Summary of results from the 2014/2015 Hydrocarbon Intercalibration Experiment (HIE)

Prepared by

Christopher M. Reddy

and

Stephen A. Wise, Lane C. Sander, and Jacolin A. Murray (NIST)

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Abstract

Following an open meeting entitled, "*Hydrocarbon Chemistry QA/QC*," at the 2014 Gulf of Mexico Oil Spill and Ecosystem Science Conference in Mobile, Alabama, the Gulf of Mexico Research Initiative (GoMRI) initiated the Hydrocarbon Intercalibration Experiment (HIE). The aim of this effort was to address the need for advancing the importance of laboratory quality assurance/quality control (QA/QC) practices and for interlaboratory comparison and calibration for hydrocarbon compounds.

Over thirty laboratories expressed interest and were supplied from the National Institute of Standards and Technology (NIST) with two Standard Reference Materials (SRMs) for analysis (SRM 2779 Gulf of Mexico Crude Oil and candidate SRM 2777 Weathered Gulf of Mexico Oil). SRM 2779 was prepared from neat oil collected directly from the leaking Macondo well during the *Deepwater Horizon* disaster while candidate SRM 2777 is a field-weathered residue of the Macondo well oil dissolved in toluene.

Twenty laboratories submitted results on traditional analytes measured by gas chromatography, ultrahigh-resolution mass spectrometry, toxicity, shear viscosity, and interfacial tension, which were initially discussed in an afternoon workshop during the Gulf of Mexico Oil Spill and Ecosystem Science Conference in Houston, TX on February 16, 2015.

The majority of the participants focused on the traditionally measured analytes (saturates, aromatics, and biomarkers) found in crude oil and its refined products, and overall performed very well compared to known values for SRM 2779. The field-weathered candidate SRM 2777 presented greater challenges due to the lower concentrations of analytes. A more comprehensive report on these analyses will be published in a future NIST internal report.

One exciting outcome of this exercise is that this is the first ever published comparison for oil and weathered oil by Fourier Transform ion cyclotron resonance mass spectrometry (FT-ICR-MS), a powerful, high-resolution technique shown to expand the analytical window of oil-spill science, especially for native compounds and breakdown products that are not amenable to gas chromatography. Three participating laboratories submitted results. Despite having different operating platforms and methods, there was very good agreement amongst them.

Results on toxicity, shear viscosity, and interfacial tension were each provided by only one laboratory and are listed.

Based on discussions at the 2015 Houston meeting, review of the results, follow-up meetings with participants, some members of the GoMRI board, and other experts, we recommend:

1. Continued usage of certified reference materials in routine analysis along with other means to elevate accuracy and minimalize systematic error.
2. Taking advantage of the supplemental information section, now commonplace in peer-review journals, and providing detailed content on analytical methods and QA/QC, allowing readers an opportunity to learn and compare results.

3. Planning for additional intercomparisons that may include other matrices such as animal tissues, water, or sediment samples.
4. Publishing the results from the HIE in one or more peer-reviewed journals.

Overall, the HIE was a great success. For many of the participants, this was their first introduction to both certified reference materials and an opportunity to compare and gauge their methods and techniques with other researchers in the field.

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I. Background

On the afternoon of January 26, 2014, the Gulf of Mexico Research Initiative (GoMRI) held a meeting entitled, "*Hydrocarbon Chemistry QA/QC*" at the Gulf of Mexico Oil Spill and Ecosystem Science Conference in Mobile, Alabama (See Appendix I for agenda). The goals of the meeting were to discuss the current state of knowledge on the analysis of oil and oil residues in water, sediment, soil, and tissue and to elucidate best principles for assessing and confirming high-quality and reproducible results. Of particular interest were refining and improving current methodologies, increasing awareness of new techniques, and expanding target analytes in native oils and weathering products following acute and chronic releases of oil and its refined products to the marine environment.

The meeting was attended by experts in various subfields of oceanography and chemistry as well as those new to or interested in the analytical chemistry of oil spills. Several researchers and GoMRI Research Board members made presentations and then there was an open and engaging discussion amongst the audience and presenters. The presentations are available at http://gulfresearchinitiative.org/hydrocarbon-intercalibration-experiment/.

After discussions with members of the community, the GoMRI board concluded that an intercomparison would be timely and fruitful. Intercomparison studies are an excellent tool for assessing the comparability of analytical measurements. In addition, they provide an opportunity for researchers to compare their methods and approaches as well as to report and increase awareness on novel or typically untargeted analytes that may eventually become more standard. Lastly, they provide an opportunity for new researchers to understand and appreciate the demands and rigor needed to contribute positively to the field via a rigorous quality control and quality assurance plan.

In cooperation with the National Institute of Standards and Technology (NIST), which has helped benchmark and improve the quality of analytical data gathered on the marine environment by administering intercomparison exercises, GoMRI then launched the hydrocarbon intercalibration[1] experiment (HIE) to address the need for advancing the importance of laboratory quality assurance/quality control (QA/QC) practices and for interlaboratory comparison and calibration for hydrocarbon compounds.

The GoMRI Research Board strongly encouraged all GoMRI-funded principal investigators, co-principal investigators, and other GoMRI collaborating laboratories to participate. Other members of the scientific community were invited and two commercial analytical laboratories (Alpha Analytical; Mansfield, MA and Battelle Memorial Institute; Duxbury, MA) who have analyzed 1000s of samples following the *Deepwater Horizon* disaster were contracted to be

[1] While originally termed an "intercalibration", the spirit and goals of this effort are more akin to an "intercomparison". Hence, the latter term will be used in this report.

involved in this effort. Researchers who studied other physical, chemical, and biological properties beyond hydrocarbons were invited to participate.

It is important to note that the HIE was not intended to be a proficiency test, and that laboratory-specific results would be anonymous to all, including the GoMRI Research Board members, except for the HIE coordinators and their teams.

It was expected that each participant would:

- Report their results by December 1, 2014;
- Share information on analytical methods used;
- Allow NIST and GoMRI to use their results;
- Be open to co-author a peer-reviewed manuscript;
- Make a significant effort to attend a workshop to discuss the results of this study at the 2015 GoMRI meeting in Houston, TX (February 16, 2015).

Over thirty laboratories expressed interest and were supplied with two different Standard Reference Materials (SRMs) for analysis as described in the next section. Due to delays and requests from many participants for additional time, the deadline was extended until noon February 16, 2015. Ultimately, 20 laboratories submitted results on traditional analytes measured by gas chromatography (GC), an expanded range of analytes detected by Fourier Transform ion cyclotron resonance mass spectrometry (FT-ICR-MS), toxicity, shear viscosity, and interfacial tension, all of which was discussed at a Houston, TX workshop on February 16, 2015 (See Appendix 2).

This report provides a summary and discussion of the HIE results from all participants. The majority of the participants focused on the saturates, aromatics, and biomarkers in the SRMSs. A more comprehensive report will be prepared by NIST in an internal report and will be made available at a later date. To preview what to expect from the NIST internal report, refer to a previous report on intercomparisons of Macondo well (MW) oil from the *Deepwater Horizon* disaster (NIST 2011). The HIE is also the first ever FT-ICR-MS intercomparison for oil and weathered oils and the results are reported in detail here. A brief overview on toxicity, shear viscosity, and interfacial tension are also provided. Lastly, recommendations are presented.

II. Description of the samples and instructions

Participants received two ampoules each of SRM 2779 Gulf of Mexico Crude Oil and the candidate SRM 2777 Weathered Gulf of Mexico Oil. Each ampoule contained 1.3 mL of material.

I. **SRM 2779.** The petroleum crude oil for SRM 2779 was collected on May 21, 2010, on the drillship *Discoverer Enterprise* from the insertion tube that was receiving oil directly from the Macondo well (MW) during response operations (Figure 1). Using the data from three independent methods of analysis performed at NIST as well as one set of data from an interlaboratory study of 36 participating laboratories coordinated by NIST and the National Oceanic and Atmospheric Administration (NOAA) (NIST 2011), certified and reference values (as mass fractions) are provided for a number of polycyclic aromatic hydrocarbons (PAHs) along with reference values (as mass fractions) for a number of alkylated PAH groups, hopanes, and steranes, but not *n*-alkanes. (NIST 2012).

II. **Candidate SRM 2777.** This material was prepared from the Soxhlet extraction (90/10 dichloromethane/methanol) of oiled sand-patties collected on August 31, 2012 at Gulf Shores Beach, Alabama (Figure 2). Geochemical analysis revealed that the residue is weathered MW oil (Aeppli *et al*., 2014; sample B105; Table S2). Solvent was removed to yield a dark, syrupy liquid (Figure 3) that was diluted in toluene at approximately 71 mg/g.

    This material was chosen as a true "field" weathered sample and not a laboratory-weathered sample in light of recent studies showing that field weathering via biodegradation had removed some normal alkanes, branched alkanes, and other saturates (Aeppli *et al.* 2012, Ruddy *et al.* 2014, Gros *et al*. 2014, Figure 4). In addition, the field-based studies have shown a formation of residues non-amenable to GC during "real world" conditions following the release, as revealed by mass balance tracked by elemental analysis, thin-layer chromatography, GC, and FT-ICR-MS (Aeppli *et al*. 2012, Ruddy *et al*. 2014). It was critical to include a field-weathered sample, with an increased amount of non-GC amenable materials relative to the majority of the traditionally measured analytes, as it would be critical for any participants using analytical techniques or assays not employing GC, e.g. FT-ICR-MS.

Each participant was informed that the candidate SRM 2777 should be treated as an unknown sample and SRM 2779 as a control material with assigned values for many analytes. They were asked to remove three subsamples from one ampoule of SRM 2779 and three subsamples from one ampoule of candidate SRM 2777 and treat each subsample with their laboratory's and/or program's analytical protocols. An Excel spreadsheet (see Appendix 3) was sent to each participant with specific instructions on how to report values for only the analytes they typically measure and other details. If the spreadsheet did not fit within the analytes or properties studied, reports or memos were accepted.

The remaining ampoule of each material would be available to the participants for their own use.

III. Overview on saturates, aromatics, and biomarkers by gas chromatography

This section provides an overview on the reported results on the alkane, aromatic, and biomarkers typically studied in oil-spill science (see Tables 1-4 for a listing of analytes reported by each laboratory). Again, please note that these results will be discussed in detail in a NIST internal report.

The laboratories reporting values for alkane, aromatic, and biomarkers were assigned numerical identification codes. Twenty laboratories reported results for one or more of these analytes (Tables 1-4). (Please note that some research groups used more than one analytical method, such as using two different types of gas chromatographs). For ease, we treated each analytical method as a "laboratory".

The intercalibration data were collected and input into ProLab Plus (quo data GmbH, Dresden Germany, version 2.14) for data analysis using ISO 5725-2 standard (ISO 1994). For each analyte reported, a summary chart was generated. See Figure 5 for an example of a summary chart. It should be noted that only a select few summary charts will be shown here, however, all summary charts will be shown in the NIST internal report. These summary charts show the results obtained from each participating laboratory, the mean of all reported values, the certified or reference value for SRM 2779 when available, the uncertainty representing the 95 % confidence level, and the range of z-scores from -3 to 3 (indicated as red lines labeled "limit of tolerance", see Figure 5 caption). The reproducibility standard deviation and repeatability standard deviation were calculated for each analyte using ISO 5725-2. The reproducibility standard deviation describes the variability between laboratories and the repeatability standard deviation describes the variability within the laboratories. To assess the accuracy of each laboratory, z-scores were calculated for each laboratory for each analyte. Generally, the z-score is calculated using the following equation:

$z = (x-x_a)/\sigma$;

where x is the result from an individual laboratory, x_a is the assigned value and σ is the standard deviation of the test results (Miller and Miller 2010). In this study, z-scores were calculated using the mean of all laboratories for x_a and the reproducibility standard deviation for σ. Outlier detection was limited to removal of data only if the laboratory exceeded an absolute z-score value greater than 3 (the Grubbs and Cochran tests indicated in ISO 5725-2 were not applied). Consequently, almost all of the data were used in calculation of the means. Outliers are indicated in the summary charts in red.

Here, we will first discuss the results for SRM 2779 and then candidate SRM 2777. There were fewer target analytes reported in candidate SRM 2777 due to significant weathering in this material, and many analytes were below the participants' detection limits. As a result, the discussion of this report will be focused on SRM 2779. In addition, the goal of this effort was for each laboratory to "compare" their results, so focusing on the results from SRM 2779 is more appropriate based on the number of detectable compounds reported.

Results for SRM 2779

a. ***Normal alkanes***. Five to twelve labs reported some data for *n*-alkanes and the branched hydrocarbons, pristane and phytane (Table 1). The mean mass fractions for each laboratory for *n*-alkanes in SRM 2779 are listed in Table 5. It was surprising that more laboratories did not submit results since these are the most abundant class of compounds in the MW oil, analytical standards are readily available, and they resolve enough by GC, especially for the Macondo well oil. In addition, they are frequently used for gauging the extent of weathering, especially evaporation and biodegradation. The results varied. For example, *n*-pentadecane ranged from 2890 to 6020 mg/kg with an HIE mean and uncertainty of 4650 ± 654 mg/kg (Table 5). However, within each laboratory, the relative standard deviations were excellent (as an example see Figure 5). Figure 6 shows the mean mass fraction and standard deviation for *n*-alkanes ranging from C_{10}-C_{25}, with greater variability in the smaller and more volatile alkanes. This could be a result of sample handling or calibration differences among laboratories. Three laboratories (9, 10, and 14) that reported values for normal alkanes with some sample preparation or clean-up beyond dilution did not have any apparent patterns due to this additional handing.

GC-MS, GC-FID, and comprehensive two-dimensional gas chromatography (GC×GC) were used to measure *n*-alkanes, which was unprecedented. We compared the results from one participating research group who used GC-MS and GC×GC-FID with two different analysts using internal- and external-based calculations, respectively (Figure 7). The results were excellent with the GC×GC-FID skewed slightly higher than the GC-MS results but comparable. A more comprehensive comparison for each value for *n*-pentadecane from each laboratory is shown in Figure 8.

b. ***Polycyclic aromatic hydrocarbons***. Parent and alkylated PAHs had the most participants (2 to 16; Tables 2-3) submitting results despite these analytes occurring at much lower concentrations than the *n*-alkanes. This could be because these analytes are the most measured compound class for oil-spill studies due to their known bioactivity. PAH are frequently used to identify sources (petrogenic vs. pyrogenic) (Lima *et al*. 2005) the degree of abiotic and biotic weathering (Wang *et al*. 1998), and fingerprinting oils (e.g., alkylated phenanthrenes/anthracenes vs. alkylated dibenzothiophenes; Douglas *et al.* 1996). The Certificate of Analysis of SRM 2779 (NIST 2012) has both certified and reference values available for many of the analytes in this study to which the participants could refer to before submitting results.

The mean values of each laboratory for PAHs and alkylated PAHs are listed in Tables 6 and 7, respectively. Overall, the range in participant reported values for parent PAHs and alkylated PAHs was similar to one another and compared well to the values listed in the Certificate of Analysis (NIST 2012). For example, the summary figures for the HIE results for phenanthrene (287±31.9 mg/kg) were within the uncertainty of the certified value (258±27 mg/kg; Figure 9). At lower concentrations, the mean HIE

values were also similar to those in the Certificate of Analysis, but with a greater uncertainty (e.g., benzo[*e*]pyrene (12.7±3.01 mg/kg vs. certified value 10.8±0.6 mg/kg) and fluoranthene (5.01±1.42 mg/kg vs. certified value 4.4±0.4 mg/kg)).

The mean HIE values for alkylated PAHs, e.g., C_1-phenanthrenes/anthracenes (724±90.1 mg/kg vs. reference value 670±90 mg/kg) were not as tightly grouped as for phenanthrene even though they occurred at much higher concentrations (Figure 10). This can be explained as the reported values are the sum of numerous peaks, often not baseline resolved by GC-MS, which can introduce a subjective bias to peak integration. Each laboratory used the standard method of using a response factor of the parent compound (or one similar) as the internal standard for any series of parent and alkylated PAHs, which may have also introduced some variability. Please note that the reference values for SRM 2779 were derived from the 2010 intercomparison, with a majority of the labs using the response factors of the parent PAHs.

One participating research group also measured the alkylated PAHs with a compound more representative than the parent PAHs (Figure 11). For example, this laboratory used the response factor of 1-methylphenanthrene for the C_1-phenanthrenes/anthracenes. Generally, using a "representative compound", although possibly more accurate, led to values considerably different from those reported by the HIE participants and listed in the Certificate of Analysis of SRM 2779. Thus, it is important that labs describe how they determine alkylated PAHs to ensure values from different laboratories can be compared.

Figures 12-14 summarize the mean and uncertainties (error bars) of select parent PAHs and alkylated PAHs depicted from the highest to lowest concentrations. These three figures also capture the variability of the laboratories' results.

Five laboratories (5, 7, 9, 10, and 14) that reported values for aromatics performed sample preparation or clean-up beyond dilution without any apparent patterns due to this additional handing.

c. ***Biomarkers***. Only eight out of twenty laboratories provided biomarker results for SRM 2779 (Table 4), despite the fact that biomarkers are one of the cornerstones of oil spill forensics and that reference values were available in the Certificate of Analysis (NIST 2012). For each specific biomarker, between two to eight laboratories (Table 4) provided results. The analysis of petroleum biomarkers (or molecular fossils) relies on their fidelity for fingerprinting and source specificity. Due to their relative recalcitrance towards abiotic and biotic degradation processes, these biomarkers are often used as reference compounds to which the weathering of relatively less stable compounds or the formation of new compounds can be compared and/or normalized.

The mean values reported for biomarkers for SRM 2779 are listed in Table 8. For 17α(H),21β(H)-hopane, the biomarker most often used as an "internal" standard for weathering and fingerprinting, the results were reasonably good (Figure 14). Seven of

the eight laboratories were within the mean uncertainty range (51.4±6.2 mg/kg vs. reference value 42±10 mg/kg) and five were within the uncertainty range of the reference value in the Certificate of Analysis (Figure 15). Alternatively, the results for 17α(H),22,29,30-trisnorhopane (9.19±2.02 mg/kg vs. reference value 7.29±0.79 mg/kg) and 5α(H),14β(H),17β(H)-cholestane-20R (29.3±6.04 mg/kg vs. reference value 23.7±2.7 mg/kg) were within the uncertainties of the reference, but there was greater scatter among the data reported by the laboratories (Figure 14). A summary of all results is shown in Figure 15. Unlike the *n*-alkanes and PAHs, pure standards and isotope-labeled biomarker internal standards are costly and often not commercially available, which may explain the variability among the data for the biomarkers. In fairness, it is well recognized that biomarker analysis need only be internally consistent within each laboratory (Douglas *et al.* 2016), although laboratories should strive for more external consistency.

Perhaps the most accurate means by which to compare the HIE results for SRM 2779 is to compare them to the values in the Certificate of Analysis (NIST 2012) (Figures 17 to 20 from highest to lowest concentrations). The results are quite good. At higher concentrations, the analytes that strayed the farthest were some alkylated PAHs, but as explained previously, this could be due to the subjective manner of how these isomers are quantified.

To provide a snapshot on the HIE results from SRM 2779, the output for phenanthrene is compared to the results to the NIST 2010 intercomparison, which included the then candidate SRM 2779 as an unknown (Figure 21). Thirty-six laboratories participated in the analysis of PAHs and biomarkers. Generally, the results from both intercomparisons were quite similar for phenanthrene.

Overall, the HIE participants did very well compared to available values. Differences were largest at lower concentrations; where pure standards are less available; and for some alkylated PAHs where integration of multiple peaks is subjective and approaches to quantification can differ.

Results from Candidate SRM 2777

A more comprehensive discussion on the results from candidate SRM 2777 will be presented in the NIST internal report and will be included in the Certificate of Analysis of this candidate SRM. The mean values reported for alkanes, PAHs, alkylated PAHs, and biomarkers for candidate SRM 2777 are listed in Tables 9-12, respectively. This sample presented significant challenges to most of the laboratories due to extreme weathering, which had removed many of the analytes, and because the residue was diluted in toluene (see Figure 4). For example, the reported value from the HIE, for phenanthrene was 287±31.9 mg/kg in SRM 2779 vs. 0.607±0.244 mg/kg in candidate SRM 2777 (Tables 6 and 10).

To highlight the results from select analytes, Figures 21 and 22 shows the HIE values for *n*-pentatricontane and phenanthrene and also C_1-phenanthrenes/anthracenes and 17α(H),21β(H)-hopane, respectively. These are the same analytes from Figures 9, 10, and 15 except *n*-

pentadecane was replaced by *n*-pentatricontane (Normal pentadecane was lost due to weathering in candidate SRM 2777).

As biomarkers are less likely to be weathered and their concentrations are less likely to be affected by weathering, the same compounds in Figure 16 from SRM 2779 are shown in Figure 24.

In summary, candidate SRM 2777 presented significant challenges that limited the number of analytes.

IV. Overview on measurements by ultrahigh resolution mass spectrometry

For the past 15 years, advances in ultrahigh resolution mass spectrometry, specifically, FT-ICR-MS, have expanded the analytical window of complex mixtures through selective ionization of high molecular weight, nonvolatile, thermally unstable, and/or highly polar acidic and basic species that are not GC-amenable (Marshall *et al.* 1998, Marshall and Rodgers 2008). A major advantage of this technique is its ultrahigh resolving power ($m/\Delta m50\% > 100{,}000$, in which $\Delta m50\%$ is mass spectral peak width at half-maximum peak height) with mass accuracy of < 1 ppm uncertainty, which has led to the development of petroleomics (McKenna *et al*. 2013, Rodgers *et al*. 2005, Rodgers and Marshall 2007).

FT-ICR-MS has been recently applied to oil spill characterization from the the *Cosco Busan* oil spill (Corilo *et al*. 2013, Lemkau *et al*. 2014), *Deepwater Horizon* (McKenna *et al*. 2013, Ruddy *et al*. 2014), naturally seeped oil (McKenna *et al.* 2014), oil residues found along the Texas Coast (Koolen *et al.* 2015), and water-soluble fractions of the neat Macondo surrogate oil (Liu and Kujawinski 2015).

The GoMRI HIE had three laboratories (hereafter referred to as FT1, FT2, and FT3), each with uniquely distinct FT-ICR mass spectrometers, that contributed analytical results facilitating the first intercomparison of FT-ICR mass spectra collected for petroleum and weathered oil residues.

Advancements in ionization, ion accumulation, ion transfer, and excitation and detection events of the FT-ICR-MS experiment continue to improve incrementally in mass resolution, mass measurement accuracy (mass error), and number of peaks detected. The complexity of petroleum and weathered products challenges all FT-ICR mass spectrometers and pushes the limits of commercial systems in nearly all figures of merit. Custom-built FT-ICR-MS systems and commercial upgrades are essential for achieving improved performance. Importantly, mass resolving power in FT-ICR-MS increases linearly with applied magnetic field, and eight other FT-ICR-MS performance parameters increase linearly (quadrupolar axialization efficiency, data acquisition speed, upper mass limit for peak coalescence) or quadratically (upper mass limit due to trapping potential, maximum ion kinetic energy maximum number of trapped ions, maximum ion trapping duration, FT-ICR-MS mass resolving power) with increasing magnetic field strength (Marshall *et al.* 1998). In addition, ionization mechanisms are highly variable amongst different ion sources typically coupled to FT-ICR-MS (e.g. electrospray ionization (ESI), atmospheric pressure photoionization), and can preferentially favor the ionization of certain species (e.g. acidic in ESI operated in negative mode) (Oldenburg *et al*. 2014). Finally, since all the possible isomers of a compound have the same exact *m/z*, they cannot be resolved using the FTICR-MS, thus limiting isomer-specific measurements. These unique characteristics of FT-ICR-MS mean that its quantitative capabilities are relative and cannot be directly compared to the absolute concentrations derived from GC-MS. However, a correlation between the relative abundances in FT-ICR-MS and GC-MS concentrations has been demonstrated, suggesting rudimentary quantitative capabilities of FT-ICR-MS (Oldenburg *et al*. 2014). Therefore, unlike discrete measurements of absolute concentrations of targeted individual compounds (such as phenanthrene) using GC-MS, it was expected that the FT-ICR-MS results from each participant would provide untargeted screening of a plethora of non-GC amenable species. Relative

abundances may vary among laboratories, due to the different characteristics of the FT-ICR-MS instrumentation and the sample analysis and data processing methods.

Each laboratory provided experimental results typically reported in FT-ICR-MS studies (see Table 13 for sample preparation, instrument details, and operating procedures for the three participating laboratories) for SRM 2779 and candidate SRM 2777. Here is a select overview of their results and discussion on them:

a. ***Elemental ratios via positive and negative ion electrospray ionization*** (Table 14): Because each FT-ICR-MS spectrum contains thousands of peaks, a summary table was used to compare chemical characteristics of SRM 2779 and the candidate SRM 2777 by the three participants. The elemental ratios provide insight into heteroatom contributions within detected peaks with assigned formulas. The dominant heteroatom classes (isoabundance > 1%, where isoabundance = Σ(Intensities within a compound class)/ Σ(Intensities of all detected peaks) × 100) provide further details on the formula types of the heteroatom-containing compounds. Laboratory FT1 reported only one value per ratio while the other two participants analyzed each sample three times. Despite the inherent differences expected from individual FT-ICR MS platforms (Table 13), the parameters reported by the three participants agreed well. This suggests that each platform effectively captured the overall chemical character of the most easily ionized (and therefore, highest signal to noise) species in both samples. In ESI operated in negative mode, these would be acidic species which are easy to deprotonate (e.g. carboxylic acids, alcohols, pyrroles), while in positive mode basic, readily protonated species would be detected (e.g. compounds with pyridinic nitrogen atoms) (Oldenburg *et al.* 2014).

b. ***Mass scale expanded inset at less than one nominal mass for SRM 2779 and candidate SRM 2777*** (Figure 25): This figure shows differences at one randomly selected nominal mass window among the different participants. The trends observed in such a narrow section of the spectra can be indicative of the overall compositional trends shown in Table 14 and Figures 26 and 27; however, this figure primarily illustrates the unprecedented level of detailed species characterization in such a narrow region as one nominal mass, which is afforded by ultrahigh mass resolving power of FT-ICR-MS. Each participating laboratory captured similar characteristics and highlighted the decreased relative abundance of O_1 and concurrent increase in relative abundance for O_2, O_3, and O_4 from SRM 2779 to candidate SRM 2777 with a similar number of peaks detected above the baseline noise level. Note the mass resolving capability of FT-ICR-MS which is able to distinguish ^{13}C isotopologs of identified compounds.

c. ***Distribution of the number of assigned formulae for all compound classes detected in ESI negative mode*** (Figures 26 and 27): The distributions of carbon number (Figure 26) and double bond equivalents (number of rings and/or double bonds involving carbon; DBE) (Figure 27) provide a broad overview of the chemical characteristics of the neat crude oil (SRM 2779) and weathered oil (SRM 2777). These figures also reduced the amount of information generated by the FT-ICR-MS and hence allowed more straightforward comparisons between labs and samples on the global compositional

features. All three laboratories showed carbon number distributions above C_{65} (Figure 26) and reported higher DBE (Figure 27) in SRM 2779, which suggests overall higher aromaticity in the original crude oil. The most abundant compounds in both SRM 2779 and candidate SRM 2777 contain between C_{25}-C_{40} for all three labs, with the maxima slightly shifted toward lower carbon numbers in the candidate SRM 2777. On the other hand, DBE distribution is notably shifted from the most abundant DBE values situated around 15 approx. in SRM 2779 to lower DBE values in candidate SRM 2777. This comparison may be revealing as to which compound classes are most affected by weathering, and to which types of species are they being transformed to. For example, the apparent shift to lower DBE upon weathering might be due to the oxygenation of parent oil compounds involving species with aromatic double bonds, which lowers their DBE, while the introduction of acidic oxygen allows them to be preferentially detected by ESI in negative mode. On the other hand, the slight shift towards lower carbon numbers in candidate SRM 2777 indicates that the oxygenation is coupled to degradation (e.g., decarboxylation) of the larger parent oil compounds, which was also reflected in carbon distributions as all laboratories observed lower carbon numbers in SRM 2777.

d. ***NegESI SRM2779 DBE versus carbon number image for N1 class only*** (Figure 28): In negative ion electrospray ionization, the N_1 class corresponds to pyrrolic (five-membered ring) nitrogen compounds. Isobundance color-coded contour plots of DBE versus carbon number and relative abundance are used to visualize rapidly compositional trends within a heteroatom class for both samples collected at all three labs. Compounds with the highest relative abundance are indicated by the warm (i.e., red, orange) colors. All three laboratories, regardless of instrumental parameters or experimental methods, report highly abundant compounds across the same carbon number and DBE ranges. Because peak intensities in the FT-ICR-MS are a proxy of ionization efficiencies, Figure 28 indicates that ionization was consistent for the most acidic and therefore easily ionized compounds at all three labs.

