in a way that is understandable by a general audience.** *

The most exciting component of this project the collection of over 600 crude oil samples and over 40 tar balls from across the globe. Sources include on- and off-shore wells in the Gulf of Mexico, North and South America, and the Middle East. These samples provide an exciting opportunity to develop a library of "fingerprints" that can be used to identify, group, and prioritize future crude oil samples in terms of public health concern.

Our project fills a critical gap in the ability to evaluate the public health impact of oil spills, being among the first to implement recent Academy recommendations for improving risk-related evaluations using novel paradigms in exposure science, toxicology, and risk assessment. By bringing together researchers, federal/state/local agencies, emergency response professionals, and oil industry representatives, we hope to move innovative research capabilities into public health practice. By enabling more rapid, cost-effective, and accurate assessment of the public health effects of oil spills, our project will ultimately lead to better protection of public health and more efficient use of societal resources.

**7.2. Do you have any stories that capture the impact of this project? (optional)**

If so, please share one or two. Examples of what we are interested in include stories of people/communities that the project has helped; lives that have changed; work that led to policy change, such as legislation or regulation; and research breakthroughs.

None noted.

**7.3. Have any communications, outreach, or dissemination activities occurred in relation to your project?***

Please describe:

- Any press releases issued (other than that issued by the National Academies of Sciences, Engineering, and Medicine) about the project.
- Any media coverage or news stories about the project.
- Any social media accounts, websites, listservs, or other communication vehicles used to communicate information about this project. Please include relevant web addresses if available.

https://vetmed.tamu.edu/news/press-releases/texas-ams-chiu-receives-grant-through-gulf-research-program/