In summary, this was the first intercomparison of FT-ICR-MS analyses of petroleum and weathered petroleum using ultrahigh resolution FT-ICR-MS. The three participating laboratories submitted generally similar results despite significantly different instrument platforms and operational and data processing protocols. This shows great promise for continued and increasing usage of FT-ICR-MS for neat and weathered crude and refined oils that cannot be characterized fully by gas chromatography due to the presence of high molecular weight, polar and non-volatile compounds. However, there were slight differences that indicate minor challenges for direct comparison of results. Differences stem primarily from the fact that, at this point, the FTMS instrumentation platforms, sample analysis and data processing protocols are highly individualized for each FTMS laboratory. Due to these differences, a common reference material, specific to a petroleum product, could be helpful for development of more standardized FTMS protocols, which, in the future, would enable more direct comparisons of the results from different laboratories.

V. Non-chemical analyses (cytotoxicity, shear viscosity, and interfacial tension)

a. ***Cytotoxicity and activation of Ah receptor signaling by fresh and aged Macondo oil samples:*** Both oil samples were diluted in water and dimethylsulfoxide (DMSO). Cytotoxicity was detected in the DMSO-soluble components but not in the aqueous-soluble components for the concentrations tested. Both samples activated Ah receptor-directed signaling of a reporter gene, which is a well known property of polycyclic aromatic hydrocarbons and other compounds in crude oil. Activation of Ah receptor signaling was most apparent in the DMSO extract of SRM2779 and was weaker for candidate SRM 2777, suggesting that field-weathering lowered the bioactivity of the Macondo well oil. However, the cytotoxic activity detected in the samples did not strictly correlate with the ability to activate AhR signaling. This indicates that different chemicals are linked to these two effects. The aqueous extracts of samples 2779 and 2777 yielded similar (low) levels of bioactivity in the AhR signaling bioassays. The participant concluded that coupling bioactivity with analytical methods may be useful for the characterization of oil samples.

b. ***Report on interfacial tension:*** A microtensiometer was used to measure the dynamic interfacial tension of two samples, SRM 2779 and Candidate SRM 2777 (Box 5, Ampule 10), against simulated sea water and deionized water. Measurements were taken at room temperature. The interfacial tension values of SRM 2779 are 10-15mN/m higher than the values of candidate SRM 2777 throughout the measurement. Equilibrium interfacial tension values could not reliably be obtained due to continued decreases in the interfacial tension values even at long experimental times.

c. ***Shear viscosity***: The shear viscosity of two samples, SRM 2779 and candidate SRM 2777 were both studied on a rotational rheometer (TA Instruments AR 2000) over a range of shear-rates, specifically over the range of 1 to 1000 s-1. Both samples showed Newtonian behavior, i.e., exhibited a constant viscosity over the range of shear-rates. The viscosities for SRM 2779 and candidate SRM 2777 (note that the SI unit of viscosity is used here, which is Pas; 1 mPas = 1 centipoise) were 5.16±0.01 mPas and 6.48±0.16 mPas, respectively.

VI. Summary and Recommendations

Twenty laboratories participated in the first GoMRI sponsored HIE. Overall, it was a great success. A wide range of analytes and new techniques were contributed.

The following is recommended:

General

1. Continued usage of certified reference materials in routine analysis along with other means to elevate accuracy and minimalize systematic error.
2. Take advantage of the supplemental information section, now commonplace in peer-review journals, and provide detailed content on analytical methods and QA/QC, allowing readers an opportunity to learn and compare results.
3. Plan for additional intercomparisons that may include other matrices such as animal tissue, water, and sediment samples.
4. Publish the results from the HIE in one or more peer-reviewed journals.

GC analysis for alkanes, aromatics, and biomarkers

1. Challenges were faced with the lower amounts of analytes in candidate SRM 2777, which may limit it to a reference for biomarkers and other compounds that were the least weathered.
2. Encourage laboratories to expand their target analytes list if it does not demand significantly more work. For example, add alkane analysis if already performing PAH and biomarkers by GC-MS.
3. Vigilance regarding the means by which compounds are quantified, especially alkylated PAHs.

FT-ICR-MS

1. This technique shows great promise for continued and increasing usage of FT-ICR-MS for neat and weathered crude and refined oils that cannot be characterized by gas chromatography. However, there were slight differences, and to overcome them, a common reference material, specific to a petroleum product, could be helpful for development of more standardized FTMS protocols, which, in the future, would enable more direct comparisons of the results from different laboratories.
2. Notably, this technique did not face as much challenges for candidate SRM2777. Hence, it could be a more suitable reference material.

VII. Disclaimer

Certain commercial equipment, instruments, materials, or methods are identified in this report to specify adequately procedures performed by participants in the interlaboratory study. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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IX. Tables

Table 1. List of alkanes that each lab reported values for SRM 2779 and candidate SRM 2777.

	Lab number																																							
	1		2		3		4		5		6		7		8		9		10		11		12		13		14		15		16		17		18		19		20	
Analyte	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777
n-decane	✓		✓		✓												✓		✓		✓		✓		✓								✓							
n-undecane	✓		✓		✓												✓		✓	✓	✓		✓		✓						✓		✓							
n-dodecane	✓		✓		✓												✓		✓	✓	✓		✓		✓						✓		✓							
n-tridecane	✓		✓		✓												✓		✓	✓	✓		✓		✓						✓		✓							
n-tetradecane	✓		✓		✓												✓		✓		✓		✓		✓		✓				✓		✓							
n-pentadecane	✓		✓		✓												✓		✓		✓		✓		✓		✓				✓		✓							
n-hexadecane	✓		✓		✓										✓	✓	✓		✓		✓	✓	✓		✓		✓				✓		✓							
n-heptadecane			✓		✓												✓		✓		✓	✓	✓		✓	✓	✓				✓		✓							
n-octadecane			✓		✓												✓		✓		✓	✓	✓		✓	✓	✓				✓		✓							
n-nonadecane	✓	✓	✓		✓												✓		✓		✓	✓	✓		✓		✓				✓		✓							
n-eicosane	✓	✓	✓		✓												✓		✓		✓	✓	✓		✓		✓				✓		✓							
n-henicosane	✓	✓	✓		✓												✓		✓		✓	✓	✓		✓		✓				✓		✓							
n-docasane	✓	✓	✓		✓												✓		✓		✓	✓	✓		✓		✓				✓		✓							
n-tricosane	✓	✓	✓		✓												✓		✓		✓	✓	✓		✓		✓				✓		✓							
n-tetracosane	✓	✓	✓		✓												✓		✓	✓	✓	✓	✓		✓		✓				✓		✓							
n-pentacosane	✓	✓	✓		✓												✓		✓	✓	✓	✓	✓		✓		✓				✓		✓							
n-hexacosane	✓	✓	✓		✓												✓		✓	✓	✓	✓	✓		✓		✓				✓		✓							
n-heptacosane	✓	✓	✓		✓												✓		✓		✓	✓	✓		✓		✓				✓		✓							
n-octacosane	✓	✓	✓		✓												✓		✓		✓	✓	✓		✓		✓				✓		✓							
n-nonacosane	✓	✓	✓		✓	✓											✓		✓		✓	✓	✓		✓		✓				✓		✓							
n-triacontane	✓	✓	✓		✓	✓											✓		✓	✓	✓	✓	✓		✓		✓	✓			✓									
n-hentriacontane	✓	✓	✓		✓	✓											✓		✓	✓	✓	✓	✓		✓	✓	✓	✓			✓			✓						
n-dotriacontane	✓	✓	✓	✓	✓	✓											✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓			✓			✓						
n-tritriacontane			✓	✓	✓	✓											✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓			✓			✓						
n-tetratriacontane			✓	✓	✓	✓											✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓			✓			✓						
n-pentatriacontane			✓	✓	✓	✓											✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓			✓									
n-hexatriacontane			✓	✓	✓	✓											✓	✓					✓		✓	✓	✓	✓			✓									
n-heptatriacontane			✓	✓	✓	✓											✓	✓					✓		✓	✓	✓	✓			✓									
n-octatriacontane			✓	✓	✓	✓											✓	✓					✓				✓	✓			✓									
n-nonatriacontane			✓	✓	✓	✓											✓	✓					✓				✓	✓												
n-tetracontane			✓	✓	✓	✓											✓	✓					✓				✓													
norpristane			✓		✓	✓																	✓																	
pristane			✓		✓	✓											✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓												
phytane			✓		✓	✓											✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓												

Table 2. List of PAHs that each lab reported values for SRM 2779 and candidate SRM 2777.

	Lab number																																							
	1		2		3		4		5		6		7		8		9		10		11		12		13		14		15		16		17		18		19		20	
Analyte	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777
naphthalene	✓		✓	✓	✓		✓		✓	✓	✓	✓	✓	✓			✓		✓	✓	✓	✓	✓		✓	✓	✓	✓	✓								✓	✓		
biphenyl	✓		✓		✓		✓	✓			✓	✓					✓	✓	✓				✓														✓	✓		
acenaphthene	✓		✓				✓		✓		✓	✓	✓	✓			✓						✓				✓													
acenaphthylene	✓		✓				✓		✓		✓	✓	✓				✓						✓				✓													
fluorene	✓		✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓			✓	✓			✓	✓	✓		✓	✓	✓	✓									✓	✓		
phenanthrene	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓		✓		✓	✓	✓	✓							✓	✓		
anthracene	✓						✓	✓		✓	✓	✓	✓	✓			✓	✓			✓	✓	✓				✓	✓												
fluoranthene	✓	✓	✓	✓			✓	✓	✓	✓	✓	✓	✓				✓	✓			✓	✓	✓		✓		✓	✓												
pyrene	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓			✓	✓			✓	✓	✓	✓	✓		✓	✓							✓	✓	✓	✓		
benzo[*b*]fluorene			✓																				✓				✓	✓												
benz[*a*]anthracene	✓		✓				✓	✓			✓	✓	✓				✓				✓	✓	✓		✓		✓	✓									✓	✓		
chrysene	✓	✓									✓	✓	✓	✓							✓	✓			✓		✓	✓	✓	✓							✓	✓		
triphenylene	✓	✓									✓	✓																												
chrysene+triphenylene			✓	✓			✓	✓	✓	✓							✓	✓					✓	✓																
benzo[*b*]fluoranthene	✓	✓	✓	✓					✓	✓	✓	✓	✓	✓			✓	✓			✓	✓	✓														✓	✓		
benzo[*j*]fluoranthene																																								
benzo[*k*]fluoranthene	✓						✓	✓					✓				✓				✓						✓													
benzo[*a*]fluoranthene																																								
benzo[*e*]pyrene	✓	✓	✓	✓					✓	✓	✓	✓					✓	✓			✓	✓	✓	✓											✓	✓	✓	✓		
benzo[*a*]pyrene	✓		✓				✓	✓	✓		✓	✓	✓				✓				✓	✓	✓				✓													
perylene	✓										✓	✓					✓	✓			✓																			
indeno[*1,2,3-cd*]pyrene										✓	✓	✓	✓				✓	✓									✓	✓												
benzo[*ghi*]perylene	✓		✓						✓	✓		✓	✓				✓	✓			✓	✓	✓				✓	✓												
dibenz[*a,h*]anthracene	✓		✓				✓	✓					✓				✓	✓			✓						✓	✓												
cis/trans-decalin			✓																				✓																	
dibenzofuran	✓		✓				✓	✓			✓	✓							✓	✓			✓																	
retene			✓	✓			✓	✓	✓	✓							✓	✓																						
benzothiophene			✓				✓																✓																	
dibenzothiophene	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓					✓	✓	✓	✓	✓	✓	✓		✓		✓													
naphthobenzothiophene			✓				✓	✓													✓	✓	✓	✓																

Table 3. List of alkylated PAHs that each lab reported values for SRM 2779 and SRM 2777

	Lab number																																							
	1		2		3		4		5		6		7		8		9		10		11		12		13		14		15		16		17		18		19		20	
Analyte	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777
1-methylnaphthalene	✓		✓	✓			✓		✓	✓	✓	✓					✓	✓	✓	✓			✓		✓	✓	✓	✓									✓			
2-methylnaphthalene	✓		✓	✓			✓		✓	✓	✓	✓	✓	✓			✓	✓	✓	✓			✓		✓	✓	✓	✓									✓			
2,6-dimethylnaphthalene			✓	✓			✓		✓	✓	✓	✓	✓	✓			✓	✓					✓				✓										✓			
1,6,7-trimethylnaphthalene			✓						✓	✓	✓	✓											✓														✓			
1-methylphenanthrene	✓	✓	✓	✓			✓	✓	✓	✓	✓	✓					✓	✓	✓	✓			✓	✓	✓	✓	✓	✓									✓	✓		
2-methylphenanthrene			✓	✓			✓	✓			✓	✓					✓	✓	✓	✓			✓	✓	✓	✓	✓	✓												
3-methylphenanthrene			✓	✓			✓	✓	✓	✓	✓	✓	✓	✓			✓	✓	✓	✓			✓	✓	✓	✓	✓	✓												
9-methylphenanthrene			✓	✓			✓	✓	✓	✓			✓	✓			✓	✓	✓	✓			✓	✓			✓	✓												
2-methylanthracene			✓				✓	✓									✓						✓		✓		✓	✓												
C_1-decalins			✓																		✓		✓																	
C_2-decalins			✓																				✓																	
C_3-decalins			✓																				✓																	
C_4-decalins			✓																				✓																	
C_1-naphthalenes	✓		✓	✓	✓	✓			✓	✓	✓	✓					✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓										✓	
C_2-naphthalenes	✓		✓	✓	✓	✓			✓	✓	✓	✓					✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓										✓	
C_3-naphthalenes	✓	✓	✓		✓	✓			✓	✓	✓	✓							✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓										✓	✓
C_4-naphthalenes	✓	✓	✓		✓	✓			✓	✓									✓	✓	✓	✓	✓		✓	✓	✓												✓	✓
C_1-benzothiophenes			✓																				✓																	
C_2-benzothiophenes			✓																				✓																	
C_3-benzothiophenes			✓																				✓																	
C_4-benzothiophenes			✓																				✓																	
C_1-fluorenes	✓	✓	✓	✓	✓	✓			✓	✓	✓	✓					✓	✓			✓	✓	✓		✓	✓													✓	✓
C_2-fluorenes	✓	✓	✓	✓	✓	✓			✓	✓											✓	✓	✓	✓	✓	✓													✓	✓
C_3-fluorenes	✓	✓	✓	✓					✓	✓											✓	✓	✓	✓	✓	✓													✓	✓
C_1-phenanthrenes/anthracenes	✓	✓	✓	✓	✓	✓			✓	✓	✓	✓					✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓									✓	✓
C_2-phenanthrenes/anthracenes	✓	✓	✓	✓	✓	✓			✓	✓	✓	✓							✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓									✓	✓
C_3-phenanthrenes/anthracenes	✓	✓	✓	✓					✓	✓	✓	✓									✓	✓	✓	✓	✓	✓	✓	✓	✓	✓									✓	✓
C_4-phenanthrenes/anthracenes	✓	✓	✓	✓					✓	✓											✓	✓	✓	✓	✓	✓													✓	✓
C_1-dibenzothiophenes	✓	✓	✓	✓	✓	✓			✓	✓							✓	✓	✓	✓	✓	✓	✓	✓			✓	✓											✓	✓
C_2-dibenzothiophenes	✓	✓	✓	✓	✓	✓			✓	✓	✓	✓							✓	✓	✓	✓	✓	✓			✓												✓	✓
C_3-dibenzothiophenes	✓	✓	✓	✓					✓	✓											✓	✓	✓	✓															✓	✓
C_4-dibenzothiophenes	✓	✓	✓	✓					✓	✓													✓	✓															✓	✓
C_1-fluoranthenes/pyrenes	✓	✓	✓	✓	✓	✓			✓	✓	✓	✓					✓	✓			✓	✓	✓	✓			✓	✓											✓	✓
C_2-fluoranthenes/pyrenes	✓	✓	✓	✓	✓	✓			✓	✓											✓	✓	✓	✓			✓	✓											✓	✓
C_3-fluoranthenes/pyrenes	✓	✓	✓	✓					✓	✓											✓	✓	✓	✓			✓												✓	✓
C_4-fluoranthenes/pyrenes	✓	✓	✓	✓					✓	✓											✓	✓	✓	✓															✓	✓
C_1-naphthobenzothiophenes			✓	✓																	✓	✓	✓	✓																
C_2-naphthobenzothiophenes			✓	✓																	✓	✓	✓	✓																
C_3-naphthobenzothiophenes			✓	✓																	✓	✓	✓	✓																
C_4-naphthobenzothiophenes			✓																				✓																	
C_1-chrysenes	✓	✓	✓	✓					✓	✓	✓	✓					✓	✓			✓	✓	✓	✓			✓	✓	✓	✓									✓	✓
C_2-chrysenes	✓	✓	✓	✓					✓	✓	✓	✓									✓	✓	✓	✓			✓	✓	✓	✓									✓	✓
C_3-chrysenes	✓	✓	✓	✓					✓	✓											✓	✓	✓	✓					✓	✓									✓	✓
C_4-chrysenes			✓						✓	✓											✓	✓	✓																	

Table 4. List of biomarkers that each lab reported values for SRM 2779 and candidate SRM 2777.

	Lab number																																					
	1		2		3		4		5		6		7		8		9		10		11		12		13		14		15		16		17		18		19		20	
Analyte	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777	2779	2777
Carbazole			✓				✓	✓															✓																	
18α(H)-22,29,30-Trisnorneohopane			✓	✓			✓	✓											✓	✓			✓	✓	✓	✓	✓	✓												
17α(H)-22,29,30-Trisnorhopane	✓	✓	✓	✓			✓	✓									✓	✓	✓	✓			✓	✓	✓	✓	✓	✓												
17α(H),21β(H)-30-Norhopane	✓	✓	✓	✓			✓	✓									✓	✓					✓		✓	✓	✓	✓												
18α(H)-30-Norneohopane			✓	✓															✓	✓			✓	✓	✓	✓														
17α(H)-Diahopane			✓																✓	✓			✓	✓	✓	✓														
17α(H),21β(H)-Hopane	✓	✓	✓	✓			✓	✓									✓	✓	✓	✓			✓	✓	✓	✓	✓	✓												
17α(H),21β(H)-22R-Homohopane	✓	✓	✓	✓			✓	✓									✓	✓	✓	✓			✓	✓	✓	✓	✓	✓												
17α(H),21β(H)-22S-Homohopane	✓	✓	✓	✓			✓	✓									✓	✓	✓	✓			✓	✓	✓	✓	✓	✓												
13β(H),17α(H)-Diacholestane 20S			✓	✓																			✓	✓	✓	✓	✓	✓												
5α(H),14α(H),17α(H)-Cholestane 20S			✓	✓			✓	✓											✓	✓			✓	✓			✓	✓												
5α(H),14α(H),17α(H)-Cholestane 20R	✓	✓	✓	✓			✓	✓									✓	✓	✓	✓			✓	✓	✓	✓	✓	✓												
5α(H),14α(H),17α(H)-24-Ethylcholestane 20S			✓	✓			✓	✓											✓	✓			✓	✓	✓	✓	✓	✓												
5α(H),14αH),17α(H)-24-Ethylcholestane 20R	✓	✓	✓	✓			✓	✓									✓	✓	✓	✓			✓	✓	✓	✓	✓	✓												
5α(H),14β(H),17β(H)-Cholestane 20R	✓	✓	✓	✓			✓	✓									✓	✓	✓	✓			✓	✓			✓	✓												
5α(H),14β(H),17β(H)-Cholestane 20S			✓	✓			✓	✓											✓	✓			✓	✓	✓	✓	✓	✓												
5α(H),14β (H),17β(H)-24-Ethylcholestane 20R	✓	✓	✓	✓			✓	✓									✓	✓	✓	✓			✓	✓	✓	✓	✓	✓												
5α(H),14β (H),17βb(H)-24-Ethylcholestane 20S			✓	✓			✓	✓											✓	✓			✓	✓	✓	✓	✓	✓												
C_{20}-triaromatic steroid (pregnane derivative)			✓	✓															✓	✓																		
C_{21}-triaromatic steroid (homopregnane)			✓	✓															✓	✓																		
C_{26}-20S-triaromatic steroid (cholestane derivative)			✓	✓															✓	✓																		
C_{26}-20R-triaromatic steroid (cholestane derivative)																																						
C_{27}-20S-triaromatic steroid (methylcholestane derivative)																																						
C_{27}-20R-triaromatic steroid (methylcholestane derivative)			✓	✓															✓	✓			✓	✓														
C_{28}-20S-triaromatic steroid (ethylcholestane derivative)			✓	✓															✓	✓			✓	✓														
C_{28}-20R-triaromatic steroid (ethylcholestane derivative)			✓	✓															✓	✓			✓	✓														

Table 5. Laboratory means and standard deviations (in parentheses) in mg/kg for *n*-alkanes reported in SRM 2779. The interlaboratory mean, uncertainty, and number of reporting labs are also displayed. No values indicate that values were not reported.

	Lab number												
Analyte	1	2	3	4	5	6	7	8	9	10	interlab mean	uncertainty	n
n-decane	8100 (417)	9047 (263)	8198 (170)						8647 (142)	1693 (64.3)	7179	1160	9
n-undecane	7033 (357)	8252 (308)	7250 (187)						8379 (252)	1840 (79.4)	6437	1427	10
n-dodecane	6107 (323)	7436 (257)	5945 (395)						7079 (118)	2083 (98.7)	5688	1140	10
n-tridecane	5530 (282)	6903 (235)	5789 (210)						6001 (64.5)	2437 (104)	5600	1107	10
n-tetradecane	5037 (265)	5899 (232)	4770 (153)						5587 (52.7)	2683 (103)	4875	741	11
n-pentadecane	4423 (226)	5741 (192)	4443 (102)						5278 (54.5)	2893 (95.0)	4649	654	11
n-hexadecane	3903 (185)	4943 (129)	3724 (131)					5928 (200)	4388 (42.3)	2670 (75.5)	4260	637	12
n-heptadecane		4241 (162)	3335 (119)						4017 (39.3)	2563 (85.0)	3563	615	10
n-octadecane		3605 (112)	2690 (109)						3375 (56)	2137 (63.5)	3039	501	10
n-nonadecane	2613 (131)	2794 (80.9)	1920 (31.9)						3472 (172)	1973 (75.7)	2596	425	11
n-eicosane	2277 (116)	2721 (109)	1922 (84.6)						2686 (6.33)	1733 (58.6)	2340	368	11
n-henicosane	1997 (100)	2165 (65.4)	1751 (116)						2164 (11.5)	1533 (58.6)	1978	297	11
n-docasane	1690 (85.4)	1904 (59.9)	1561 (166)						2050 (21.2)	1377 (55.1)	1761	266	11
n-tricosane	1610 (85.4)	1678 (56.0)	1487 (182)						1766 (7.26)	1200 (52.9)	1546	238	11
n-tetracosane	1403 (70.2)	1512 (48.8)	1386 (114)						1611 (12.1)	1123 (49.3)	1416	206	11
n-pentacosane	1147 (60.3)	1349 (45.1)	961 (70.6)						1578 (10.1)	959 (35.9)	1237	170	11
n-hexacosane	986 (50.4)	1100 (44.6)	888 (154)						1187 (53.3)	835 (32.3)	1078	144	11
n-heptacosane	838 (45.9)	886 (44.5)	795 (55.3)						936 (1.52)	623 (30.8)	916	149	11
n-octacosane	697 (40.3)	732 (38.5)	415 (23.4)						814 (15.8)	494 (24.6)	779	208	11
n-nonacosane	624 (40.3)	598 (9.75)	603 (74.7)						759 (10.9)	443 (21.7)	791	328	11
n-triacontane	539 (33.2)	568 (23.9)	479 (77.2)						656 (1.63)	382 (18.5)	570	105	10
n-hentriacontane	486 (28.6)	546 (26.5)	406 (58.4)						645 (2.27)	353 (16.1)	534	108	10
n-dotriacontane	398 (22.6)	443 (25.4)	352 (20.7)						534 (45.1)	296 (7.57)	445	78.1	10
n-tritriacontane		365 (28.9)	220 (28.1)						480 (39.1)	228 (11.3)	362	93.4	9
n-tetratriacontane		304 (5.88)	211 (33.9)						462 (32.0)	181 (9.01)	301	75.7	9
n-pentatriacontane		272 (4.80)	267 (38.3)						415 (10.3)	151 (11.6)	270	58.4	9
n-hexatriacontane		190 (6.24)	158 (10.4)						321 (17.6)		213	56.8	7
n-heptatriacontane		181 (3.45)	139 (11.4)						310 (23.6)		187	63	7
n-octatriacontane		164 (5.38)	101 (18.4)						273 (14.7)		152	69.4	6
n-nonatriacontane		159 (4.18)	94.6 (15.3)						230 (15.9)		135	64.9	5
n-tetracontane		160 (7.47)	65.1 (20.4)						245 (23.0)		131	78.5	5
norpristane		1718 (112)	1132 (124)								1403	341	3
pristane		2577 (29.9)	1621 (47.6)						2775 (82.4)	1127 (37.9)	2245	437	8
phytane		1409 (24.0)	808 (134)						1631 (88.9)	841 (29.9)	1325	245	8

Table 5, continued.

	Lab number												
Analyte	11	12	13	14	15	16	17	18	19	20	interlab mean	uncertainty	n
n-decane	4250 (26.5)	8017 (242)	8153 (250)				8509 (93.0)				7179	1160	9
n-undecane	3777 (32.1)	7617 (216)	7637 (240)			4470 (437)	8113 (150)				6437	1427	10
n-dodecane	3633 (11.5)	6633 (155)	6953 (250)			4050 (328)	6959 (317)				5688	1140	10
n-tridecane	3520 (20.0)	6277 (197)	6437 (183)			4507 (309)	8599 (306)				5600	1107	10
n-tetradecane	3450 (10.0)	5667 (162)	5637 (246)	6340 (1162)		3137 (208)	5419 (213)				4875	741	11
n-pentadecane	3377 (11.5)	5360 (149)	5390 (305)	6016 (450)		3140 (250)	5077 (23.5)				4649	654	11
n-hexadecane	3123 (20.9)	4917 (110)	4700 (252)	5845 (280)		2607 (235)	4366 (540)				4260	637	12
n-heptadecane	2990 (10.0)	4067 (120)	4353 (285)	5206 (383)		2037 (221)	2825 (79.6)				3563	615	10
n-octadecane	2817 (15.3)	3407 (90.2)	3510 (156)	4393 (537)		1623 (147)	2838 (96.6)				3039	501	10
n-nonadecane	2280 (10.0)	2813 (104)	3107 (224)	3816 (447)		1437 (57.7)	2331 (98.0)				2596	425	11
n-eicosane	2200 (10.0)	2697 (66.6)	2913 (142)	3376 (432)		1220 (91.7)	1999 (49.9)				2340	368	11
n-henicosane	1900 (0.00)	2220 (45.8)	2460 (123)	2889 (382)		1053 (68.1)	1622 (63.6)				1978	297	11
n-docasane	1690 (10.0)	2000 (52.9)	2210 (106)	2535 (345)		950 (47.4)	1402 (15.9)				1761	266	11
n-tricosane	1517 (5.70)	1670 (45.8)	2020 (131)	2151 (269)		777 (68.6)	1134 (51.3)				1546	238	11
n-tetracosane	1463 (11.5)	1550 (52.0)	1767 (32.1)	1964 (303)		722 (12.5)	1080 (28.1)				1416	206	11
n-pentacosane	1423 (15.3)	1483 (41.6)	1450 (62.4)	1427 (197)		667 (48.0)	1165 (18.8)				1237	170	11
n-hexacosane	1320 (0.00)	1223 (35.1)	1227 (58.6)	1297 (184)		550 (50.9)	1248 (40.7)				1078	144	11
n-heptacosane	1063 (5.77)	933 (31.2)	1123 (55.1)	1032 (138)		461 (35.6)	1381 (31.2)				916	149	11
n-octacosane	1006 (6.89)	719 (22.7)	902 (32.9)	846 (113)		331 (21.5)	1609 (52.8)				779	208	11
n-nonacosane	873 (2.98)	686 (22.0)	814 (43.5)	676 (84.8)		272 (18.7)	2351 (89.8)				791	328	11
n-triacontane	831 (3.31)	661 (15.0)	737 (58.1)	583 (54.4)		264 (33.5)					570	105	10
n-hentriacontane	823 (7.58)	604 (19.3)	669 (31.2)	576 (39.7)		230 (40.2)					534	108	10
n-dotriacontane	660 (2.74)	504 (23.7)	562 (31.1)	440 (22.8)		265 (88.1)					445	78.1	10
n-tritriacontane	570 (1.90)	426 (8.74)	481 (19.6)	335 (14.1)		155 (40.2)					362	93.4	9
n-tetratriacontane	408 (1.67)	364 (13.5)	395 (17.7)	250 (18.0)		134 (52.5)					301	75.7	9
n-pentatriacontane	329 (1.94)	300 (13.4)	337 (7.57)	168 (25.6)		186 (49.0)					270	58.4	9
n-hexatriacontane		234 (6.90)	278 (15.9)	126 (5.64)		119					213	56.8	7
n-heptatriacontane		209 (13.3)	243 (13.2)	74.6 (13.2)		86.4					187	63.0	7
n-octatriacontane		198 (12.5)		48.1 (9.65)		86.5					152	69.4	6
n-nonatriacontane		153 (6.00)		37.8 (9.04)							135	64.9	5
n-tetracontane		164 (7.81)		23.3 (13.9)							131	78.5	5
norpristane		1360 (52.0)									1403	341	3
pristane	1930 (20.0)	2527 (127)	2857 (98.1)	2547 (190)							2245	437	8
phytane	1280 (0.00)	1503 (61.1)	1360 (52.9)	1772 (258)							1325	245	8

Table 6. Laboratory means and standard deviations (in parentheses) in mg/kg for parent PAHs reported in SRM 2779. The interlaboratory mean, uncertainty, and number of reporting labs are also displayed. Certified (bold) and reference values for SRM 2779 as listed in the Certificate of Analysis (COA) are also displayed. Values in red indicate outliers and were not used to determine the interlaboratory mean and uncertainty. No values indicate that values were not reported.

	Lab number														
Analyte	1	2	3	4	5	6	7	8	9	10	interlab mean	uncertainty	n	COA value	uncertainty
naphthalene	906 (46.9)	640 (12.9)	677 (34.2)	990 (233)	935 (3.46)	886 (17.3)	726 (64.5)		855 (14.5)	855 (25.1)	808	59.2	14	**855**	**46**
biphenyl	174 (8.92)	172 (3.07)	98.8 (3.90)	178 (34.4)		186 (4.58)			170 (12.2)	24.8 (1.33)	246	201	9	195	19
acenaphthene	40.2 (2.63)	14.1 (0.645)		63.9 (13.1)	13.8 (0.451)	17.0 (0.208)	20.9 (0.950)		19.4 (0.569)		24.2	11.6	9		
acenaphthylene	10.9 (0.622)	8.34 (0.261)		7.49 (1.52)	17 (0.306)	8.03 (0.286)	8.00 (2.16)		8.28 (0.1)		8.61	2.46	9	8.09	0.1
fluorene	149 (7.43)	153 (3.01)	107 (1.12)	231 (44.1)	161 (1.53)	132 (4.00)	162 (20.8)		121 (6.11)		148	21.1	12	145	43
phenanthrene	273 (13.5)	303 (1.83)	254 (10.0)	466 (76.3)	304 (4.36)	315 (9.00)	337 (15.1)	341 (0.529)	224 (3.46)	273 (8.25)	287	31.9	15	**258**	**27**
anthracene	6.01 (0.474)			6.49 (1.07)		3.10 (0.290)	3.20 (0.200)		9.25 (0.385)		6.02	2.07	8	**3.42**	**0.59**
fluoranthene	4.74 (0.263)	4.97 (0.110)		7.53 (0.450)	6.35 (0.00577)	9.27 (0.258)	3.60 (0.436)		5.44 (0.247)		5.01	1.42	11	**4.36**	**0.4**
pyrene	12.9 (0.993)	16.8 (0.631)	6.25 (0.269)	82.1 (24.9)	19.4 (0.400)	14.7 (0.681)	17.4 (1.57)		12.8 (0.557)		15.5	5.36	13	**14.81**	**0.39**
benzo[*b*]fluorene		11.8 (1.04)									8.63	3.15	3		
benz[*a*]anthracene	6.83 (0.0797)	6.15 (0.226)		36.3 (0.781)		7.69 (0.380)	7.63 (0.416)		5.30 (0.363)		13.9	10.7	11	**7.03**	**0.85**
chrysene	26.9 (1.52)		28.1 (0.602)			41.8 (3.84)	51.2 (5.55)				48.1	12.9	9	23.3	5.2
triphenylene	25 (1.31)					27.3 (1.08)					26.1	2.31	2	17.7	6.7
chrysene+triphenylene		51.7 (1.63)		91.5 (9.73)	66.9 (1.63)				38.3 (0.289)		57.9	19.6	5	**47.4**	**1.7**
benzo[*b*]fluoranthene	5.17 (0.450)	6.3 (0.0503)			6.49 (0.288)	5.97 (0.137)	5.57 (0.416)		5.11 (0.356)		5.95	1.02	9	**5.62**	**0.34**
benzo[*k*]fluoranthene	3.31 (0.197)			15.3 (2.83)			1.30 (0.100)		0.221 (0.0458)		5.24	5.18	6	0.66	0.28
benzo[*e*]pyrene	11.7 (0.822)	11.0 (0.443)			13.2 (0.0577)	10.6 (0.153)			9.88 (0.569)		12.7	3.01	9	**10.78**	**0.6**
benzo[*a*]pyrene	3.93 (0.278)	2.03 (0.139)		89.3 (10.4)	1.54 (0.0557)	2.24 (0.352)	2.33 (0.569)		1.88 (0.145)		12.6	17.4	10	1.36	0.35
perylene	1.22 (0.0912)					0.558 (0.118)			0.496 (0.0482)		0.671	0.368	4	0.71	0.17
indeno[*1,2,3-cd*]pyrene						0.801 (0.268)	1.10 (0.100)		0.271 (0.0580)		1.41	1.41	4	0.48	0.14
benzo[*ghi*]perylene	2.02 (0.263)	1.74 (0.0945)			1.36 (0.0346)		2.20 (0.173)		1.57 (0.211)		1.59	0.271	8	**2.11**	**0.26**
dibenz[*a,h*]anthracene	1.19 (0.0737)	1.56 (0.208)		29.6 (2.61)			1.57 (0.115)		1.81 (0.133)		5.53	8.04	7	**0.574**	**0.091**
cis/trans-decalin		679 (12.6)									662	35.3	2		
dibenzofuran	25.1 (1.24)	27.8 (0.552)		35.0 (7.65)		36.9 (0.700)				22.3 (0.727)	28.3	5.11	6	25.7	3.6
retene		16.6 (0.731)		34.0 (11.9)	7.90 (0.230)				25.5 (1.18)		21.0	11.3	4		
benzothiophene		7.22 (0.170)		3.65 (0.0346)							5.3	2.08	3		
dibenzothiophene	48.2 (2.36)	54.2 (1.02)	30.7 (0.276)	47.2 (8.30)	60.5 (0.872)	57.8 (2.23)			46.5 (0.721)	44.4 (2.29)	47.4	6.07	12	**51.8**	**2.1**
naphthobenzothiophene		31.6 (2.20)		25.7 (5.48)							20.2	10.0	4		

Table 6, continued.

	Lab number														
Analyte	11	12	13	14	15	16	17	18	19	20	interlab mean	uncertainty	n	COA value	uncertainty
naphthalene	638 (2.57)	738 (24.0)	775 (13.0)	861 (448)	825 (79.5)				5902 (216)		808	59.2	14	**855**	**46**
biphenyl		176 (5.03)							1039 (35.9)		246	201	9	195	19
acenaphthene		21.7 (0.971)		6.93 (4.92)							24.2	11.6	9		
acenaphthylene		5.79 (0.215)		3.73 (2.39)							8.61	2.46	9	8.09	0.1
fluorene	124 (0.989)	116 (2.08)	119 (6.24)	197 (96.8)					569 (24.1)		148	21.1	12	145	43
phenanthrene	232 (0.865)	239 (6.11)	246 (10.6)	255 (34.4)	255 (22.9)				731 (1.24)		287	31.9	15	**258**	**27**
anthracene	4.84 (0.0304)	11.3 (0.306)		4.03 (2.12)							6.02	2.07	8	**3.42**	**0.59**
fluoranthene	6.56 (0.0267)	2.16 (0.165)	2.88 (0.132)	1.63 (0.387)							5.01	1.42	11	**4.36**	**0.4**
pyrene	13.9 (0.0297)	10.3 (0.153)	9 (0.515)	7.01 (1.63)				15.6	44.8 (1.54)		15.5	5.36	13	**14.81**	**0.39**
benzo[*b*]fluorene		7.27 (0.254)		6.85 (1.87)							8.63	3.15	3		
benz[*a*]anthracene	5.26 (0.0213)	4.6 (0.101)	4.51 (0.269)	8.58 (5.77)					59.5 (3.46)		13.9	10.7	11	**7.03**	**0.85**
chrysene	45.7 (0.0828)		42.2 (2.00)	40.7 (29.4)	87.3 (9.87)				69.3 (2.60)		48.1	12.9	9	23.3	5.2
triphenylene											26.1	2.31	2	17.7	6.7
chrysene+triphenylene		41.2 (0.361)									57.9	19.6	5	**47.4**	**1.7**
benzo[*b*]fluoranthene	4.76 (0.0237)	4.60 (0.129)							9.62 (1.76)		5.95	1.02	9	**5.62**	**0.34**
benzo[*k*]fluoranthene	0.421 (0.00248)			10.9 (12.9)							5.24	5.18	6	0.66	0.28
benzo[*e*]pyrene	11.0 (0.0803)	9.19 (0.202)						13.3	24.2 (1.75)		12.7	3.01	9	**10.78**	**0.6**
benzo[*a*]pyrene	1.74 (0.0122)	1.91 (0.189)		18.8 (10.3)							12.6	17.4	10	1.36	0.35
perylene	0.413 (0.00149)										0.671	0.368	4	0.71	0.17
indeno[*1,2,3-cd*]pyrene				3.47 (1.58)							1.41	1.41	4	0.48	0.14
benzo[*ghi*]perylene	1.44 (0.0113)	1.33 (0.0907)		1.03 (0.266)							1.59	0.271	8	**2.11**	**0.26**
dibenz[*a,h*]anthracene	1.82 (0.0128)			1.13 (0.0556)							5.53	8.04	7	**0.574**	**0.091**
cis/trans-decalin		644 (24.0)									662	35.3	2		
dibenzofuran		22.8 (1.08)									28.3	5.11	6	25.7	3.6
retene											21	11.3	4		
benzothiophene		5.04 (0.159)									5.3	2.08	3		
dibenzothiophene	41.3 (0.286)	38.4 (0.666)	34.3 (1.61)	64.9 (16.5)							47.4	6.07	12	**51.8**	**2.1**
naphthobenzothiophene	10.8 (0.0569)	12.9 (0.265)									20.2	10.0	4		

Table 7. Laboratory means and standard deviations (in parentheses) in mg/kg for alkyl-PAHs reported in SRM 2779. The interlaboratory mean, uncertainty, and number of reporting labs are also displayed. Certified (bold) and reference values for SRM 2779 as listed in the Certificate of Analysis (COA) are also displayed. No values indicate that values were not reported.

	Lab number														
Analyte	1	2	3	4	5	6	7	8	9	10	interlab mean	uncertainty	n	COA value	uncertainty
1-methylnaphthalene	1207 (60.3)	1020 (16.8)		1089 (164)	1220 (0.00)	1193 (25.2)			994 (18.8)	721 (23.8)	1215	330	11	**1140**	**20**
2-methylnaphthalene	1750 (85.4)	1500 (247)		2418 (565)	2153 (5.77)	1683 (32.1)	950 (105)		1463 (25.4)	1157 (32.4)	1877	533	12	**1630**	**50**
2,6-dimethylnaphthalene		894 (13.5)		494 (216)	1060 (10.0)	436 (6.66)	605 (65.9)		949 (94.8)		1184	925	9		
1,6,7-trimethylnaphthalene		315 (5.17)			227 (16.5)	244 (3.06)					377	286	5	306	63
1-methylphenanthrene	176 (8.69)	192 (3.61)		354 (70.3)	231 (3.79)	192 (4.58)			170 (6.03)	132 (2.85)	224	85.6	11	**169**	**10**
2-methylphenanthrene		182 (3.16)		409 (49.7)		240 (4.93)			204 (4.36)	168 (4.18)	210	61.7	8	**230**	**14**
3-methylphenanthrene		163 (3.10)		444 (14.5)	248 (3.06)	223 (5.20)	244 (32)		205 (4.36)	151 (3.53)	215	58.4	10	**206**	**32**
9-methylphenanthrene		214 (4.14)		403 (26.7)	325 (4.04)		224 (31.7)		232 (5.51)	198 (6.13)	234	63.5	8	**232**	**19**
2-methylanthracene		13.4 (0.493)		53.1 (9.27)					25.6 (0.666)		20.1	14.2	6	23.3	2.5
C_1-decalins		1045 (34.2)									1000	89.6	2	1040	410
C_2-decalins		903 (18.7)									887	31.5	2	1060	470
C_3-decalins		399 (12.0)									432	67.1	2	1460	600
C_4-decalins		379 (29.0)									416	75.3	2		
C_1-naphthalenes	2007 (91.2)	1482 (20.0)	2254 (14.5)		3370 (10.0)	3023 (58.6)			2457 (44.2)	1877 (58.6)	2262	373	13		
C_2-naphthalenes	2393 (127)	2014 (28.5)	2971 (87.6)		3970 (26.5)	3783 (280)			1815 (90.4)	2227 (152)	2596	545	13	2170	360
C_3-naphthalenes	1743 (90.7)	1464 (22.5)	1959 (94.9)		3050 (26.5)	2033 (47.3)				1307 (110)	1780	377	12	1380	270
C_4-naphthalenes	966 (57.6)	756 (9.83)	959 (84.1)		1360 (26.5)					282 (23.0)	794	321	10	700	130
C_1-benzothiophenes		27.5 (1.99)									24.2	6.56	2		
C_2-benzothiophenes		32.9 (0.626)									26.5	12.7	2	36	13
C_3-benzothiophenes		42.3 (3.14)									37.4	9.69	2		
C_4-benzothiophenes		23.2 (0.479)									24	1.67	2	30	4
C_1-fluorenes	340 (17.9)	342 (7.66)	296 (3.24)		334 (6.81)	562 (22.6)			217 (5.77)		342	71.9	10	300	60
C_2-fluorenes	487 (20.7)	459 (14.5)	334 (13.2)		419 (9.29)						421	97.2	8	380	30
C_3-fluorenes	411 (20.5)	362 (12.8)			334 (6.43)						325	109	7	270	40
C_1-phenanthrenes/anthracenes	679 (34.7)	730 (16.3)	698 (9.28)		964 (16.0)	979 (44.2)			837 (19.7)	649 (16.7)	724	90.1	13	670	90
C_2-phenanthrenes/anthracenes	729 (38.4)	820 (13.9)	750 (5.89)		940 (13.0)	1387 (80.8)				639 (13.3)	755	156	12	630	60
C_3-phenanthrenes/anthracenes	527 (27.3)	487 (19.9)			733 (171)	1917 (56.9)					661	340	10	400	50
C_4-phenanthrenes/anthracenes	292 (14.9)	193 (8.80)			311 (7.23)						259	161	7	200	30
C_1-dibenzothiophenes	169 (8.41)	158 (4.95)	130 (4.38)		169 (2.52)				99.1 (1.08)	94.6 (4.62)	139	33.9	10	130	20
C_2-dibenzothiophenes	224 (11.3)	224 (7.44)	254 (8.70)		234 (3.21)	399 (12.5)				71.7 (3.68)	204	75.0	10	160	20
C_3-dibenzothiophenes	173 (8.75)	159 (2.86)			152 (3.21)						155	53.2	6	110	10
C_4-dibenzothiophenes	94.7 (9.92)	72.7 (2.94)			73.2 (0.608)						87.2	33.1	5	56	10
C_1-fluoranthenes/pyrenes	97.2 (4.78)	99.4 (3.24)	52.5 (0.452)		86.2 (1.72)	135 (11.2)			64.7 (0.379)		92.9	19.9	10	67	7
C_2-fluoranthenes/pyrenes	153 (8.77)	151 (8.59)	126 (0.793)		137 (5.00)						139	28.3	8	130	20
C_3-fluoranthenes/pyrenes	156 (7.66)	173 (6.96)			151 (2.31)						144	42.2	7	120	20
C_4-fluoranthenes/pyrenes	133 (5.38)	108 (7.71)			101 (2.34)						117	34.4	6	87	21
C_1-naphthobenzothiophenes		68.6 (2.68)									49.9	18.7	3	57	15
C_2-naphthobenzothiophenes		84.2 (4.31)									61.0	24.0	3	70	19
C_3-naphthobenzothiophenes		54.4 (2.79)									41.9	14.7	3	48	12
C_4-naphthobenzothiophenes		20.1 (1.29)									26.0	11.8	2	31	10
C_1-chrysenes	125 (6.78)	120 (3.20)	77.3 (1.03)		113 (0.577)	137 (1.73)			84 (1.85)		114	14.2	11	110	7
C_2-chrysenes	132 (7.13)	139 (10.2)	117 (10.6)		146 (2.52)	175 (3.79)					140	29.3	10	130	10
C_3-chrysenes	128 (4.91)	104 (4.50)			95.7 (3.54)						119	48.8	7	93	12
C_4-chrysenes		67.9 (2.78)			68.6 (0.929)						69.8	15.2	4	71	16

Table 7, continued.

	Lab number														
Analyte	11	12	13	14	15	16	17	18	19	20	interlab mean	uncertainty	n	COA value	uncertainty
1-methylnaphthalene		1029 (31.5)	1022 (36.6)	1052 (625)					2813 (111)		1215	330	11	**1140**	**20**
2-methylnaphthalene		1607 (40.4)	1530 (36.1)	1781 (987)					4532 (163)		1877	533	12	**1630**	**50**
2,6-dimethylnaphthalene		951 (21.5)		439 (269)					4829 (150)		1184	925	9		
1,6,7-trimethylnaphthalene		157 (2.08)							941 (243)		377	286	5	306	63
1-methylphenanthrene		96.1 (2.12)	153 (9.29)	161 (46.6)					603 (9.34)		224	85.6	11	**169**	**10**
2-methylphenanthrene		117 (3.79)	187 (7.00)	175 (55.2)							210	61.7	8	**230**	**14**
3-methylphenanthrene		103 (2.65)	167 (6.66)	197 (72.8)							215	58.4	10	**206**	**32**
9-methylphenanthrene		142 (2.65)		137 (45.7)							234	63.5	8	**232**	**19**
2-methylanthracene		8.16 (0.0700)	8.48 (0.380)	11.8 (7.06)							20.1	14.2	6	23.3	2.5
C_1-decalins		955 (36.5)									1000	89.6	2	1040	410
C_2-decalins		871 (31.4)									887	31.5	2	1060	470
C_3-decalins		466 (6.03)									432	67.1	2	1460	600
C_4-decalins		454 (26.1)									416	75.3	2		
C_1-naphthalenes	1250 (0.129)	1557 (50.3)	2553 (77.7)	2833 (1611)	1738 (54.0)					3010 (151)	2262	373	13		
C_2-naphthalenes	1387 (11.5)	1837 (60.3)	3373 (136)	1840 (1055)	1776 (93.0)					4367 (227)	2596	545	13	2170	360
C_3-naphthalenes	842 (5.63)	1137 (25.2)	2053 (139)	1754 (792)	1238 (131)					2780 (141)	1780	377	12	1380	270
C_4-naphthalenes	270 (1.10)	534 (12.7)	1247 (85)	31.6 (8.25)						1537 (92.9)	794	321	10	700	130
C_1-benzothiophenes		21 (0.306)									24.2	6.56	2		
C_2-benzothiophenes		20.2 (0.569)									26.5	12.7	2	36	13
C_3-benzothiophenes		32.6 (0.839)									37.4	9.69	2		
C_4-benzothiophenes		24.8 (1.42)									24	1.67	2	30	4
C_1-fluorenes	214 (1.75)	234 (8.74)	396 (20.2)							481 (25.3)	342	71.9	10	300	60
C_2-fluorenes	249 (1.70)	290 (6.51)	440 (20.4)							689 (29.2)	421	97.2	8	380	30
C_3-fluorenes	163 (0.709)	215 (4.04)	211 (5.29)							581 (29.0)	325	109	7	270	40
C_1-phenanthrenes/anthracenes	454 (0.311)	477 (10.6)	733 (31.1)	681 (226)	633 (87.4)					893 (45.6)	724	90.1	13	670	90
C_2-phenanthrenes/anthracenes	459 (2.08)	481 (11.5)	751 (38.6)	442 (325)	631 (108)					1035 (52.1)	755	156	12	630	60
C_3-phenanthrenes/anthracenes	245 (1.85)	269 (3.21)	428 (15.9)	212 (98.6)	527 (79.7)					1263 (61.1)	661	340	10	400	50
C_4-phenanthrenes/anthracenes	110 (0.722)	113 (4.36)	95.2 (4.80)							699 (35.7)	259	161	7	200	30
C_1-dibenzothiophenes	116 (0.399)	111 (2.52)		78.0 (40.4)						262 (13.0)	139	33.9	10	130	20
C_2-dibenzothiophenes	145 (0.665)	131 (3.06)		9.08 (1.74)						346 (17.5)	204	75.0	10	160	20
C_3-dibenzothiophenes	88.2 (0.743)	93.3 (1.55)								267 (13.6)	155	53.2	6	110	10
C_4-dibenzothiophenes		48.6 (0.361)								147 (15.4)	87.2	33.1	5	56	10
C_1-fluoranthenes/pyrenes	77.2 (0.545)	57 (1.74)		118 (64.0)						142 (7.00)	92.9	19.9	10	67	7
C_2-fluoranthenes/pyrenes	106 (0.717)	91.9 (1.76)		124 (8.72)						224 (12.8)	139	28.3	8	130	20
C_3-fluoranthenes/pyrenes	115 (0.928)	116 (3.21)		34.0 (21.2)						228 (11.2)	144	42.2	7	120	20
C_4-fluoranthenes/pyrenes	79.4 (0.164)	87.7 (1.80)								195 (7.86)	117	34.4	6	87	21
C_1-naphthobenzothiophenes	40.1 (0.00462)	41 (0.557)									49.9	18.7	3	57	15
C_2-naphthobenzothiophenes	44.1 (0.0266)	54.7 (0.416)									61.0	24.0	3	70	19
C_3-naphthobenzothiophenes	29 (0.0219)	42.3 (1.14)									41.9	14.7	3	48	12
C_4-naphthobenzothiophenes		31.9 (1.68)									26.0	11.8	2	31	10
C_1-chrysenes	95.1 (0.764)	105 (1.15)		151 (80.3)	103 (4.73)					141 (7.66)	114	14.2	11	110	7
C_2-chrysenes	111 (0.553)	123 (1.53)		102 (44.3)	102 (10.4)					256 (13.9)	140	29.3	10	130	10
C_3-chrysenes	73.2 (0.298)	136 (1.00)			47.7 (4.04)					248 (9.55)	119	48.8	7	93	12
C_4-chrysenes	52.9 (0.400)	89.8 (4.57)									69.8	15.2	4	71	16

Table 8. Laboratory means and standard deviations (in parentheses) in mg/kg for biomarkers reported in SRM 2779. The interlaboratory mean, uncertainty, and number of reporting labs are also displayed. Certified (bold) and reference values for SRM 2779 as listed in the Certificate of Analysis (COA) are also displayed. No values indicate that values were not reported.

	Lab number														
Analyte	1	2	3	4	5	6	7	8	9	10	interlab mean	uncertainty	n	COA value	uncertainty
Carbazole		7.95 (0.371)		5.33 (0.785)							5.64	2.50	3		
18α(H)-22,29,30-Trisnorneohopane		7.02 (0.376)		12.7 (0.879)						13.4 (0.260)	10.0	2.99	6	6.9	1.1
17α(H)-22,29,30-Trisnorhopane	9.84 (0.467)	6.48 (0.197)		10.2 (1.08)					13 (2.11)	11.2 (0.512)	9.19	2.02	8	7.29	0.79
17α(H),21β(H)-30-Norhopane	25.8 (1.51)	18.7 (0.849)		23.1 (1.91)					31.4 (2.11)		19.4	8.42	7	17.0	4.6
18α(H)-30-Norneohopane		7.73 (0.605)								11.4 (0.315)	10.7	3.19	4		
17α(H)-Diahopane		4.80 (0.332)								11.0 (0.166)	7.90	2.73	4	4.5	1.2
17α(H),21β(H)-Hopane	45.4 (2.64)	43.0 (1.27)		45.8 (2.54)					56.1 (1.51)	69.2 (2.98)	51.4	6.17	8	42.1	9.9
17α(H),21β(H)-22R-Homohopane	16.9 (1.39)	11.6 (0.787)		19.8 (1.08)					22.8 (0.416)	30.9 (1.12)	20.0	3.91	8	13.8	3.6
17α(H),21β(H)-22S-Homohopane	24.5 (1.53)	17.04 (0.617)		23.9 (1.64)					32.8 (1.01)	20.8 (0.176)	22.9	3.83	8	17.3	4.3
13β(H)17α(H)-Diacholestane 20S		40.8 (3.13)									48.1	17.6	4	41.2	6.7
5α(H),14α(H),17α(H)-Cholestane 20S		49.5 (1.79)		24.3 (0.176)							42.7	14.2	4		
5α(H),14α(H),17α(H)-Cholestane 20R	14.7 (0.790)	45.3 (4.55)		23.0 (0.981)					15.8 (0.100)	20.7 (0.798)	24.5	13.2	8		
5α(H),14α(H),17α(H)-24-Ethylcholestane 20S		18.6 (1.07)		15.7 (0.951)						24.6 (0.767)	22.6	4.61	6		
5α(H),14α(H),17α(H)-24-Ethylcholestane 20R	22.8 (1.99)	17.5 (0.111)		16.1 (0.596)					15.9 (1.15)	18.4 (0.429)	19.9	2.39	8	16.9	5.0
5α(H),14β(H),17β(H)-Cholestane 20R	36.6 (2.24)	22.4 (1.98)		24.2 (0.797)					40.2 (2.03)	31.4 (0.566)	29.3	6.04	7	23.7	2.7
5α(H),14β(H),17β(H)-Cholestane 20S		22.9 (2.17)		23.3 (2.27)						24.1 (0.270)	25.0	2.71	6	22.3	7.5
5α(H),14β(H),17β(H)-24-Ethylcholestane 20R	17.9 (1.04)	27.7 (2.24)		20.1 (1.17)					28.1 (0.586)	29.8 (1.07)	31	6.97	8	21.3	8.2
5α(H),14β(H),17β(H)-24-Ethylcholestane 20S		23.0 (1.79)		20.3 (1.09)						24.5 (0.732)	24.4	2.65	6	23.1	6.4
C_{20}-triaromatic steroid (pregnane derivative)		10.8 (0.193)								16.4 (0.567)	13.6	5.54	2		
C_{21}-triaromatic steroid (homopregnane)		9.58 (0.130)								15.6 (0.378)	12.6	6.05	2		
C_{26}-20S-triaromatic steroid (cholestane derivative)		4.69 (0.308)								8.10 (0.170)	6.42	3.46	2		
C_{27}-20R-triaromatic steroid (methylcholestane derivative)		10.0 (0.136)								14.3 (0.387)	29.6	35.0	3		
C_{28}-20S-triaromatic steroid (ethylcholestane derivative)		13.3 (0.372)								21.9 (0.403)	39.3	43.6	3		
C_{28}-20R-triaromatic steroid (ethylcholestane derivative)		9.22 (1.28)								17.3 (0.713)	30.1	34.1	3		

Table 8, continued.

	Lab number														
Analyte	11	12	13	14	15	16	17	18	19	20	interlab mean	uncertainty	n	COA value	uncertainty
Carbazole		3.64 (0.275)									5.64	2.50	3		
18α(H)-22,29,30-Trisnorneohopane		10.3 (0.891)	12.6 (0.252)	4.29 (0.667)							10.0	2.99	6	6.9	1.1
17α(H)-22,29,30-Trisnorhopane		8.37 (0.446)	10.3 (0.208)	3.98 (0.354)							9.19	2.02	8	7.29	0.79
17α(H),21β(H)-30-Norhopane		4.66 (1.32)	28.3 (0.462)	3.59 (0.617)							19.4	8.42	7	17.0	4.6
18α(H)-30-Norneohopane		8.79 (0.528)	14.9 (0.265)								10.7	3.19	4		
17α(H)-Diahopane		6.65 (0.294)	9.11 (0.0896)								7.90	2.73	4	4.5	1.2
17α(H),21β(H)-Hopane		50.1 (0.306)	55.7 (0.896)	45.5 (1.07)							51.4	6.17	8	42.1	9.9
17α(H),21β(H)-22R-Homohopane		17.5 (0.404)	20.9 (0.252)	19.9 (1.03)							20.0	3.91	8	13.8	3.6
17α(H),21β(H)-22S-Homohopane		21.4 (0.493)	26.9 (0.379)	16.2 (1.12)							22.9	3.83	8	17.3	4.3
13β(H)17α(H)-Diacholestane 20S		46.4 (2.55)	73 (0.777)	32.1 (9.26)							48.1	17.6	4	41.2	6.7
5α(H),14α(H),17α(H)-Cholestane 20S		57.3 (1.05)		39.9 (3.75)							42.7	14.2	4		
5α(H),14α(H),17α(H)-Cholestane 20R		59.8 (2.37)	12.8 (0.00)	3.88 (0.824)							24.5	13.2	8		
5α(H),14α(H),17α(H)-24-Ethylcholestane 20S		32.1 (1.47)	21.5 (0.0577)	23.2 (3.45)							22.6	4.61	6		
5α(H),14α(H),17α(H)-24-Ethylcholestane 20R		23.6 (0.208)	20.4 (0.208)	24.3 (2.2)							19.9	2.39	8	16.9	5.0
5α(H),14β(H),17β(H)-Cholestane 20R		31.9 (0.458)		18.1 (1.01)							29.3	6.04	7	23.7	2.7
5α(H),14β(H),17β(H)-Cholestane 20S		30.2 (0.351)	27.9 (0.907)	21.7 (2.71)							25.0	2.71	6	22.3	7.5
5α(H),14β(H),17β(H)-24-Ethylcholestane 20R		42.2 (1.89)	45.5 (0.513)	36.5 (2.93)							31.0	6.97	8	21.3	8.2
5α(H),14β(H),17β(H)-24-Ethylcholestane 20S		25.2 (1.91)	30.1 (0.173)	23.5 (0.97)							24.4	2.65	6	23.1	6.4
C_{20}-triaromatic steroid (pregnane derivative)											13.6	5.54	2		
C_{21}-triaromatic steroid (homopregnane)											12.6	6.05	2		
C_{26}-20S-triaromatic steroid (cholestane derivative)											6.42	3.46	2		
C_{27}-20R-triaromatic steroid (methylcholestane derivative)		64.5 (2.87)									29.6	35.0	3		
C_{28}-20S-triaromatic steroid (ethylcholestane derivative)		82.6 (1.50)									39.3	43.6	3		
C_{28}-20R-triaromatic steroid (ethylcholestane derivative)		63.9 (1.31)									30.1	34.1	3		

Table 9. Laboratory means and standard deviations (in parentheses) in mg/kg for n-alkanes reported in candidate SRM 2777. The interlaboratory mean, uncertainty, and number of reporting labs are also displayed. No values indicate that values were not reported.

	Lab number												
Analyte	1	2	3	4	5	6	7	8	9	10	interlab mean	uncertainty	n
n-decane													
n-undecane										0.496 (0.102)	0.496		1
n-dodecane										0.426 (0.0455)	0.426		1
n-tridecane										0.416 (0.0445)	0.416		1
n-tetradecane													
n-pentadecane													
n-hexadecane								8.81 (0.154)			4.45	8.74	2
n-heptadecane											2.38	3.25	2
n-octadecane											2.42	3.11	2
n-nonadecane	2.48 (0.0451)										1.92	1.12	2
n-eicosane	2.04 (0.127)										2.39	0.701	2
n-henicosane	2.17 (0.163)										1.51	1.31	2
n-docasane	1.69 (0.0351)										1.20	0.976	2
n-tricosane	2.52 (0.164)										1.58	1.90	2
n-tetracosane	1.33 (0.0503)									1.48 (0.172)	1.13	0.564	3
n-pentacosane	1.44 (0.150)									11.2 (1.39)	7.81	6.38	3
n-hexacosane	0.660 (0.0173)									5.57 (0.679)	4.25	3.63	3
n-heptacosane	0.740 (0.0173)										0.899	0.318	2
n-octacosane	2.38 (0.156)										1.67	1.42	2
n-nonacosane	6.89 (0.152)		4.21 (0.127)								3.99	3.48	3
n-triacontane	2.28 (0.0907)		12.8 (1.55)							2.33 (0.095)	3.95	4.44	5
n-hentriacontane	2.06 (0.132)		4.62 (0.157)							3.58 (0.307)	4.82	3.21	7
n-dotriacontane	2.50 (0.129)	7.06 (1.01)	10.5 (0.556)						5.57 (0.503)	2.38 (0.075)	5.62	2.59	9
n-tritriacontane		10.7 (3.37)	11.5 (1.45)						11.7 (1.08)	3.29 (0.485)	7.99	3.43	8
n-tetratriacontane		20.5 (3.44)	13 (1.73)						19.1 (1.97)	8.65 (0.529)	12.9	6.14	8
n-pentatriacontane		18.4 (2.79)	15.1 (1.84)						21.7 (2.15)	8.53 (1.02)	11.6	5.83	7
n-hexatriacontane		16.2 (0.702)	15.9 (2.29)						16.6 (2.37)		13.2	5.06	5
n-heptatriacontane		16.0 (1.89)	18.6 (0.500)						20.5 (3.03)		14.5	6.12	5
n-octatriacontane		14.9 (1.28)	22.5 (2.96)						22.7 (4.01)		15.6	9.63	4
n-nonatriacontane		14.9 (0.784)	15.8 (1.72)						26.5 (3.12)		15.0	9.65	4
n-tetracontane		21.4 (7.17)	9.10 (0.216)						25.1 (4.71)		18.5	9.67	3
norpristane			4.19 (0.144)								4.19		1
Pristane			12.2 (0.620)						18.4 (1.26)	8.04 (0.371)	12.5	2.73	6
Phytane			17.9 (2.53)						21.5 (1.29)	13.8 (0.721)	17.9	3.28	7

Table 9, continued.

	Lab number												
Analyte	11	12	13	14	15	16	17	18	19	20	interlab mean	uncertainty	n
n-decane													
n-undecane											0.496		1
n-dodecane											0.426		1
n-tridecane											0.416		1
n-tetradecane													
n-pentadecane													
n-hexadecane	0.0782 (0.00105)										4.45	8.74	2
n-heptadecane	0.762 (0.00409)		4.01 (0.0777)								2.38	3.25	2
n-octadecane	0.861 (0.00344)		3.97 (0.154)								2.42	3.11	2
n-nonadecane	1.36 (0.0114)										1.92	1.12	2
n-eicosane	2.74 (0.0121)										2.39	0.701	2
n-henicosane	0.861 (0.00414)										1.51	1.31	2
n-docasane	0.717 (0.00555)										1.20	0.976	2
n-tricosane	0.628 (0.00228)										1.58	1.9	2
n-tetracosane	0.570 (0.0014)										1.13	0.564	3
n-pentacosane	10.8 (0.0118)										7.81	6.38	3
n-hexacosane	6.51 (0.0554)										4.25	3.63	3
n-heptacosane	1.06 (0.00756)										0.899	0.318	2
n-octacosane	0.956 (0.00987)										1.67	1.42	2
n-nonacosane	0.880 (0.00659)										3.99	3.48	3
n-triacontane	0.859 (0.00354)			1.50 (0.483)							3.95	4.44	5
n-hentriacontane	0.836 (0.00444)		10.1 (0.196)	1.23 (0.466)			11.3 (0.442)				4.82	3.21	7
n-dotriacontane	0.819 (0.00149)		10.5 (0.100)	1.91 (0.224)			9.33 (0.197)				5.62	2.59	9
n-tritriacontane	0.784 (0.00719)		11.1 (0.404)	2.56 (0.357)			12.2 (0.213)				7.99	3.43	8
n-tetratriacontane	0.728 (0.00468)		12.6 (0.100)	2.76 (0.707)			25.7 (0.135)				12.9	6.14	8
n-pentatriacontane	0.657 (0.00966)		13.4 (0.208)	3.58 (1.51)							11.6	5.83	7
n-hexatriacontane			14.0 (0.173)	3.21 (0.627)							13.2	5.06	5
n-heptatriacontane			14.5 (0.231)	3.00 (0.147)							14.5	6.12	5
n-octatriacontane				2.18 (0.168)							15.6	9.63	4
n-nonatriacontane				2.90 (0.294)							15.0	9.65	4
n-tetracontane											18.5	9.67	3
norpristane											4.19		1
Pristane	11.5 (0.0575)		11.9 (0.0577)	12.9 (1.76)							12.5	2.73	6
Phytane	15.5 (0.138)	30.8	15.1 (0.115)	19.5 (1.26)							17.9	3.28	7

Table 10. Laboratory means and standard deviations (in parentheses) in mg/kg for parent PAHs reported in candidate SRM 2777. The interlaboratory mean, uncertainty, and number of reporting labs are also displayed. Values in red indicate outliers and were not used to determine the interlab mean and uncertainty. No values indicate that values were not reported.

	Lab number												
Analyte	1	2	3	4	5	6	7	8	9	10	interlab mean	uncertainty	n
naphthalene		1.18 (0.0351)			0.00659 (0.000367)	0.0545 (0.00104)	1.51 (0.126)		0.0329 (0.00234)	0.400 (0.0212)	0.463	0.381	9
biphenyl				0.0290 (0.00173)		0.0160 (0.00257)			0.0204 (0.00618)		0.022	0.00800	3
acenaphthene						0.00848 (0.00186)	0.760 (0.0300)				0.384	0.752	2
acenaphthylene						0.00514 (0.00166)					0.00514		1
fluorene				0.0630 (0.00624)	0.0619 (0.00119)	0.0469 (0.00374)	0.653 (0.0950)		0.0477 (0.00380)		0.186	0.171	8
phenanthrene	0.543 (0.0115)	0.637 (0.0451)	0.183 (0.0446)	0.847 (0.0814)	0.518 (0.0131)	0.404 (0.0141)	1.82 (0.0757)	6.44 (0.415)	0.526 (0.0139)	0.639 (0.0493)	0.607	0.244	12
anthracene				0.0433 (0.00666)	0.150 (0.00265)	0.061 (0.0068)	0.343 (0.0115)		0.0805 (0.0106)		0.133	0.0900	7
fluoranthene	0.207 (0.0058)	0.297 (0.0208)		0.430 (0.0346)	0.349 (0.00153)	0.212 (0.0136)			0.229 (0.00651)		0.280	0.067	8
pyrene	0.427 (0.00577)	0.457 (0.0643)	0.220 (0.0149)	1.56 (0.275)	0.847 (0.0417)	0.423 (0.0303)	1.39 (0.0289)		0.504 (0.0373)		0.620	0.262	12
benzo[*b*]fluorene											1.49		1
benz[*a*]anthracene				0.587 (0.0153)		0.0861 (0.0329)					1.97	2.29	5
chrysene	1.95 (0.0493)		3.46 (0.165)			2.03 (0.0862)	5.12 (0.200)				3.16	1.16	8
triphenylene	3.10 (0.135)					3.08 (0.0252)					3.09	0.079	2
chrysene+triphenylene		5.98 (0.153)		8.41 (1.96)	3.22 (0.0361)				4.62 (0.261)		5.56	1.71	5
benzo[*b*]fluoranthene	0.477 (0.0252)	0.617 (0.0306)			0.542 (0.00200)	0.0442 (0.00476)	0.900 (0.0954)		0.559 (0.0663)		0.528	0.173	8
benzo[*k*]fluoranthene				1.36 (0.205)							1.36		1
benzo[*e*]pyrene	0.757 (0.0551)	0.857 (0.0503)			0.784 (0.00666)	0.649 (0.0219)			0.617 (0.0150)		0.854	0.160	9
benzo[*a*]pyrene				6.04 (1.868)		0.229 (0.0205)					2.12	3.92	3
perylene						0.0519 (0.00869)			0.184 (0.0139)		0.118	0.132	2
indeno[*1,2,3-cd*]pyrene					0.0235 (0.00076)	0.560 (0.0375)			0.028 (0.00581)		0.283	0.298	4
benzo[*ghi*]perylene					0.0832 (0.00449)	0.158 (0.0134)			0.117 (0.00265)		0.109	0.0270	5
dibenz[*a,h*]anthracene				1.30 (0.451)					0.0294 (0.00252)		0.500	0.801	3
cis/trans-decalin													
dibenzofuran				0.00467 (0.000577)		0.0153 (0.00444)				0.0268 (0.00155)	0.0160	0.0130	3
retene		1.73 (0.0702)		2.24 (0.211)	0.591 (0.0539)				1.76 (0.197)		1.58	0.701	4
benzothiophene													
dibenzothiophene	0.343 (0.00577)	0.400 (0.00)		0.290 (0.0346)	0.405 (0.00306)	0.294 (0.00351)			0.231 (0.0497)	0.357 (0.0248)	0.319	0.0490	8
naphthobenzothiophene				3.37 (0.162)							1.92	1.52	3

Table 10, continued.

	Lab number												
Analyte	11	12	13	14	15	16	17	18	19	20	interlab mean	uncertainty	n
naphthalene	0.0259 (0.0000513)		0.820 (0.0361)	0.126 (0.0924)							0.463	0.381	9
biphenyl											0.0220	0.00800	3
acenaphthene											0.384	0.752	2
acenaphthylene											0.00514		1
fluorene	0.031 (0.000165)		0.440	0.377 (0.334)							0.186	0.171	8
phenanthrene	0.346 (0.00297)			0.576 (0.193)	0.250 (0.0100)						0.607	0.244	12
anthracene	0.0351 (0.000122)			0.175 (0.164)							0.133	0.0900	7
fluoranthene	0.365 (0.00243)			0.155 (0.0156)							0.280	0.0670	8
pyrene	0.438 (0.00295)	0.814		0.235 (0.0903)				0.251			0.620	0.262	12
benzo[*b*]fluorene				1.49 (0.304)							1.49		1
benz[*a*]anthracene	0.340 (0.00201)			6.16 (1.68)					2.69 (0.292)		1.97	2.29	5
chrysene	4.54 (0.0310)			0.183 (0.0696)	4.00 (0.363)				4.00 (0.504)		3.16	1.16	8
triphenylene											3.09	0.0790	2
chrysene+triphenylene		5.57 (1.32)									5.56	1.71	5
benzo[*b*]fluoranthene	0.410 (0.00260)								0.677 (0.0493)		0.528	0.173	8
benzo[*k*]fluoranthene											1.36		1
benzo[*e*]pyrene	0.732 (0.00720)	0.818 (0.211)						1.38	1.10 (0.0902)		0.854	0.160	9
benzo[*a*]pyrene	0.0805 (0.000738)										2.12	3.92	3
perylene											0.118	0.132	2
indeno[*1,2,3-cd*]pyrene				0.520 (0.199)							0.283	0.298	4
benzo[*ghi*]perylene	0.0926 (0.000754)			0.0962 (0.0409)							0.109	0.0270	5
dibenz[*a,h*]anthracene				0.174 (0.108)							0.500	0.801	3
cis/trans-decalin													
dibenzofuran											0.0160	0.0130	3
retene											1.58	0.701	4
benzothiophene													
dibenzothiophene	0.229 (0.00190)										0.319	0.0490	8
naphthobenzothiophene	0.817 (0.00438)	1.56 (0.563)									1.92	1.52	3

Table 11. Laboratory means and standard deviations (in parentheses) in mg/kg for alkylated PAHs reported in candidate SRM 2777. The interlaboratory mean, uncertainty, and number of reporting labs are also displayed. No values indicate that values were not reported.

	Lab number												
Analyte	1	2	3	4	5	6	7	8	9	10	interlab mean	uncertainty	n
1-methylnaphthalene		0.27 (0.0529)			0.00948 (0.00056)	0.041 (0.00510)			0.0504 (0.00383)	0.0438 (0.00426)	0.156	0.151	7
2-methylnaphthalene		0.43 (0.0872)			0.0119 (0.000721)	0.0798 (0.00461)	1.00 (0.100)		0.047 (0.00263)	0.0581 (0.006937)	0.403	0.368	8
2,6-dimethylnaphthalene		0.25			0.0120 (0.000503)	0.0254 (0.00187)	0.500 (0.100)		0.0520 (0.00423)		0.155	0.200	5
1,6,7-trimethylnaphthalene					0.203 (0.00404)	0.146 (0.00416)					0.175	0.0570	2
1-methylphenanthrene	2.63 (0.0351)	3.08 (0.0557)		3.22 (0.794)	2.86 (0.00577)	2.15 (0.142)			2.28 (0.135)	1.92 (0.0691)	2.69	0.362	11
2-methylphenanthrene		1.64 (0.0900)		2.19 (0.548)		1.59 (0.04)			1.57 (0.131)	1.35 (0.0432)	1.62	0.224	8
3-methylphenanthrene		2.96 (0.0493)		4.86 (1.23)	3.62 (0.0252)	3.19 (0.0808)	5.23 (0.208)		2.99 (0.186)	2.59 (0.116)	3.55	0.755	10
9-methylphenanthrene		4.12 (0.0700)		4.86 (1.19)	4.84 (0.0173)		12.6 (0.764)		4.12 (0.257)	3.61 (0.123)	5.06	2.21	8
2-methylanthracene				0.703 (0.00577)							0.533	0.427	2
C_1-decalins													
C_2-decalins													
C_3-decalins													
C_4-decalins													
C_1-naphthalenes		0.517 (0.0814)			0.0214 (0.00123)	0.114 (0.00833)			0.0969 (0.00616)	0.102 (0.0111)	0.362	0.446	8
C_2-naphthalenes		0.910			0.0655 (0.00133)	1.35 (0.127)			0.0976 (0.0118)	0.0605 (0.00512)	1.51	2.20	8
C_3-naphthalenes	1.00 (0.00)		0.856 (0.0476)		1.45 (0.00577)	1.16 (0.00577)				0.629 (0.0467)	1.03	0.283	10
C_4-naphthalenes	3.07 (0.127)		2.98 (0.0209)		3.51 (0.0839)					0.575 (0.0336)	2.38	1.26	7
C_1-benzothiophenes													
C_2-benzothiophenes													
C_3-benzothiophenes													
C_4-benzothiophenes													
C1-fluorenes	1.57 (0.0666)	1.33 (0.0700)	0.838 (0.0315)		1.11 (0.00)	2.25 (0.0557)			0.527 (0.0228)		1.38	0.415	9
C_2-fluorenes	9.13 (0.0889)	7.24 (0.347)	5.08 (0.268)		6.84 (0.0971)						7.19	2.08	8
C_3-fluorenes	12.3 (0.200)	11.1 (0.125)			9.72 (0.287)						10.5	4.04	7
C_1-phenanthrenes/anthracenes	10.02 (0.0306)	11.3 (0.235)	10.4 (0.590)		14.7 (0.379)	11.6 (0.586)			10.9 (0.7)	9.47 (0.350)	10.5	1.52	13
C_2-phenanthrenes/anthracenes	30.47 (0.289)	34.9 (1.204)	34.8 (2.56)		38.4 (0.794)	46.6 (1.18)				27.1 (0.883)	31.0	5.57	12
C_3-phenanthrenes/anthracenes	25.37 (0.252)	23.7 (0.801)			30.5 (0.416)	76.9 (2.46)					30.6	13.5	10
C_4-phenanthrenes/anthracenes	14.9 (0.300)	9.23 (0.222)			15.4 (0.346)						13.1	8.29	7
C_1-dibenzothiophenes	2.82 (0.0306)	2.68 (0.115)	1.97 (0.128)		2.31 (0.0100)				0.986 (0.212)	1.12 (0.0561)	2.20	0.616	10
C_2-dibenzothiophenes	9.90 (0.0643)	10.1 (0.081)	13 (0.813)		10.2 (0.221)	14.3 (0.907)				3.36 (0.159)	10.3	2.59	9
C_3-dibenzothiophenes	9.99 (0.115)	9.05 (0.407)			8.83 (0.0361)						9.78	2.85	6
C_4-dibenzothiophenes	6.04 (0.140)	5.53 (0.169)			4.61 (0.137)						6.23	1.63	5
C_1-fluoranthenes/pyrenes	3.64 (0.0950)	3.76 (0.183)	2 (0.0283)		2.57 (0.0321)	6.54 (0.122)			2.03 (0.0802)		3.58	0.924	10
C_2-fluoranthenes/pyrenes	4.66 (0.131)	4.61 (0.435)	3.99 (0.135)		3.59 (0.0361)						4.48	0.821	8
C_3-fluoranthenes/pyrenes	3.86 (0.0551)	5.02 (0.260)			3.5 (0.0513)						4.57	1.05	6
C_4-fluoranthenes/pyrenes	6.69 (0.363)	5.16 (0.302)			4.19 (0.0681)						6.02	1.89	6
C_1-naphthobenzothiophenes		6.31 (0.530)									5.32	2.23	3
C_2-naphthobenzothiophenes		6.61 (0.421)									5.65	2.47	3
C_3-naphthobenzothiophenes		4.01 (0.295)									3.4	2.03	3
C_4-naphthobenzothiophenes													
C_1-chrysenes	8.95 (0.423)	9.92 (0.0800)	7.16 (0.323)		5.6 (0.0755)	9.82 (0.599)			7.98 (0.269)		8.12	1.05	11
C_2-chrysenes	6.37 (0.314)	8.33 (0.202)	8.57 (0.176)		5.12 (0.0586)	10.3 (2.74)					8.16	1.80	10
C_3-chrysenes	4.33 (0.224)	4.65 (0.172)			2.28 (0.0656)						5.72	3.86	7
C_4-chrysenes					1.70 (0.0153)						1.72	0.0270	2

Table 11, continued.

	Lab number												
Analyte	11	12	13	14	15	16	17	18	19	20	interlab mean	uncertainty	n
1-methylnaphthalene			0.563 (0.0351)	0.115 (0.0583)							0.156	0.151	7
2-methylnaphthalene			1.31 (0.0854)	0.0561							0.403	0.368	8
2,6-dimethylnaphthalene											0.155	0.200	5
1,6,7-trimethylnaphthalene											0.175	0.057	2
1-methylphenanthrene		2.45 (0.437)	1.93 (0.0513)	3.52 (0.483)					3.55 (0.480)		2.69	0.362	11
2-methylphenanthrene		1.66 (0.399)	1.13 (0.0473)	1.86 (0.907)							1.62	0.224	8
3-methylphenanthrene		2.51 (0.734)	2.10 (0.0200)	5.4 (1.47)							3.55	0.755	10
9-methylphenanthrene		3.70 (1.06)		2.63 (0.25)							5.06	2.21	8
2-methylanthracene				0.278 (0.174)							0.533	0.427	2
C_1-decalins													
C_2-decalins													
C_3-decalins													
C_4-decalins													
C_1-naphthalenes	0.0378 (0.000332)		1.87 (0.115)	0.134 (0.0869)							0.362	0.446	8
C_2-naphthalenes	0.0738 (0.000414)		8.52 (0.271)	0.143 (0.0492)							1.51	2.20	8
C_3-naphthalenes	0.308 (0.00249)	2.16	1.00 (0.0808)	0.874 (0.368)						1.6 (0.00577)	1.03	0.283	10
C_4-naphthalenes	0.554 (0.00446)		1.10 (0.0458)							4.89 (0.199)	2.38	1.26	7
C_1-benzothiophenes													
C_2-benzothiophenes													
C_3-benzothiophenes													
C_4-benzothiophenes													
C_1-fluorenes	0.775 (0.00511)		1.76 (0.133)							2.22 (0.0971)	1.38	0.415	9
C_2-fluorenes	3.26 (0.0209)	7.81 (1.5)	5.22 (0.0862)							12.9 (0.100)	7.19	2.08	8
C_3-fluorenes	3.75 (0.0224)	15.6 (3.76)	3.61 (0.0208)							17.4 (0.300)	10.5	4.04	7
C_1-phenanthrenes/anthracenes	5.49 (0.0181)	11.4 (2.83)	8.22 (0.117)	13.6 (1.70)	5.86 (0.275)					13.2 (0.0577)	10.5	1.52	13
C_2-phenanthrenes/anthracenes	14.8 (0.038)	30.7 (7.55)	21.6 (0.265)	32.2 (3.87)	17.6 (1.06)					43.3 (0.436)	31.0	5.57	12
C_3-phenanthrenes/anthracenes	10.1 (0.0644)	19.7 (5.46)	14.7 (0.208)	23.5 (0.774)	20.1 (1.62)					60.8 (0.603)	30.6	13.5	10
C_4-phenanthrenes/anthracenes	4.42 (0.0232)	8.97 (2.21)	3.22 (0.0306)							35.6 (0.651)	13.1	8.29	7
C_1-dibenzothiophenes	1.52 (0.00869)	2.25 (0.484)		1.99 (0.283)						4.37 (0.0473)	2.20	0.616	10
C_2-dibenzothiophenes	5.47 (0.0228)	10.7 (2.63)								15.3 (0.0577)	10.3	2.59	9
C_3-dibenzothiophenes	4.65 (0.0396)	10.7 (2.88)								15.5 (0.153)	9.78	2.85	6
C_4-dibenzothiophenes		5.63 (1.35)								9.35 (0.215)	6.23	1.63	5
C_1-fluoranthenes/pyrenes	2.45 (0.018)	4.01 (0.786)		3.48 (0.508)						5.32 (0.135)	3.58	0.924	10
C_2-fluoranthenes/pyrenes	2.96 (0.0226)	5.13 (0.988)		4.05 (2.30)						6.81 (0.191)	4.48	0.821	8
C_3-fluoranthenes/pyrenes	3.07 (0.0172)	6.32 (1.58)								5.65 (0.0850)	4.57	1.05	6
C_4-fluoranthenes/pyrenes	3.33 (0.0223)	6.99 (1.37)								9.76 (0.511)	6.02	1.89	6
C_1-naphthobenzothiophenes	3.09 (0.0291)	6.55 (1.58)									5.32	2.23	3
C_2-naphthobenzothiophenes	3.20 (0.0145)	7.15 (1.12)									5.65	2.47	3
C_3-naphthobenzothiophenes	1.42 (0.00548)	4.76 (0.321)									3.40	2.03	3
C_4-naphthobenzothiophenes													
C_1-chrysenes	7.24 (0.0536)	9.87 (2.36)		7.19 (4.65)	5.42 (0.240)					10.1 (0.498)	8.12	1.05	11
C_2-chrysenes	5.70 (0.0242)	10.3 (2.02)		10.9 (3.88)	3.67 (0.248)					12.4 (0.611)	8.16	1.80	10
C_3-chrysenes	2.30 (0.00758)	16.1 (0.981)			1.91 (0.0929)					8.4 (0.439)	5.72	3.86	7
C_4-chrysenes	1.73 (0.0133)										1.72	0.0270	2

Table 12. Laboratory means and standard deviations (in parentheses) in mg/kg for biomarkers reported in candidate SRM 2777. The interlaboratory mean, uncertainty, and number of reporting labs are also displayed. No values indicate that values were not reported.

	Lab number												
Analyte	1	2	3	4	5	6	7	8	9	10	interlab mean	uncertainty	n
Carbazole				0.150 (0.0173)							0.150		1
18α(H)-22,29,30-Trisnorneohopane		1.74 (0.149)		2.47 (0.172)						2.55 (0.0388)	2.03	0.502	6
17α(H)-22,29,30-Trisnorhopane	1.41 (0.0200)	1.14 (0.107)		1.99 (0.241)					2.36 (0.242)	2.10 (0.156)	1.68	0.375	8
17α(H),21β(H)-30-Norhopane	3.98 (0.206)	3.55 (0.245)		4.81 (0.441)					5.58 (0.0404)		3.77	1.42	6
18α(H)-30-Norneohopane		1.76 (0.104)								2.29 (0.051)	2.31	0.563	4
17α(H)-Diahopane										2.08 (0.0769)	1.86	1.27	3
17α(H),21β(H)-Hopane	6.96 (0.413)	8.10 (0.498)		8.64 (0.649)					9.80 (0.384)	13.4 (0.720)	8.92	1.69	8
17α(H),21β(H)-22R-Homohopane	2.44 (0.0929)	2.56 (0.0781)		3.54 (0.354)					3.93 (0.189)	6.01 (0.324)	3.60	0.899	8
17α(H),21β(H)-22S-Homohopane	3.53 (0.220)	3.24 (0.164)		4.46 (0.500)					5.67 (0.285)	3.97 (0.221)	4.11	0.94	8
13β(H)17α(H)-Diacholestane 20S		7.48 (0.390)									8.57	1.82	4
5α(H),14α(H),17α(H)-Cholestane 20S		8.98 (0.378)		4.57 (0.186)							7.49	2.16	4
5α(H),14α(H),17α(H)-Cholestane 20R	2.24 (0.159)	7.41 (0.583)		4.48 (0.370)					2.51 (0.199)	3.29 (0.145)	4.35	2.71	8
5α(H),14α(H),17α(H)-24-Ethylcholestane 20S		2.87 (0.230)		3.13 (0.289)						4.47 (0.280)	3.54	0.677	6
5α(H),14α(H),17α(H)-24-Ethylcholestane 20R	2.52 (0.111)	3.02 (0.211)		2.84 (0.231)					2.93 (0.0208)	3.24 (0.149)	3.16	0.614	8
5α(H),14β(H),17β(H)-Cholestane 20R	5.64 (0.243)	3.80 (0.208)		4.89 (0.543)					7.19 (0.602)	5.65 (0.264)	5.26	0.958	7
5α(H),14β(H),17β(H)-Cholestane 20S		3.85 (0.100)		4.46 (0.710)						4.22 (0.259)	4.19	1.01	6
5α(H),14β(H),17β(H)-24-Ethylcholestane 20R	2.56 (0.0954)	5.15 (0.212)		4.07 (0.624)					4.84 (0.165)	5.26 (0.246)	5.08	1.13	8
5α(H),14β(H),17β(H)-24-Ethylcholestane 20S		3.53 (0.146)		3.03 (0.439)						4.44 (0.172)	4.03	0.721	6
C_{20}-triaromatic steroid (pregnane derivative)		0.817 (0.0379)		3.57 (0.0310)						1.26 (0.0374)	1.88	1.70	3
C_{21}-triaromatic steroid (homopregnane)		0.723 (0.0416)		3.73 (0.506)						1.14 (0.0527)	1.86	1.88	3
C_{26}-20S-triaromatic steroid (cholestane derivative)		0.407 (0.0416)								0.66 (0.0141)	0.531	0.249	2
C_{26}-20R-triaromatic steroid (cholestane derivative)													
C_{27}-20S-triaromatic steroid (methylcholestane derivative)													
C_{27}-20R-triaromatic steroid (methylcholestane derivative)		0.870 (0.115)								1.36 (0.0842)	3.17	4.12	3
C_{28}-20S-triaromatic steroid (ethylcholestane derivative)		1.13 (0.0961)								1.82 (0.0944)	4.06	5.18	3
C_{28}-20R-triaromatic steroid (ethylcholestane derivative)		0.733 (0.106)								1.49 (0.0302)	3.18	4.16	3

Table 12, continued.

	Lab number												
Analyte	11	12	13	14	15	16	17	18	19	20	interlab mean	uncertainty	n
Carbazole											0.150		1
18α(H)-22,29,30-Trisnorneohopane		2.72 (0.453)	1.79 (0.00577)	1.11 (0.0688)							2.03	0.502	6
17α(H)-22,29,30-Trisnorhopane		2.56	1.37 (0.00577)	1.09 (0.0998)							1.68	0.375	8
17α(H),21β(H)-30-Norhopane			4.16 (0.0643)	0.525 (0.154)							3.77	1.42	6
18α(H)-30-Norneohopane		3.09 (0.864)	2.12 (0.0208)								2.31	0.563	4
17α(H)-Diahopane		3.62	1.06 (0.0100)								1.86	1.27	3
17α(H),21β(H)-Hopane		10.8 (2.68)	7.85 (0.00)	5.79 (0.125)							8.92	1.69	8
17α(H),21β(H)-22R-Homohopane		4.83 (0.866)	2.89 (0.0153)	2.64 (0.235)							3.60	0.899	8
17α(H),21β(H)-22S-Homohopane		6.15 (0.906)	3.89 (0.0115)	1.99 (0.0336)							4.11	0.940	8
13β(H)17α(H)-Diacholestane 20S		9.68 (2.62)	10.5 (0.100)	6.63 (0.324)							8.57	1.82	4
5α(H),14α(H),17α(H)-Cholestane 20S		9.27 (2.39)		7.13 (0.825)							7.49	2.16	4
5α(H),14α(H),17α(H)-Cholestane 20R		12.4 (2.7)	1.76 (0.0551)	0.734 (0.0539)							4.35	2.71	8
5α(H),14α(H),17α(H)-24-Ethylcholestane 20S		4.69 (1.24)	3.33 (0.0551)	2.77 (0.305)							3.54	0.677	6
5α(H),14α(H),17α(H)-24-Ethylcholestane 20R		5.23 (1.48)	2.55 (0.0153)	3.00 (0.142)							3.16	0.614	8
5α(H),14β(H),17β(H)-Cholestane 20R		6.06 (1.47)		3.62 (0.142)							5.26	0.958	7
5α(H),14β(H),17β(H)-Cholestane 20S		6.37 (1.23)	3.53 (0.0529)	2.70 (0.369)							4.19	1.01	6
5α(H),14β(H),17β(H)-24-Ethylcholestane 20R		7.68 (2.94)	6.83 (0.0503)	4.26 (0.197)							5.08	1.13	8
5α(H),14β(H),17β(H)-24-Ethylcholestane 20S		5.45 (0.773)	4.31 (0.122)	3.41 (0.556)							4.03	0.721	6
C_{20}-triaromatic steroid (pregnane derivative)											1.88	1.70	3
C_{21}-triaromatic steroid (homopregnane)											1.86	1.88	3
C_{26}-20S-triaromatic steroid (cholestane derivative)											0.531	0.249	2
C_{26}-20R-triaromatic steroid (cholestane derivative)													
C_{27}-20S-triaromatic steroid (methylcholestane derivative)													
C_{27}-20R-triaromatic steroid (methylcholestane derivative)		7.28 (1.53)									3.17	4.12	3
C_{28}-20S-triaromatic steroid (ethylcholestane derivative)		9.23 (2.57)									4.06	5.18	3
C_{28}-20R-triaromatic steroid (ethylcholestane derivative)		7.32 (1.78)									3.18	4.16	3

Table 13. List of operating parameters.

Parameter	Laboratory FT1	Laboratory FT2	Laboratory FT3
Instrument	12 T Bruker SolariX FTICR-MS	9.4 tesla custom-built FT-ICR mass spectrometer	FT-ICR-MS ESI (+/-); hybrid 7.0 T linear ion trap (LTQ) FT-ICR-MS (LTQ FT Ultra, Thermo Scientific) coupled with ESI (+/-) at 400k resolving power
Sample preparation	Diluting whole oils to 0.25 mg/ml in toluene (for APPI-P) or in toluene 1:1 (volume fraction) methanol (for ESI-N and ESI-P)	Dissolved in toluene to yield stock solution (1 mg/mL); further diluted in 50:50 (volume fraction) MeOH:Tol to 250 ug/mL final concentration	Diluting 0.25 mg oil in 1 mL 50:50 toluene:MeOH
Solvent	ESI-N & ESI-P: toluene/MeOH 1:1	50:50 MeOH:Tol diluted to final concentration 250 ug/mL	Dissoved in 50:50 MeOH and Toluene
Dopant	ESI-N: 2 % ammonium hydroxide (NH_4OH); ESI-P: 2 % formic acid (CH_2O_2)	0.125 % TMAH for negative mode ESI; 4 % formic acid for positive mode	2 % dopant (ammonium hydroxide in negative ionization mode, formic acid in positive ionization mode)
Standard	Internal standard (reserpine, $C_{33}H_{40}N_2O_9$) in each sample to ensure mass accuracy; instrument was tuned and optimized using a set of standard compounds and oils and calibrated daily	External calibration: with standard mixtures of peptides (HP Mix, Agilent); internal calibration: based on highly abundant homologous series of peaks within each mass spectrum	Internal spike solution of reserpine (10 μL reserpine to 1 mL sample, final concentration 2×10^{-4} mg/mL); external calibration: to a mass accuracy of < 2 ppm with a standard solution from Thermo Fisher Scientific; internal calibration: based on highly abundant peaks across mass range of 140 to 1000 *m/z* and found in replicate runs of neat and weathered Macondo oils, respectively
Formula-finding algorithm/ software	Calibration and peak assignment; CaPA: FT-ICR-MS data processing/peak assignments, Ragnarok: visualization, both from Aphorist Inc.	PetroOrg software for mass analysis, data visualization (http://petroorg.com)	Compound Identification Algorithm (CIA) in Matlab (Kujawinski and Behn, 2006)

Table 14. Elemental compositions by FT-ICR-MS from the three participating laboratories with negative and positive ion ESI.

Parameter	Candidate SRM 2777						
	Laboratory FT1	Laboratory FT2			Laboratory FT3		
Elemental ratio in ESI (-)							
O:C[a]	0.106	0.108	0.108	0.130	0.110	0.111	0.111
H:C[a]	1.646	1.636	1.646	1.644	1.568	1.583	1.574
N:C[a]	0.002	0.030	0.030	0.029	0.087	0.084	0.085
S:C[a]	0.003	0.026	0.027	0.026	0.003	0.003	0.003
Double bond equivalent[a]	7.59	11	12	11	6	6	6
C number[a]	36.56	42	43	43	29	30	30
O:C[b]	0.111	-	-	-	0.132	0.132	0.133
H:C[b]	1.563	-	-	-	1.744	1.745	1.741
N:C[b]	0.004	-	-	-	0.144	0.142	0.138
S:C[b]	0.005	-	-	-	0.005	0.005	0.005
Double bond equivalent[b]	10.24	-	-	-	8	8	8
C number[b]	40.50	-	-	-	33	33	33
# Peaks assigned	13087	> 6σ = 15725	> 6σ = 15894	> 6σ = 14503	> 5σ = 7709	> 5σ = 8200	> 5σ = 7522
# Peaks w/o isotopic peaks	6251	-	-	-	-	-	-
Mass measurement accuracy for assigned peaks (RMS error)	-	140ppb	130ppb	130ppb	-	-	-
Elemental ratio in ESI (+)							
O:C[a]	0.051	-	-	-	0.061	0.051	0.072
H:C[a]	1.538	-	-	-	0.788	0.844	0.645
N:C[a]	0.014	-	-	-	0.133	0.124	0.110
S:C[a]	0.002	-	-	-	0.027	0.010	0.040
Double bond equivalent[a]	10.15	-	-	-	3	3	3
C number[a]	40.38	-	-	-	13	15	12
O:C[b]	0.0654	0.1	0.0	0.0	0.122	0.108	0.126
H:Cb	1.5309	1.6	1.5	1.5	1.886	1.923	1.855
N:C[b]	0.011	0.035	0.032	0.027	0.253	0.253	0.230
S:C[b]	0.004	0.031	0.026	0.025	0.027	0.017	0.030
Double bond equivalent[b]	11.22	13	13	13	7	6	7
C number[b]	43.7553	43	42	42	33	35	35
# Peaks assigned	13295	> 6σ = 17263	> 6σ = 19670	> 6σ = 19647	> 5σ = 1583	> 5σ = 1945	> 5σ = 1753
# Peaks w/o isotopic peaks	8755	-	-	-	-	-	-
Mass measurement accuracy for assigned peaks (RMS error)	-	190ppb	180ppb	170ppb	-	-	-

Table 14, continued.

Parameter	Candidate SRM 2777						
	Laboratory FT 1	**Laboratory FT2**			**Laboratory FT3**		
Heteroatom classes > 1% ESI (-)							
O_o	O1, O2, O3, O4, O5, O6, O7, O8	O2, O3, O4, O5, O6	O2, O3, O4, O5, O6	O2, O3, O4, O5, O6	O2, O3, O4, O5, O6	O2, O3, O4, O5, O6	O2, O3, O4, O5, O6
N_nO_o	N1O2, N1O3, N1O4, N1O5, N1O6	N1O2, N1O3, N1O4, N1O5, N1O6	N1O3, N1O4, N1O5, N1O6	N1O3, N1O4, N1O5, N1O6	N1O3, N1O4	N1O3, N1O4	N1O3, N1O4
N_n	-	-	-	-	-	-	-
S_sO_o	S1O2, S1O3, S1O4, S1O5, S1O6	S1O3, S1O4, S1O5	S1O4, S1O5	S1O4, S1O5	S1O4	S1O4	S1O4
Heteroatom classes > 1% ESI (+)							
O_o	O1, O1Na, O2, O2Na, O3Na, O4Na, O5Na	-	-	O1, O2	-	-	-
N_nO_o	N1O1, N1O2, N1O2Na, N1O3, N1O4, N1O5	N1O1, N1O2, N1O3, N1O4	N1O1, N1O2, N1O3, N1O4	N1O1, N1O2, N1O3, N1O4	-	-	-
N_n	N1	N1	N1	N1	-	-	-
S_sO_o	S1O1, S1O2, S1O2Na, S1O3Na, S1O4Na	S1O1, S1O2	S1O1, S1O2	S1O1, S1O2	-	-	-
N_nS_x	NS1	N1S1	N1S1	N1S1	-	-	-
$N_nO_oS_s$	N1O2S1	N1O1S1	N1O1S1, N1O2S1	N1O1S1, N1O2S1	-	-	-
S_s	-	S1	S1	S1	-	-	-

Table 14, continued.

Parameter	SRM 2779						
	Laboratory FT1	Laboratory FT2			Laboratory FT3		
Elemental ratio in ESI (-)							
O:C[a]	0.01	0.041	0.037	0.045	0.019	0.023	0.019
H:C[a]	1.356	1.461	1.435	1.452	1.295	1.312	1.303
N:C[a]	0.021	0.029	0.028	0.030	0.039	0.043	0.040
S:C[a]	0.001	0.023	0.024	0.023	0.001	0.001	0.001
Double bond equivalent[a]	13.15	16	16	17	12	11	12
C number[a]	37.83	47	47	46	34	34	34
O:C[b]	0.019	-	-	-	0.059	0.065	0.058
H:C[b]	1.344	-	-	-	1.453	1.492	1.457
N:C[b]	0.016	-	-	-	0.098	0.106	0.100
S:C[b]	0.004	-	-	-	0.004	0.004	0.004
Double bond equivalent[b]	15.72	-	-	-	13	12	13
C number[b]	42.79	-	-	-	37	37	37
# Peaks assigned	7711	> 6σ = 8600	> 6σ = 8296	> 6σ = 8397	> 5σ = 7214	> 5σ = 7470	> 5σ = 7198
# Peaks w/o isotopic peaks	3566	-	-	-	-	-	-
Mass measurement accuracy for assigned peaks (RMS error)	-	100ppb	130ppb	140ppb	-	-	-
Elemental ratio in ESI (+)							
O:C[a]	0.003	-	-	-	0.069	0.076	0.074
H:C[a]	1.403	-	-	-	1.194	1.192	1.196
N:C[a]	0.027	-	-	-	0.159	0.159	0.159
S:C[a]	0.002	-	-	-	0.011	0.014	0.013
Double bond equivalent[a]	13.63	-	-	-	4	4	4
C number[a]	41.28	-	-	-	21	21	21
O:C[b]	0.014	0.0	0.0	0.0	0.130	0.134	0.133
H:C[b]	1.386	1.5	1.5	1.5	1.847	1.859	1.854
N:C[b]	0.029	0.030	0.031	0.026	0.210	0.210	0.211
S:C[b]	0.008	0.027	0.026	0.020	0.017	0.018	0.018
Double bond equivalent[b]	14	20	19	22	7	7	7
C number[b]	45.91	50	50	55	36	37	36
# Peaks assigned	15262	> 6σ = 16768	> 6σ = 16014	> 6σ = 14826	> 5σ = 3426	> 5σ = 3126	> 5σ = 3243
# Peaks w/o isotopic peaks	4306	-	-	-	-	-	-
Mass measurement accuracy for assigned peaks (RMS error)	-	140ppb	130ppb	130ppb	-	-	-

Table 14, continued.

Parameter	SRM 2779						
	Laboratory FT1	Laboratory FT2			Laboratory FT3		
Heteroatom classes > 1% ESI (-)							
O_o	O1, O2	O1, O2	O1, O2	O1, O2	O1,O2	O1,O2	O1,O2
NO_o	NO1, NO2	N1O1, N1O2	N1O1, N1O2	N1O1, N1O2	NO1	NO1	NO1
N_n	N1, N2	N1, N2	N1, N2	N1, N2	N1, N2	N1, N2	N1, N2
SO_o	-	-	-	-	-	-	-
NS_s	NS1	N1S1	N1S1	N1S1	-	-	-
O_oS_s	O1S1	-	-	-	-	-	-
$N_nO_oS_s$	-	-	-	-	-	-	-
HC	-	HC	HC	HC	-	-	-
Heteroatom classes > 1% ESI (+)							
O_o	-	-	-	-	-	-	-
NO_o	NO1, NO1Na	N1O1, N1O2, N2O1, N2O2	N1O1, N1O2, N2O1	N1O1, N1O2, N2O1, N2O2	-	-	-
N_n	N1, N2	N1, N2	N1, N2	N1, N2	N1	N1	-
SO_o	-				-	-	-
N_nS_x	NS1	N1S1	N1S1	N1S1	-	-	-
O_oS_s	O1S1	-	-	-	-	-	-
$N_nO_oS_s$	N1O2S1	-	-	N1O1S1	-	-	-
S_s	-	-	-	-	-	-	-

[a] Participant relative-abundance weighted average; [b] Participant number average.

X. Figures

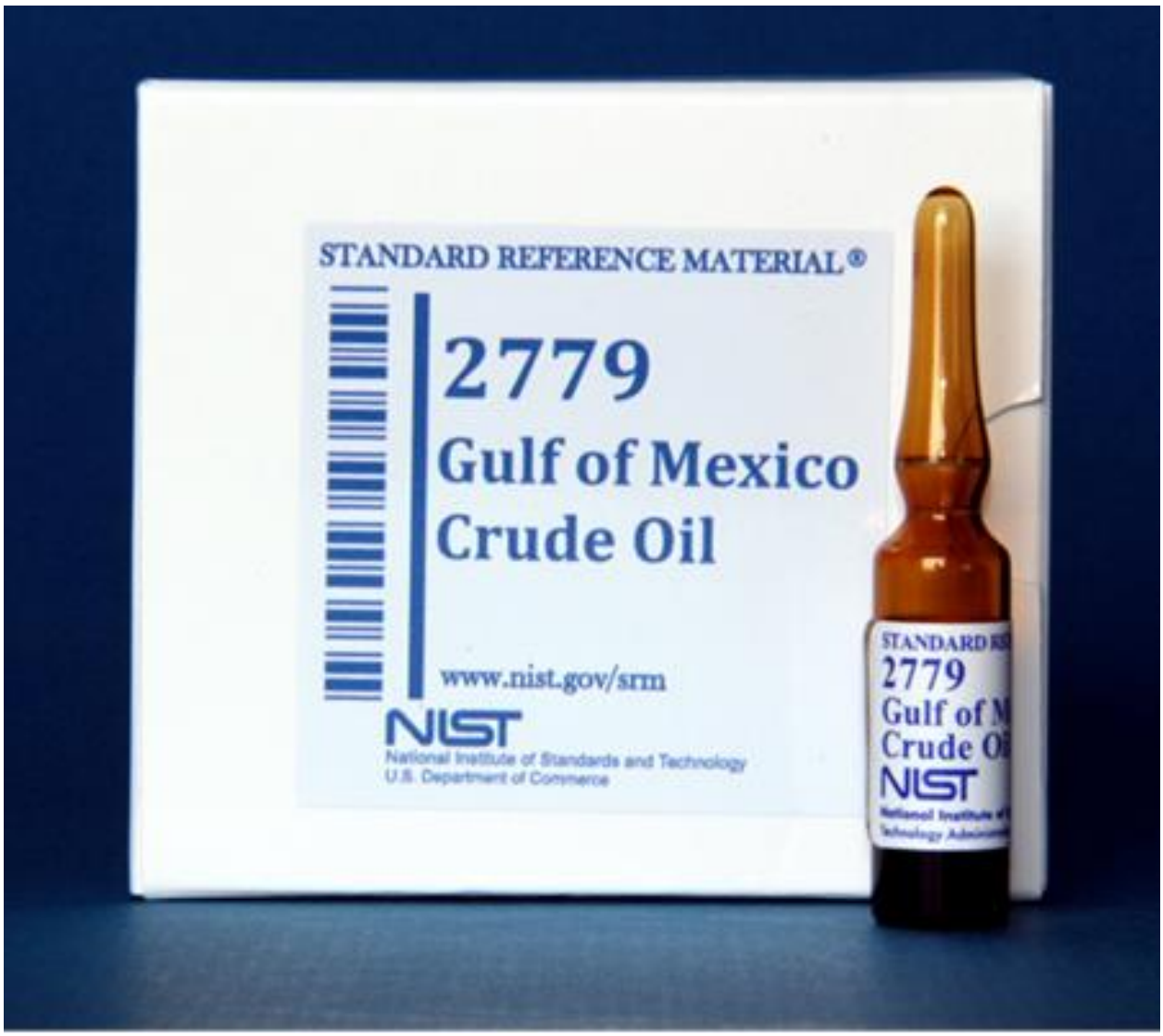


Figure 1. Image of NIST SRM 2779 Gulf of Mexico Crude Oil used in the HIE. It was collected on May 21, 2010 from the *Discoverer Enterprise* via an insertion tube that was receiving oil directly from the Macondo well during response operations. A portion was subsequently provided to NIST under the authority of the National Oceanic and Atmospheric Administration (NOAA) for use in the preparation of SRM 2779. (Credit: Lane Sander, NIST).

Figure 2. Image of oiled-sand patty typical of those collected for preparing candidate SRM 2777. Approximately 1.7 kg of sand patties were collected from Gulf Shores, Alabama in August 2012 and solvent extracted (with 90/10 dichloromethane/methanol). The solvent was removed leaving a dark syrupy liquid (Figure 3). One hundred and twenty grams was sent to the NIST who prepared a solution of 71 mg of extract/gram in toluene, added 1.3 mL of the solution in a 2 mL ampoule, and then filled the ampoules with argon prior to sealing.

Figure 3. Dark syrupy liquid from the extraction of oiled sand-patties used to prepare candidate SRM 2777.

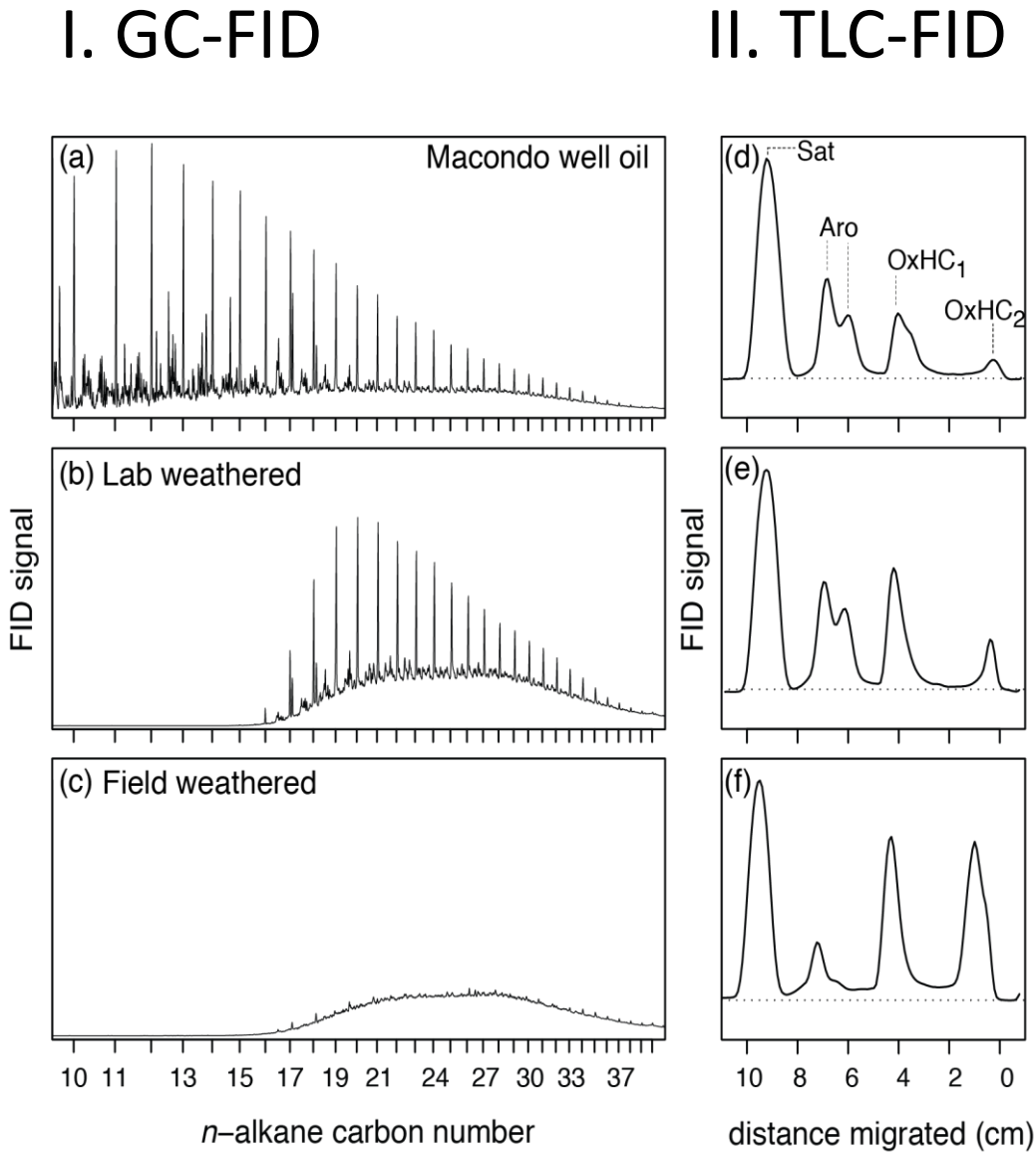


Figure 4. Chemical comparisons of SRM 2779, lab-weathered MW oil, and candidate SRM 2777; (I) GC-FID (a-c) and (II) TLC-FID (d-f). The laboratory-weathered MW oil, not used in the HIE and only presented as reference, was prepared by evaporating MW oil on a hot-plate at 90-100 °C up to the loss of compounds more volatile than *n*-pentadecane, capturing the evaporation front of candidate SRM 2777. The GC-amenable fractions and majority compositions from TLC-FID highlight the extreme weathering in candidate SRM 2777 compared to SRM 2779 (the spilled oil). Oxidized hydrocarbons ($OxHC_1$) and ($OxHC_2$) are operationally defined fractions found to be preferentially enriched from weathering (Aeppli *et al.* 2012). Furthermore, results from the lab-weathered oil reveal how different lab-weathering is vs. field weathering.

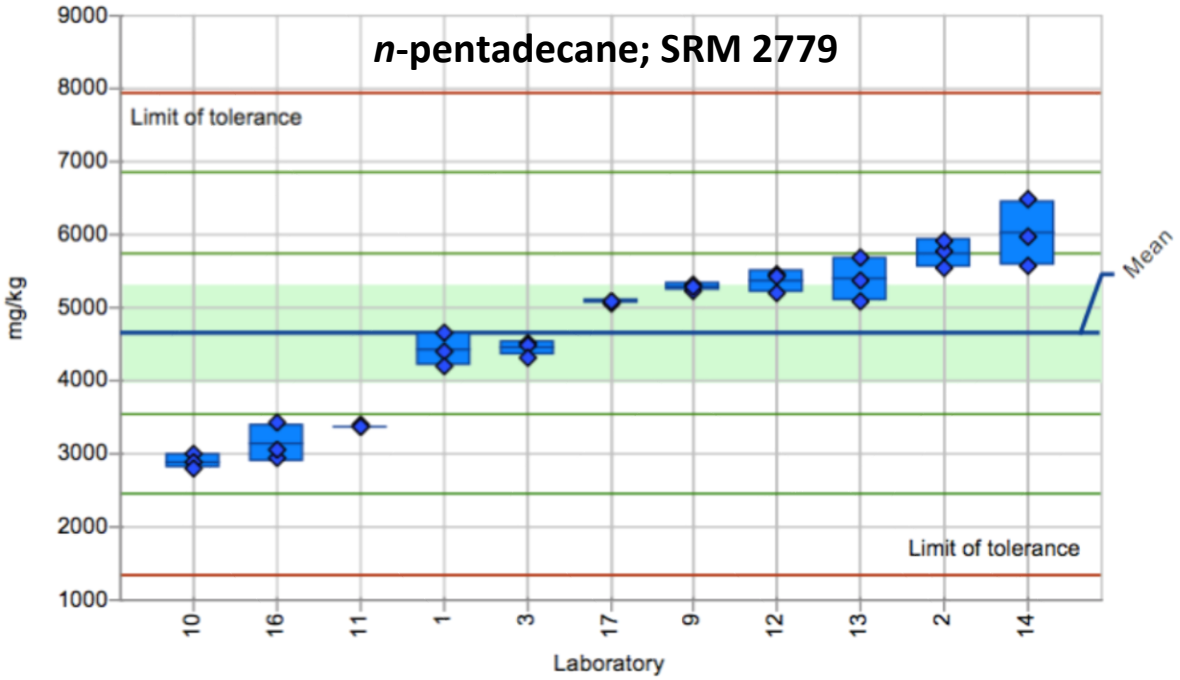


Figure 5. Summary chart for *n*-pentadecane (*n*-C_{15}) in SRM 2779. The mass fraction (mg/kg) determined by each participating lab is plotted as the blue box plot showing the three individual measurements for each lab indicated with the blue diamonds and the blue box representing the standard deviation (lab mean +/- lab standard deviation). The mean of all values reported is indicated by the thick blue line (also labeled "mean"). If available, the black line labeled "Ref. value" is the certified or reference value obtained from the Certificate of Analysis of SRM 2779. It is used as a reference value but is not used statistically. The uncertainty represented by the 95 % confidence level is indicated on the chart as the green band. The green lines represent z=+/- 1 and z=+/-2. The red lines indicate z=+/- 3. If values were outside the red lines ($|z| > 3$), they were considered outliers and not used to calculate the mean. Outliers (if present) are indicated in red in the chart.

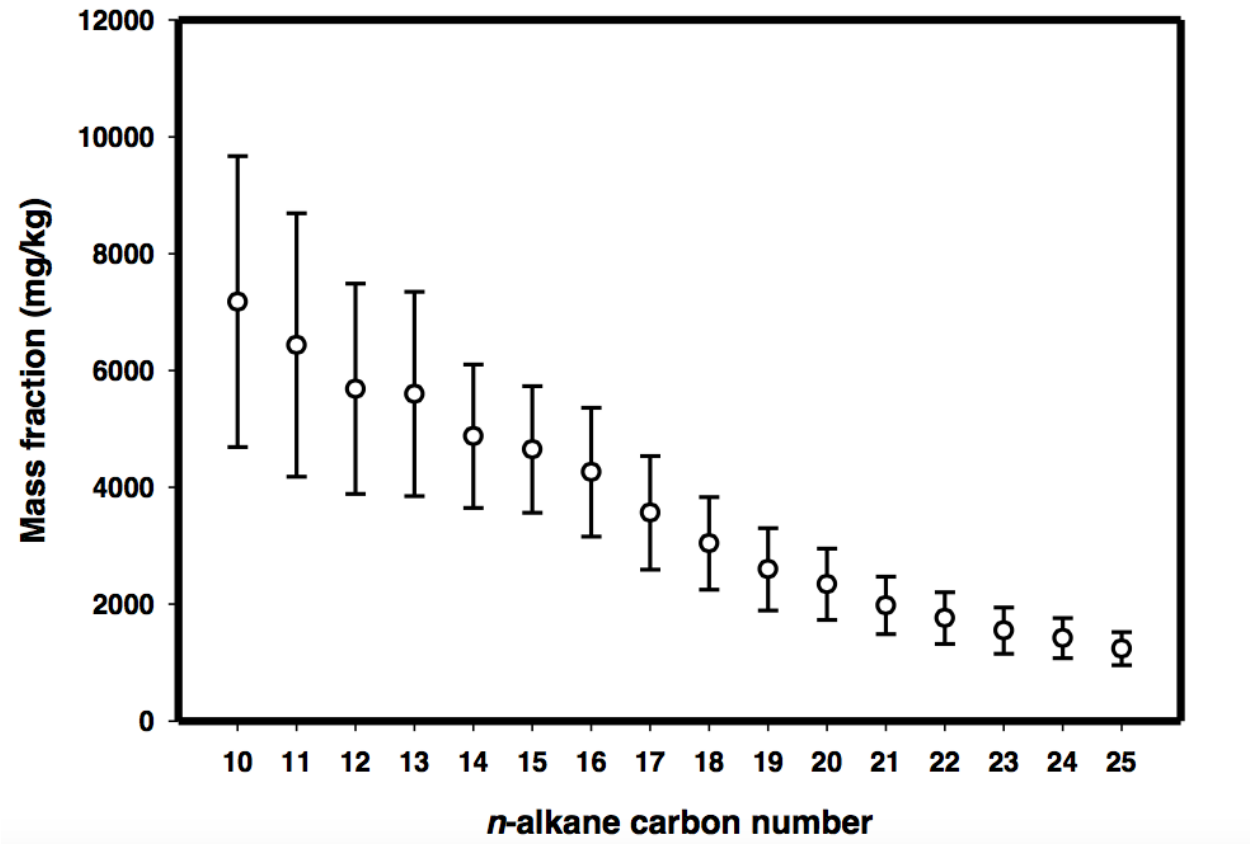


Figure 6. Mass fraction for *n*-alkanes (C_{10}-C_{25}) in SRM 2779. Nine laboratories reported values for C_{10}. Ten laboratories reported values for C_{11}, C_{12}, C_{13}, C_{17}, and C_{18}. Eleven laboratories reported values for C_{14}, C_{15}, C_{19}, C_{20}, C_{21}, C_{22}, C_{23}, C_{24}, and C_{25}. Twelve laboratories reported values for C_{16}. Error bars represents ± one standard deviation, for all reported values.

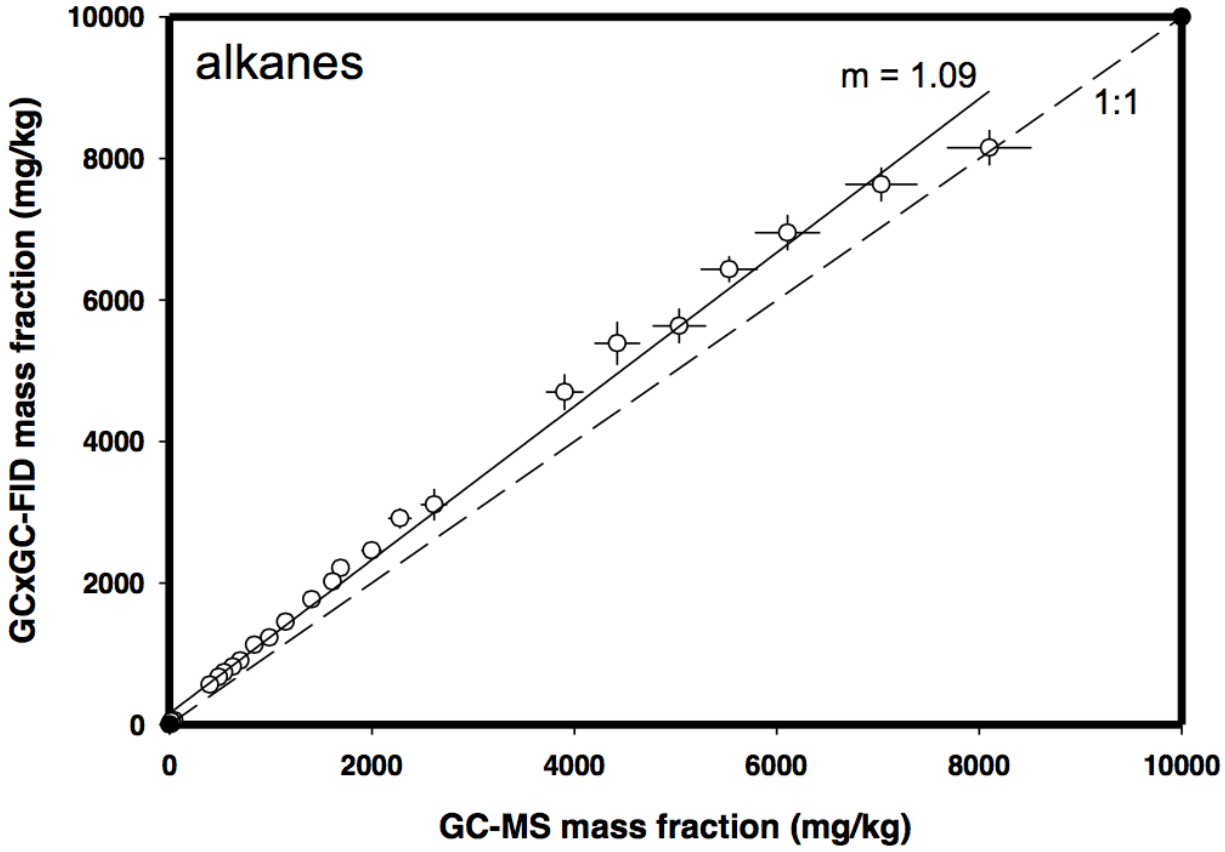


Figure 7. Comparison of *n*-alkanes in SRM 2779 measured by the same laboratory (lab numbers 1 and 13) with two different techniques: GC-MS and GC×GC-FID. The solid line is the linearly interpolated best-fit forced through zero with a slope (m) of 1.09. The dotted line is the 1:1 comparison of the mass fractions of each analyte. Error bars represents ± one standard deviation.

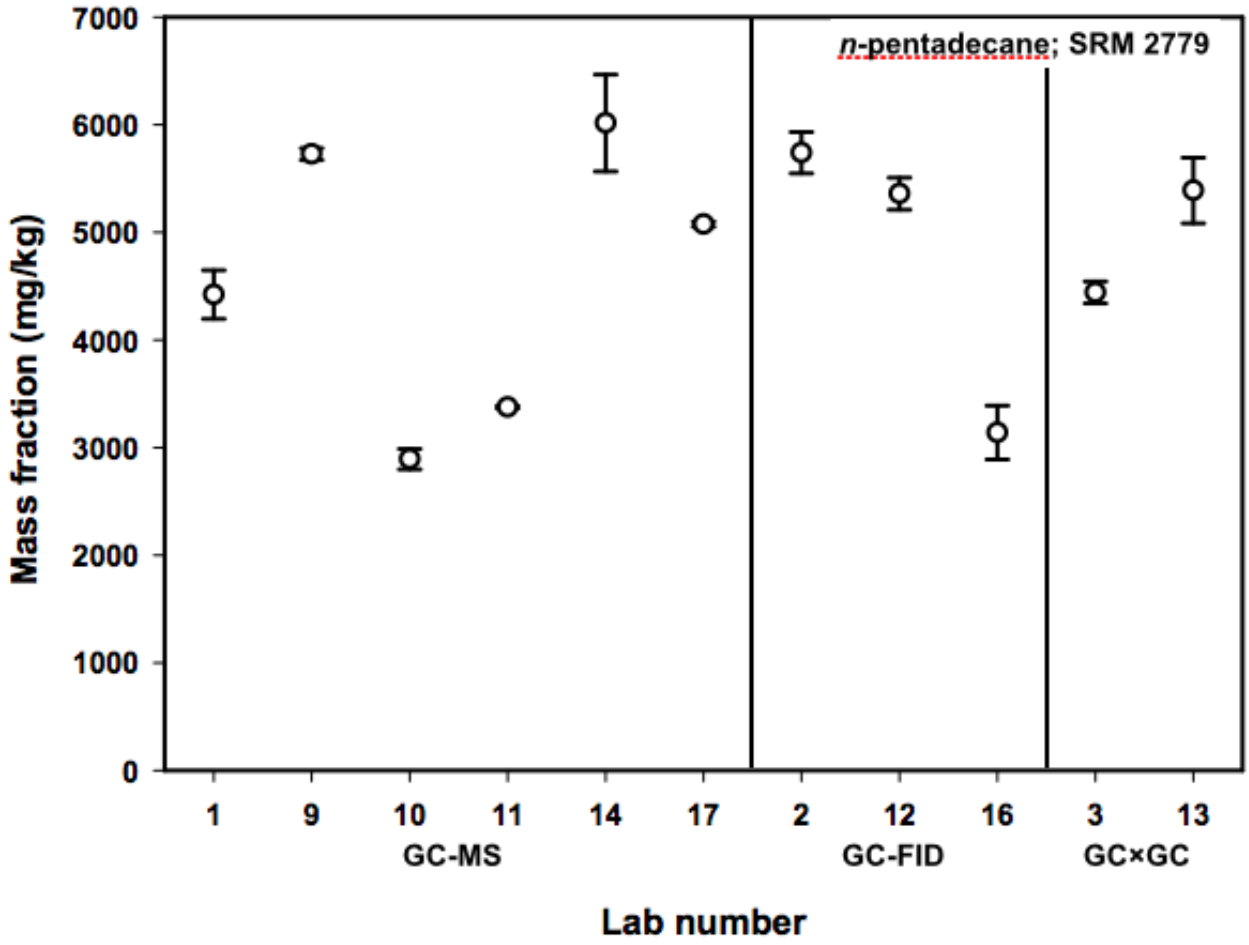


Figure 8. Comparison of *n*-pentadecane values for SRM 2779 separated by analytical method. Error bars represents ± one standard deviation, for all reported values.

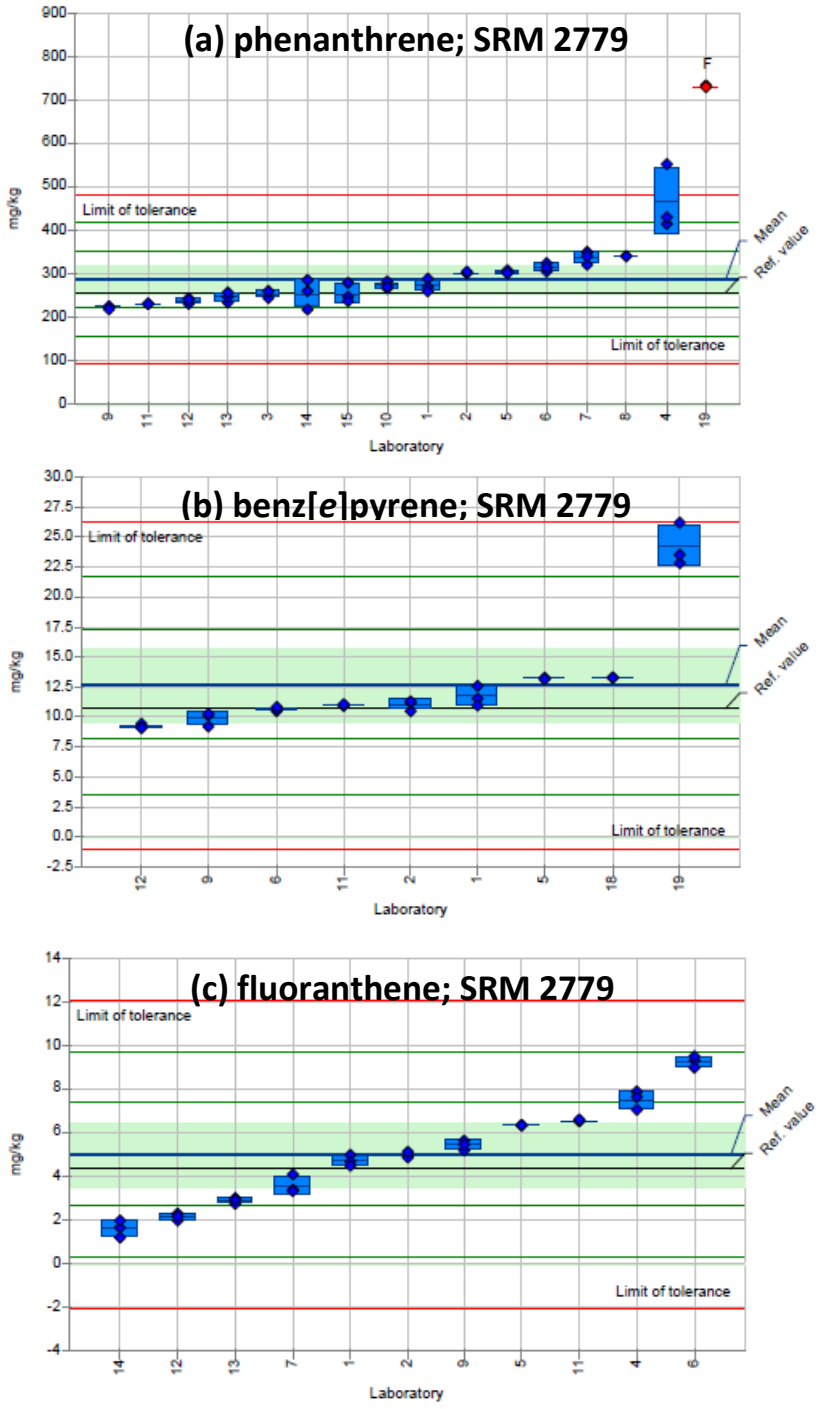


Figure 9. Summary charts for parent PAHs in SRM 2779: (a) phenanthrene, (b) benzo[*e*]pyrene, and (c) fluoranthene. See Figure 5 caption for a detailed explanation of the charts. Lab 19 for phenanthrene (a) is an outlier (z>3) and indicated in red. See Figure 5 caption for a detailed explanation of the charts.

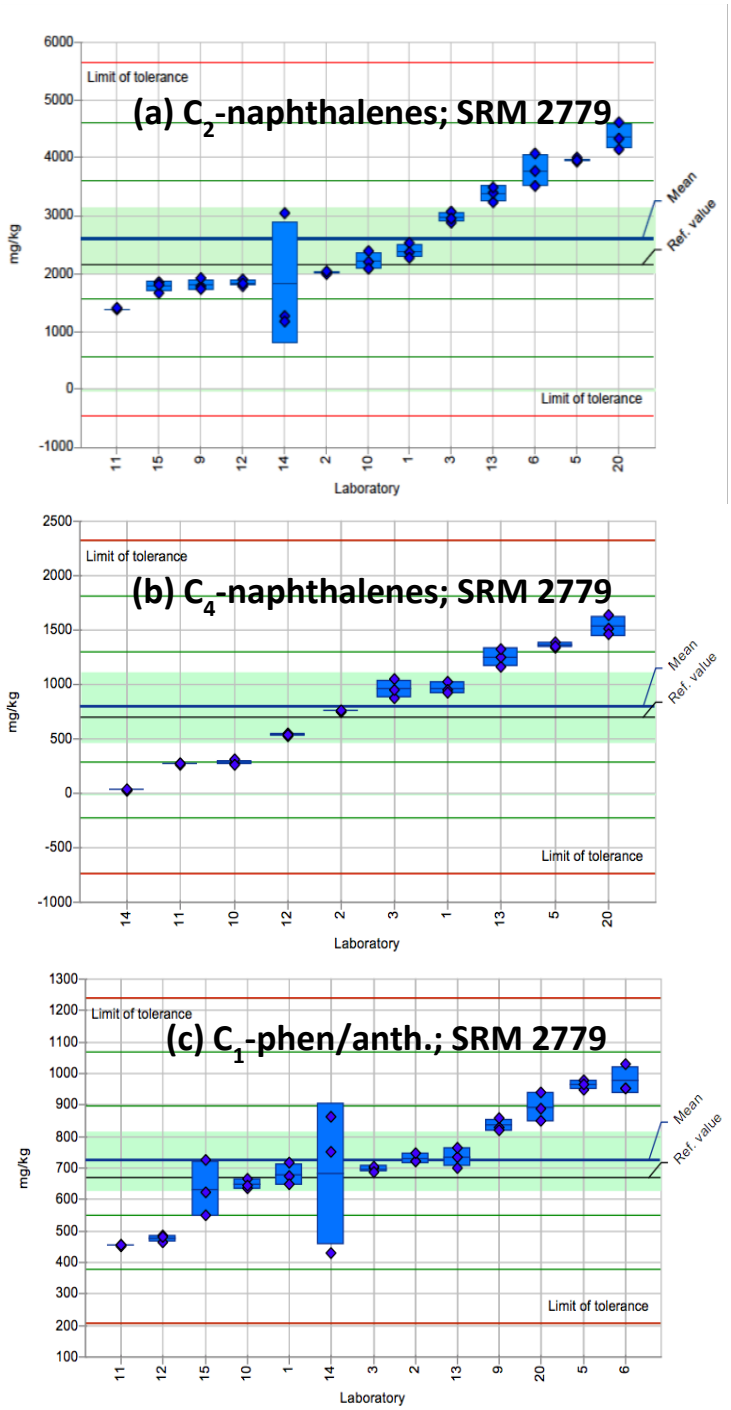


Figure 10. Summary charts for alkylated PAHs in SRM 2779: (a) C_1-naphthalenes, (b) C_4-naphthalenes, and (c) C_1-phenanthrene/anthracenes (C_1-Phen/Anth.). See Figure 5 caption for a detailed explanation of the charts.

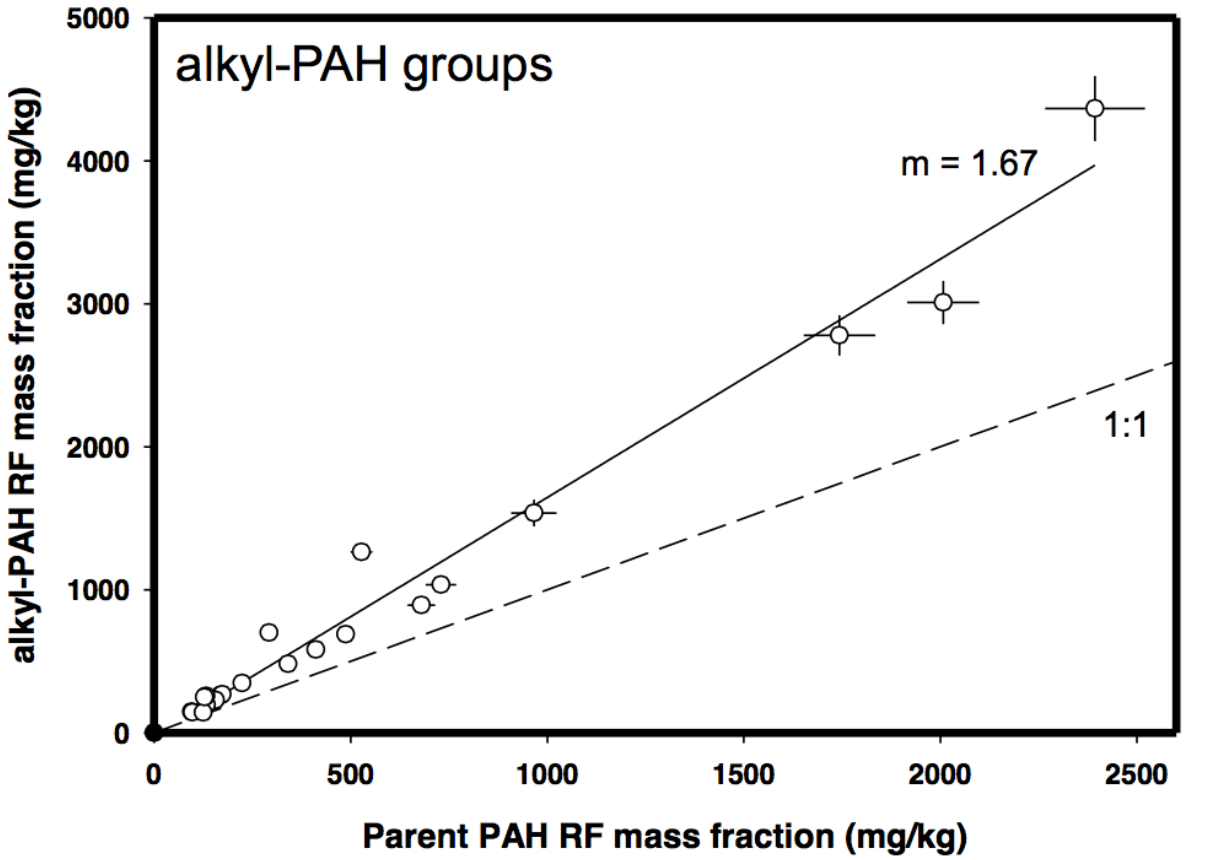


Figure 11. A comparison of response factors used for quantifying alkylated PAHs in SRM 2779. These are the results from a single laboratory who compared the typical method of using the response factor of the parent PAHs for all of the alkylated PAHs (as pure standards for every single alkylated PAHs are unavailable) within that family vs. attempting to use more representative response factors for individual alkylated PAHs that are available. For example, the response factor for C_1-phenanthrenes/anthracenes was 1-methylphenanthrene. Error bars represents ± one standard deviation.

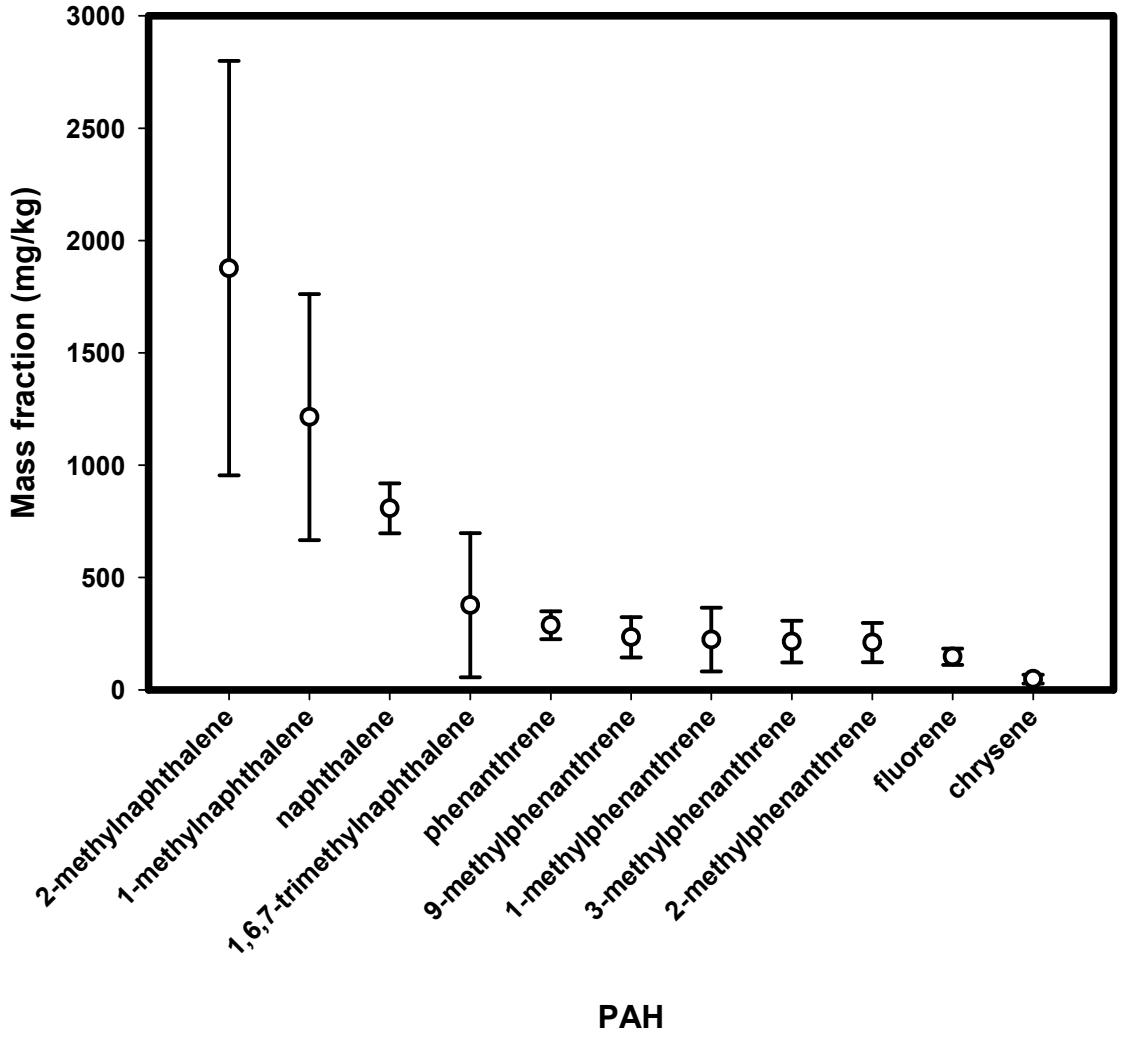


Figure 12. Mean mass fractions (mg/kg) for select PAHs in SRM 2779 on a scale of 0 mg/kg to 3000 mg/kg (see Tables 6-7). Five laboratories reported values for 1,6,7-trimethylnaphthalene. Eight laboratories reported values for 2-methylphenanthrene, and 9-methylphenanthrene. Nine laboratories reported values for chrysene. Ten laboratories reported values for 3-methylphenanthrene. Eleven laboratories reported values for 1-methylnaphthalene and 1-methylphenanthrene. Twelve laboratories reported values for 2-methylnaphthalene. Thirteen laboratories reported values for fluorene (one was an outlier). Fifteen laboratories reported values for naphthalene (one was an outlier), and sixteen laboratories reported values for phenanthrene (one was an outlier). Error bars represents ± one standard deviation, for all reported values.

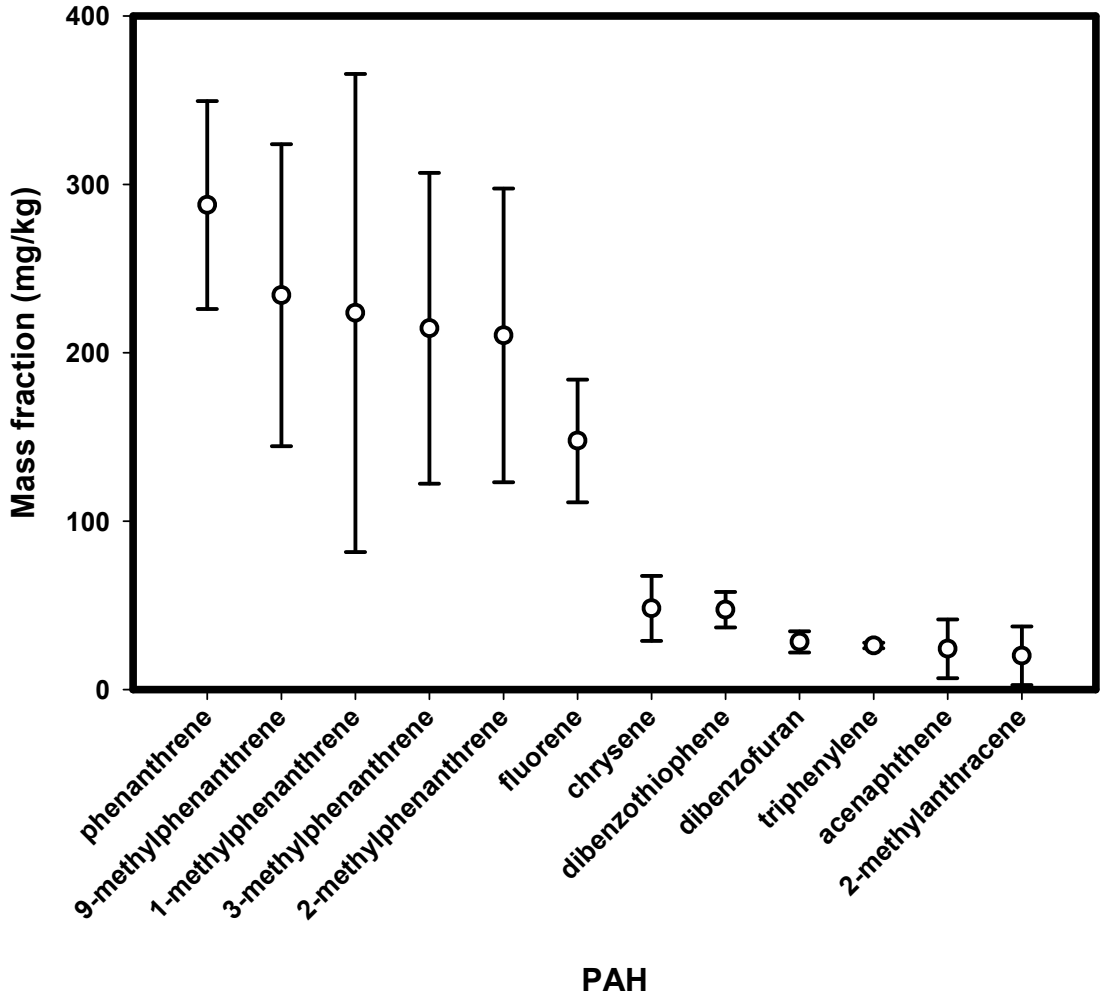


Figure 13. Mean mass fractions (mg/kg) for select aromatics in SRM 2779 on a scale from 0 mg/kg to 400 mg/kg (see Tables 6-7). Two laboratories reported values for triphenylene. Six laboratories reported values for dibenzofuran and 2-methylanthracene. Eight laboratories reported values for 2-methylphenanthrene, and 9-methylphenanthrene. Nine laboratories reported values for chrysene and acenaphthene. Ten laboratories reported values for 3-methylphenanthrene. Eleven laboratories reported values for 1-methylphenanthrene. Twelve laboratories reported values for dibenzothiophene. Thirteen laboratories reported values for fluorene (one was an outlier) and sixteen laboratories reported values for phenanthrene (one was an outlier). Error bars represents ± one standard deviation, for all reported values.

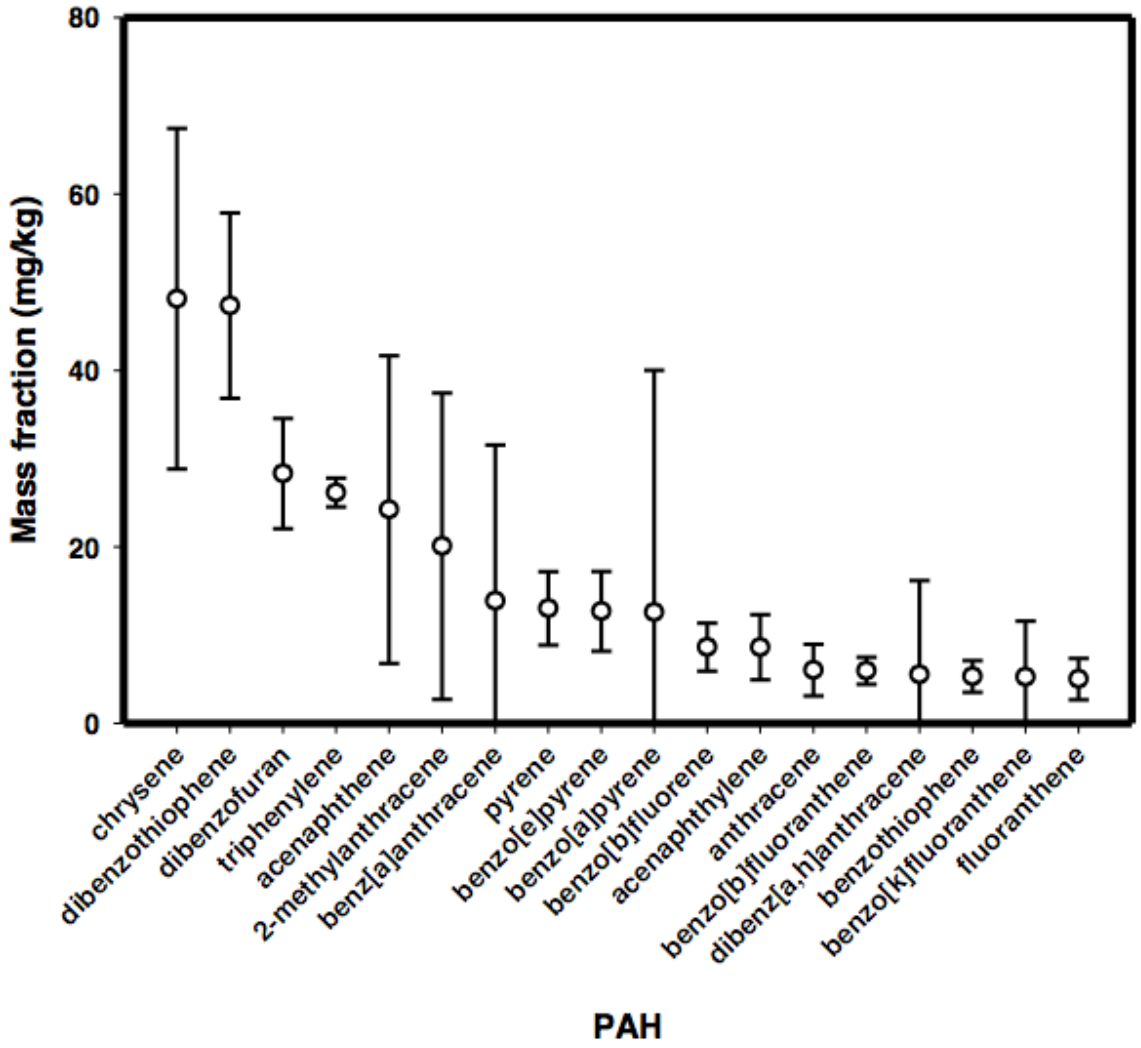


Figure 14. Mean mass fractions (mg/kg) for select PAHs in SRM 2779 on a scale from 0 to 80 mg/kg (see Tables 6-7). Two laboratories reported values for triphenylene. Three laboratories reported values for benzo[*b*]fluorene and benzothiophene. Six laboratories reported values for dibenzofuran, 2-methylanthracene and benzo[*k*]fluoranthene. Seven laboratories reported values for dibenz[*a*,*h*]anthracene. Eight laboratories reported values for anthracene. Nine laboratories reported values for chrysene, acenaphthene, benzo[*e*]pyrene, acenaphthylene, and benzo[*b*]fluoranthene. Ten laboratories reported values for benzo[*a*]pyrene. Eleven laboratories reported values for benz[*a*]anthracene and fluoranthene. Twelve laboratories reported values for dibenzothiophene. Fourteen laboratories reported values for pyrene (one was an outlier). Error bars represents ± one standard deviation, for all reported values.

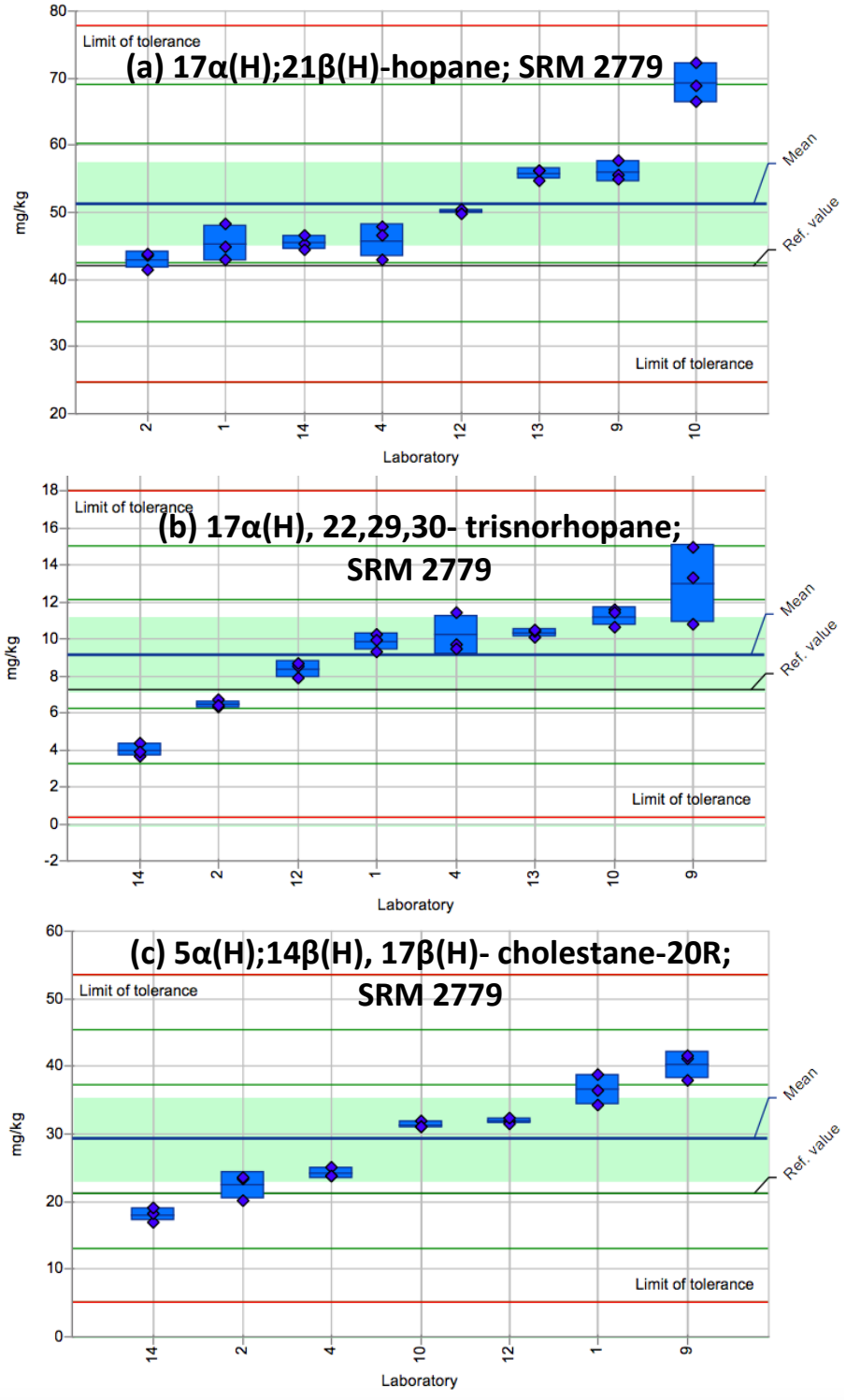


Figure 15. Summary charts for biomarkers in SRM 2779: (a) 17α(H),21β(H)-hopane, (b) 17α(H),22,29,30-trisnorhopane (c) 5α(H),14β(H),17β(H)-cholestane-20R. See Figure 5 caption for a detailed explanation of the charts.

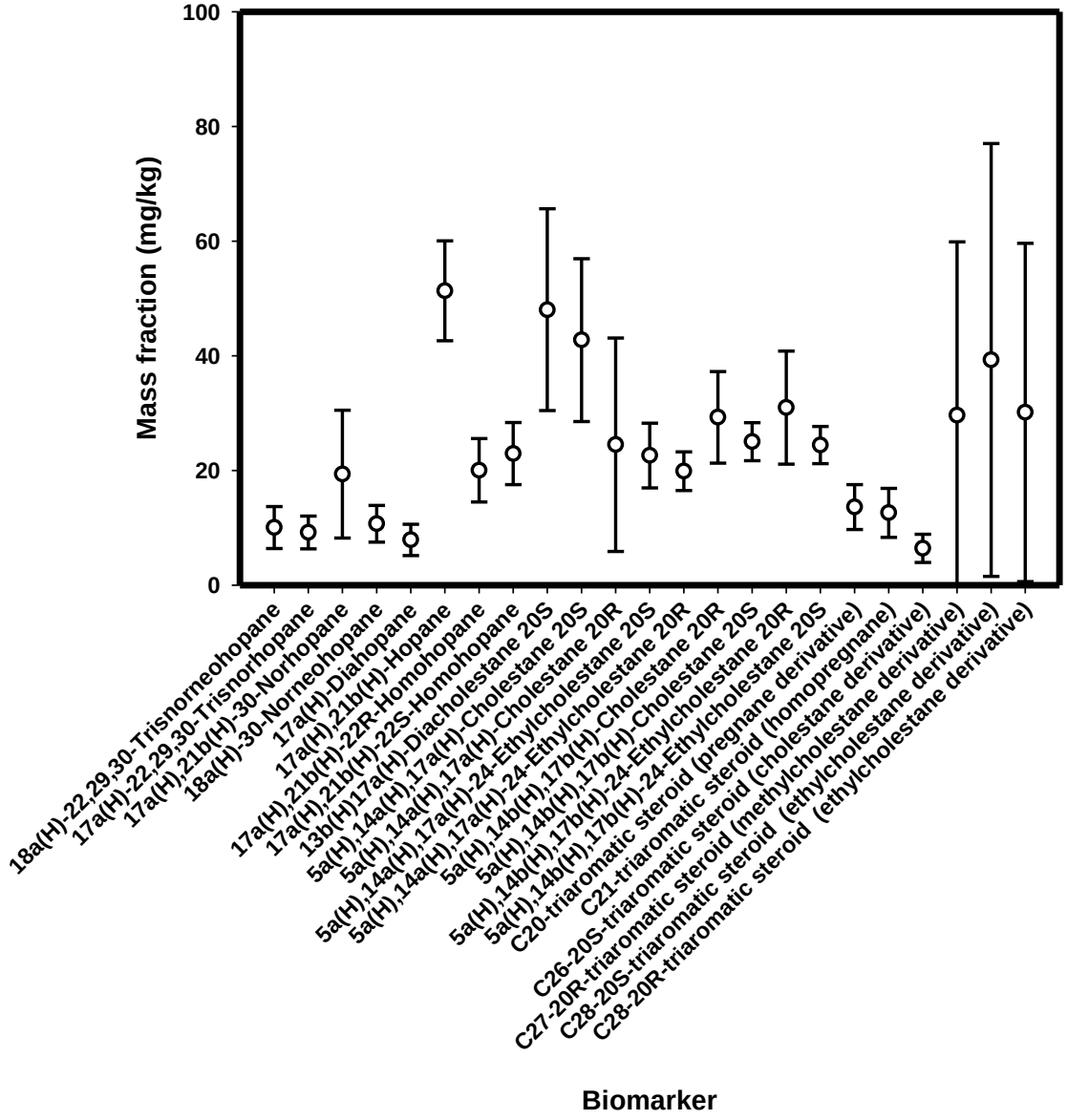


Figure 16. Mean mass fractions (mg/kg) for biomarkers in SRM 2779. Two laboratories reported values for C20-triaromatic steroid (pregnane derivative), C21-triaromatic steroid (homopregnane), and C26-20S-triaromatic steroid (cholestane derivative). Three laboratories reported values for C27-20R-triaromatic steroid (methylcholestane derivative), C28-20S-triaromatic steroid (ethylcholestane derivative), and C28-20R-triaromatic steroid (ethylcholestane derivative). Four laboratories reported values for 18α(H)-30-Norneohopane, 17α(H)-Diahopane, 13β(H)17α(H)-Diacholestane 20S, and 5α(H),14α(H),17α(H)-Cholestane 20S. Six laboratories reported values for 18α(H)-22,29,30-Trisnorneohopane, 5α(H),14α(H),17α(H)-24-Ethylcholestane 20S, 5α(H),14β(H),17β(H)-Cholestane 20S, 5α(H), and 14β(H),17β(H)-24-Ethylcholestane 20S. Seven laboratories reported values for 17α(H),21β(H)-30-Norhopane, 5α(H),14β(H),and 17β(H)-Cholestane 20R. Eight laboratories reported values for 17α(H)-22,29,30-Trisnorhopane, 17α(H),21β(H)-Hopane, 17α(H),21β(H)-22R-Homohopane, 17α(H),21β(H)-22S-Homohopane, 5α(H),14α(H),17α(H)-Cholestane 20R, 5α(H),14α(H),17α(H)-24-Ethylcholestane 20R, and 5α(H),14β(H),17β(H)-24-Ethylcholestane 20R. Error bars represents ± one standard deviation, for all reported values.

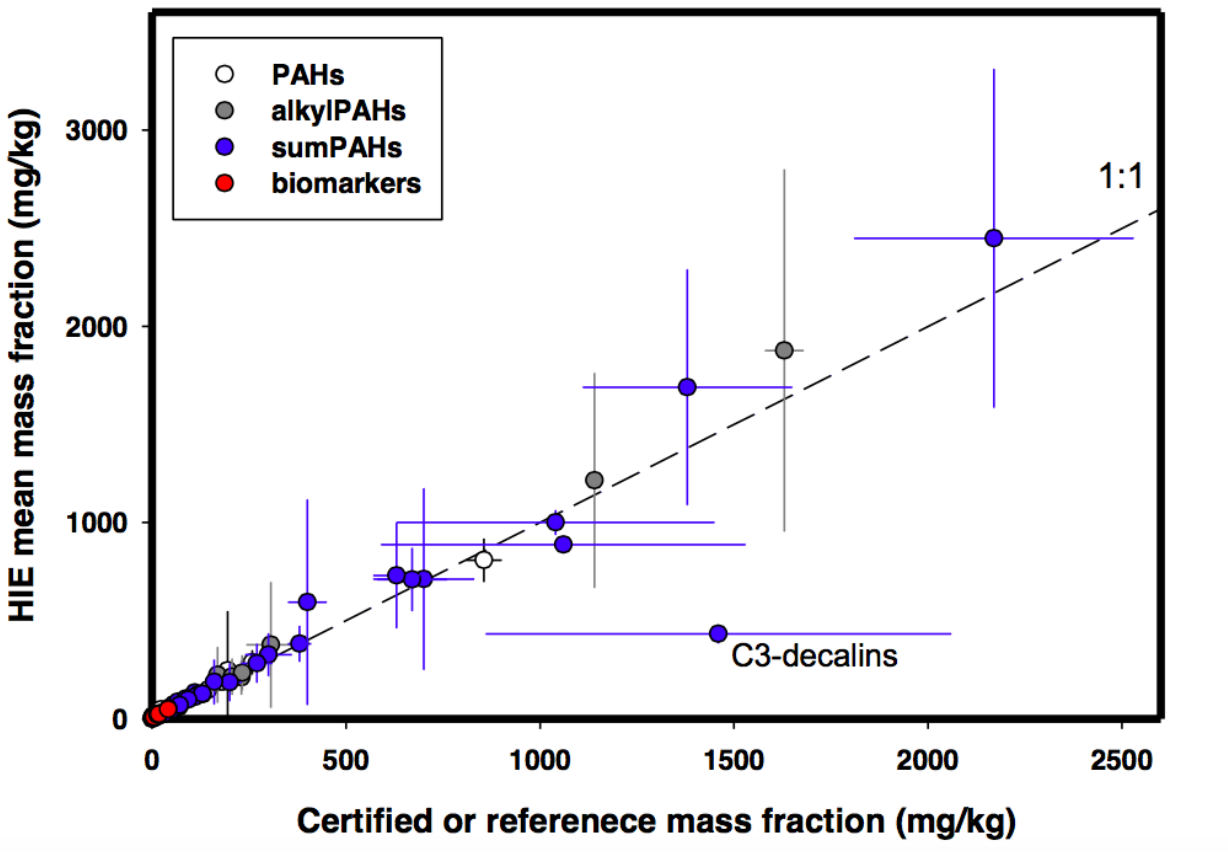


Figure 17. An expanded comparison of the results submitted for SRM 2779 versus those listed in the SRM's Certificate of Analysis in the following ranges: 0 to 2500 mg/kg. Alkylated PAHs (Alkyl PAHs) are compounds reported on an individual basis. SumPAHs is the sum of alkylated groups, such as C_3-decalins. The dotted line is the 1:1 comparison. Error bars represents ± one standard deviation.

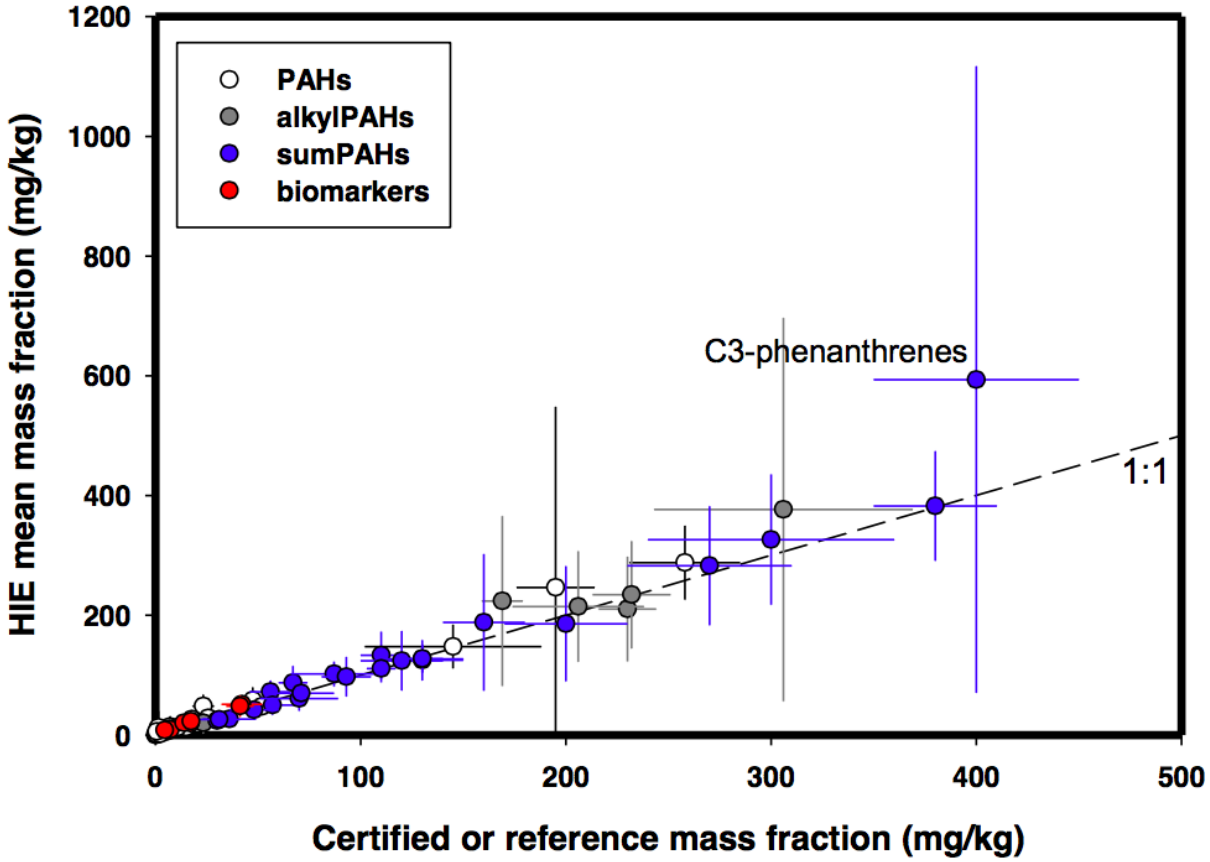


Figure 18. An expanded comparison of the results submitted for SRM 2779 versus those listed in the SRM's Certificate of Analysis in the following ranges of 0 to 500 mg/kg. Alkyl PAHs are compounds reported on an individual basis. SumPAHs is the sum of alkylated groups, such as C3-phenanthrenes. The dotted line is the 1:1 comparison. Error bars represents ± one standard deviation.

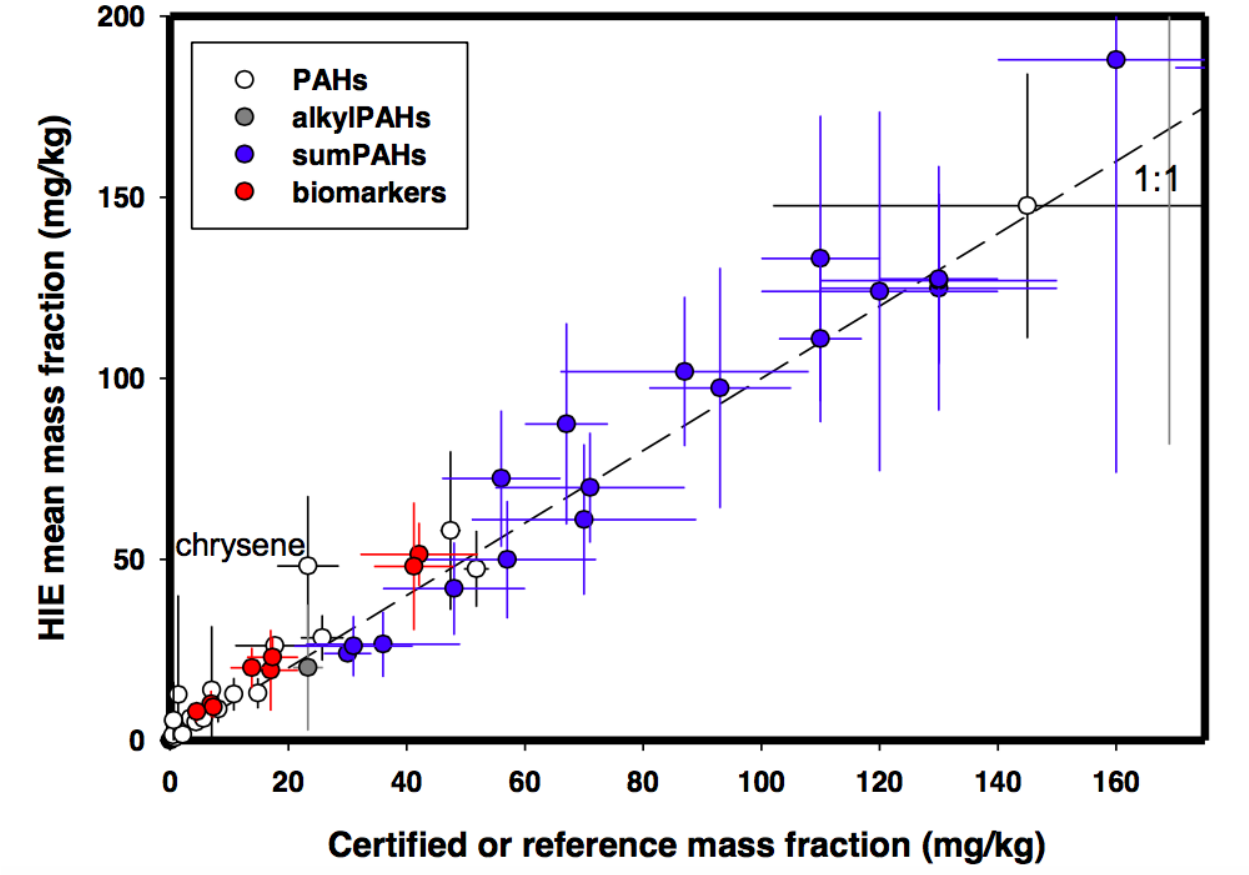


Figure 19. An expanded comparison of the results submitted for SRM 2779 versus those listed in the SRM's Certificate of Analysis in the following ranges of 0 to 200 mg/kg. Alkyl PAHs are compounds reported on an individual basis. SumPAHs is the sum of alkylated groups. The dotted line is the 1:1 comparison. Error bars represents ± one standard deviation.

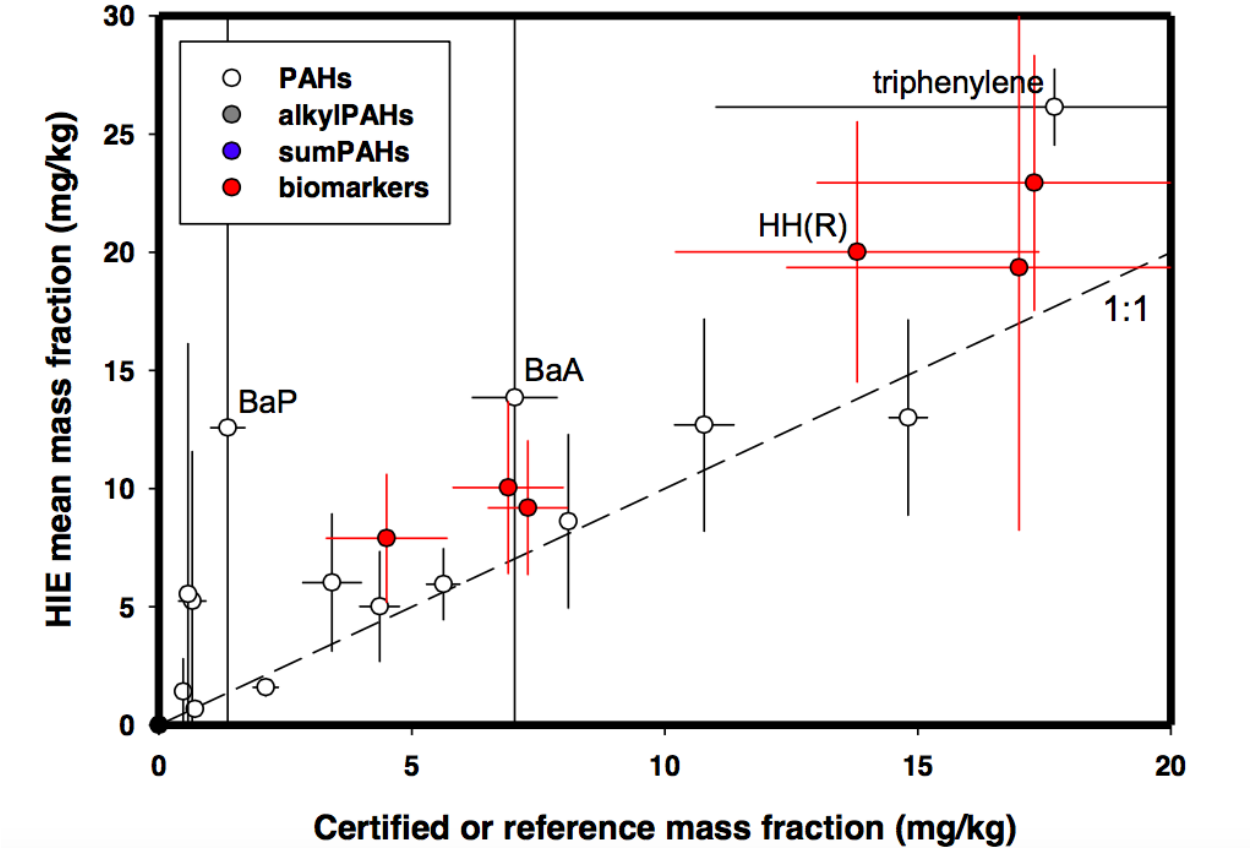


Figure 20. An expanded comparison of the results submitted for SRM 2779 versus those listed in the SRM's Certificate of Analysis in the following ranges of 0 to 20 mg/kg. Alkyl PAHs are compounds reported on an individual basis. SumPAHs is the sum of alkylated groups. The dotted line is the 1:1 comparison. Acronyms are defined as benzo[*a*]pyrene (BaP), benzo[*a*]anthracene (BaA), and homohopane R epimer, (HH(R)). Error bars represents ± one standard deviation.

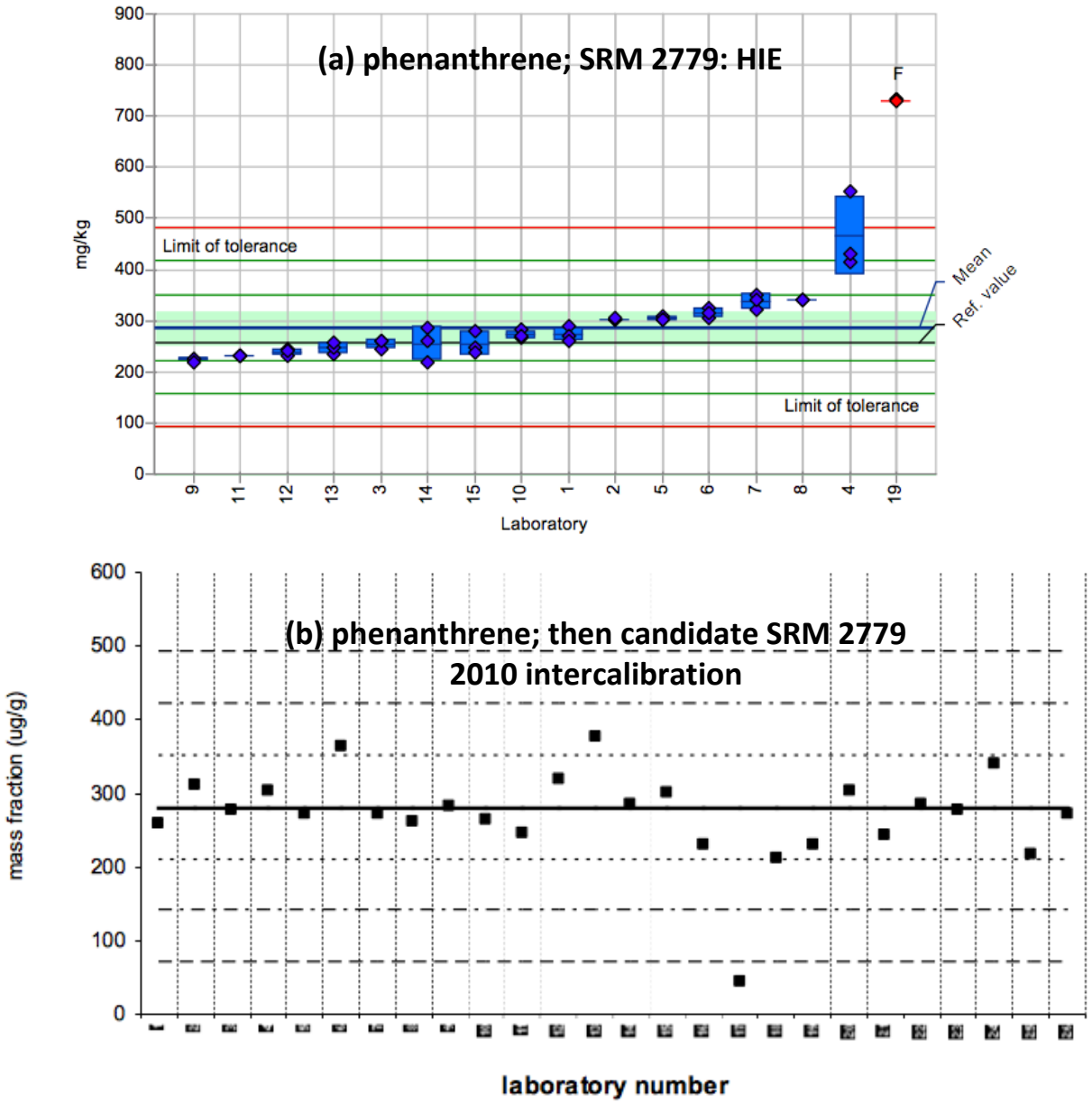


Figure 21. A comparison of the summary charts for phenanthrene: (a) HIE for SRM 2779 (See Figure 5 caption for a detailed explanation of the chart) and (b) 2010 intercomparison of then candidate SRM 2779 (NIST, 2010).

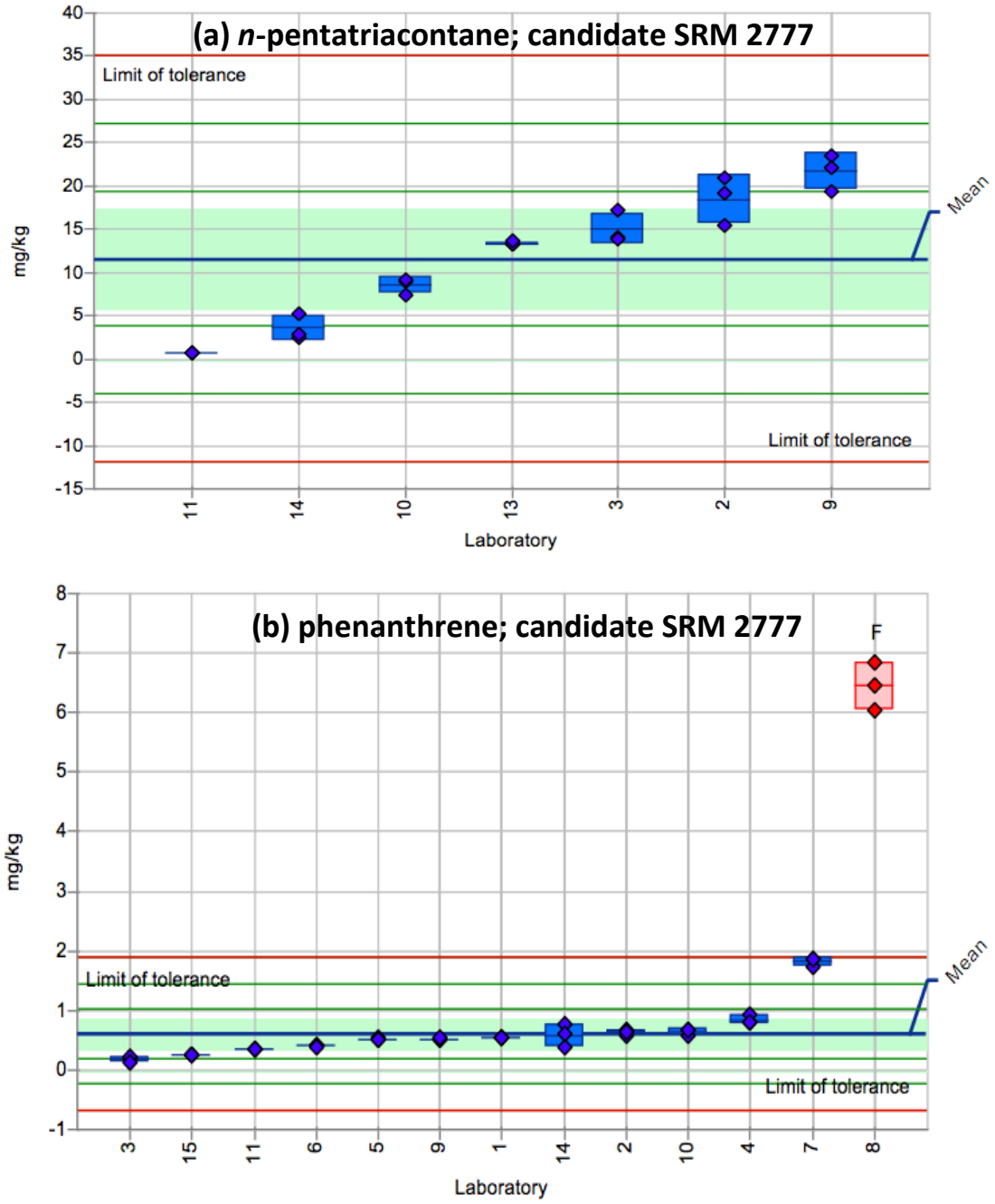


Figure 22. Summary charts for (a) *n*-pentratriacontane and (b) phenanthrene for candidate SRM 2777. See Figure 5 caption for a detailed explanation of the charts.

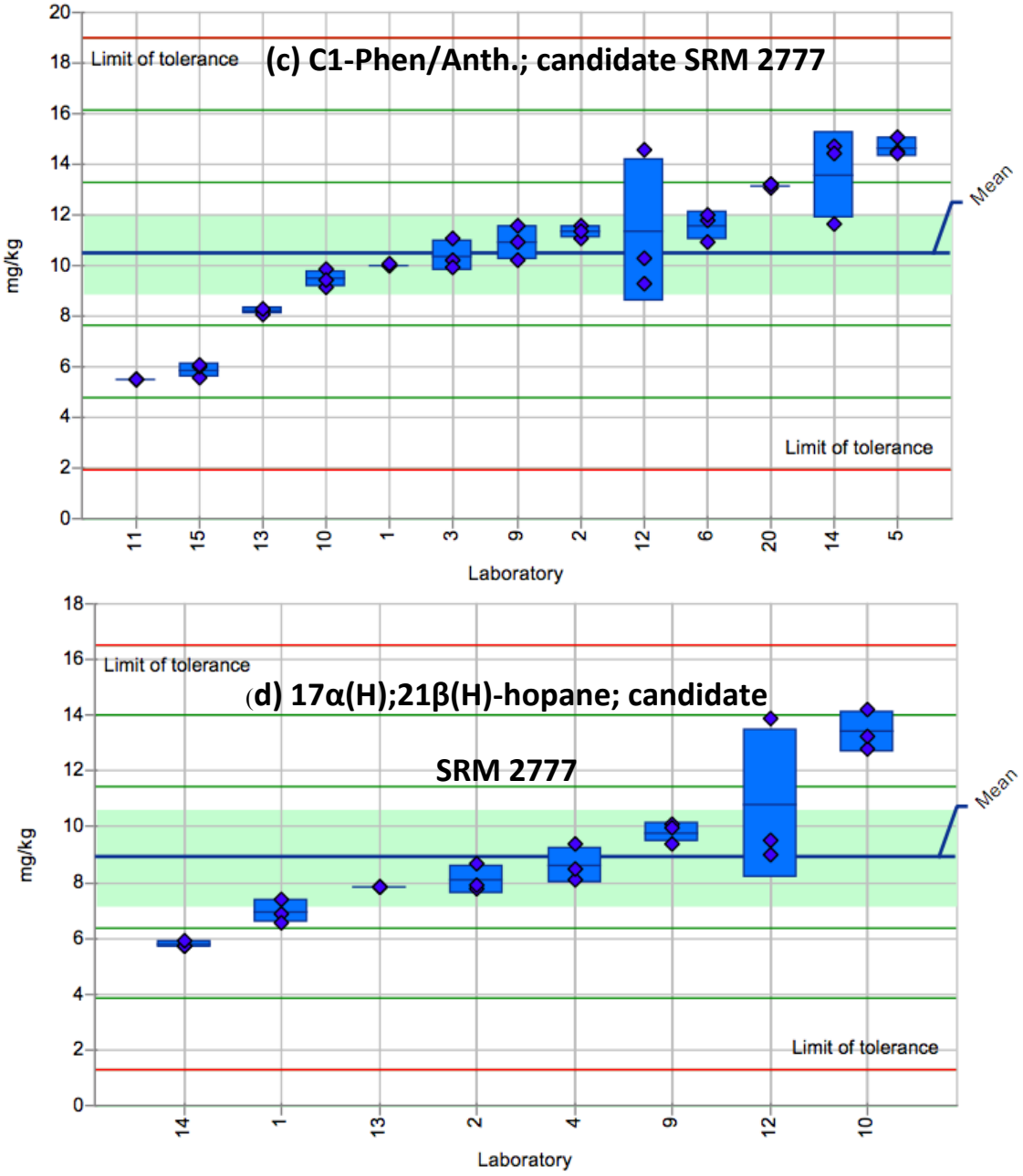


Figure 23. Summary charts for (a) C_1-phenanthrenes/anthracenes (C_1-Phen/Anth.) and (b) 17a(H); 21b(H)-hopane for candidate SRM 2777. See Figure 5 caption for a detailed explanation of the charts.

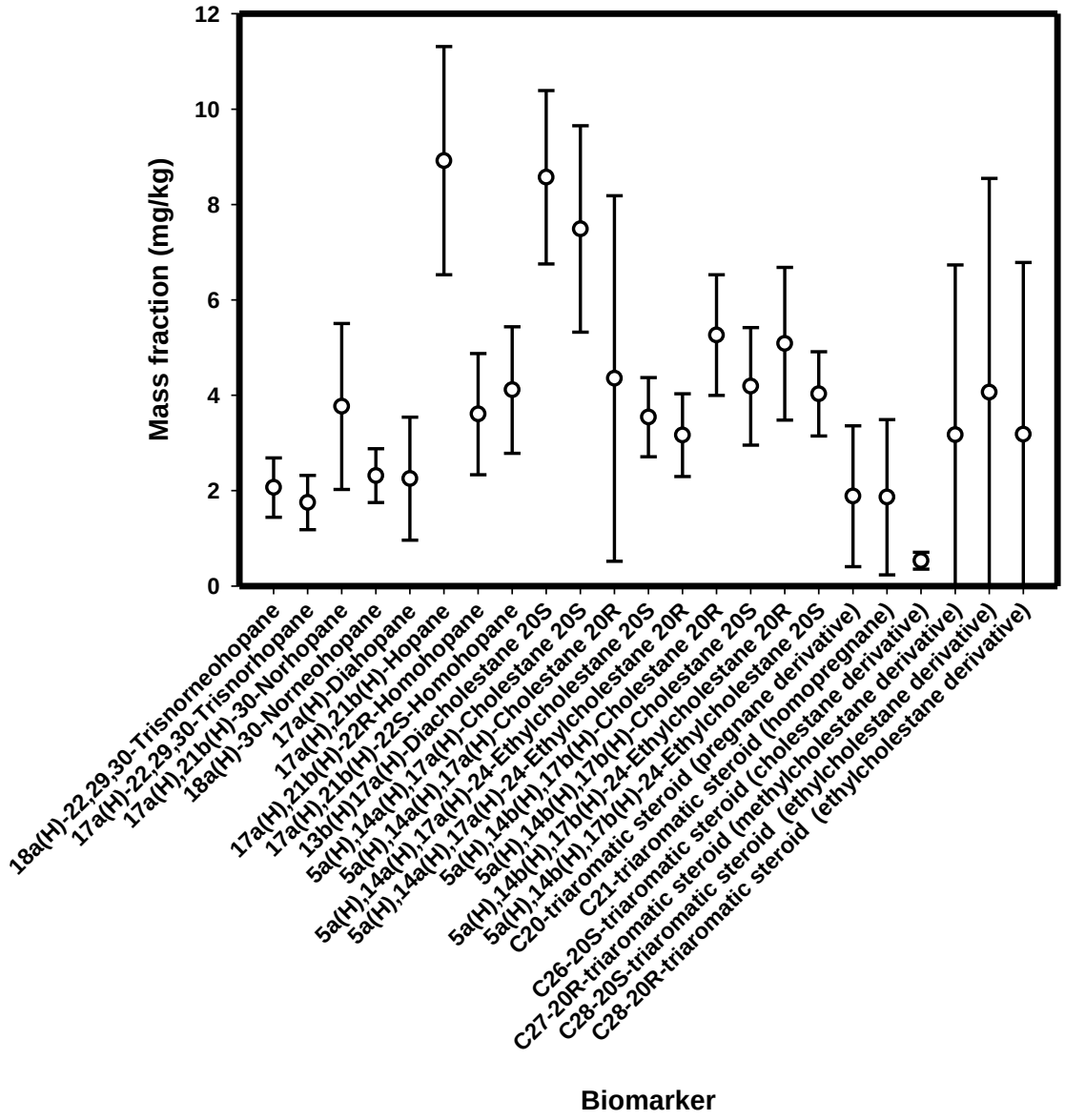


Figure 24. Mean mass fractions (mg/kg) for biomarkers in candidate SRM 2777. Two laboratories reported values for C26-20S-triaromatic steroid (cholestane derivative). Three laboratories reported values for 17α(H)-Diahopane, C27-20R-triaromatic steroid (methylcholestane derivative), C28-20S-triaromatic steroid (ethylcholestane derivative), C28-20R-triaromatic steroid (ethylcholestane derivative), C20-triaromatic steroid (pregnane derivative), and C21-triaromatic steroid (homopregnane). Four laboratories reported values for 18α(H)-30-Norneohopane,13β(H)17α(H)-Diacholestane 20S, and 5α(H),14α(H),17α(H)-Cholestane 20S. Six laboratories reported values for 17α(H),21β(H)-30-Norhopane, 18α(H)-22,29,30-Trisnorneohopane, 5α(H),14α(H),17α(H)-24-Ethylcholestane 20S, 5α(H),14β(H),17β(H)-Cholestane 20S, and 5α(H),14β(H),17β(H)-24-Ethylcholestane 20S. Seven laboratories reported values for 5α(H),14β(H),and 17β(H)-Cholestane 20R. Eight laboratories reported values for 17α(H)-22,29,30-Trisnorhopane, 17α(H),21β(H)-Hopane, 17α(H),21β(H)-22R-Homohopane, 17α(H),21β(H)-22S-Homohopane, 5α(H),14α(H),17α(H)-Cholestane 20R, 5α(H),14α(H),17α(H)-24-Ethylcholestane 20R, and 5α(H),14β(H),17β(H)-24-Ethylcholestane 20R. Error bars represents ± one standard deviation, for all reported values.

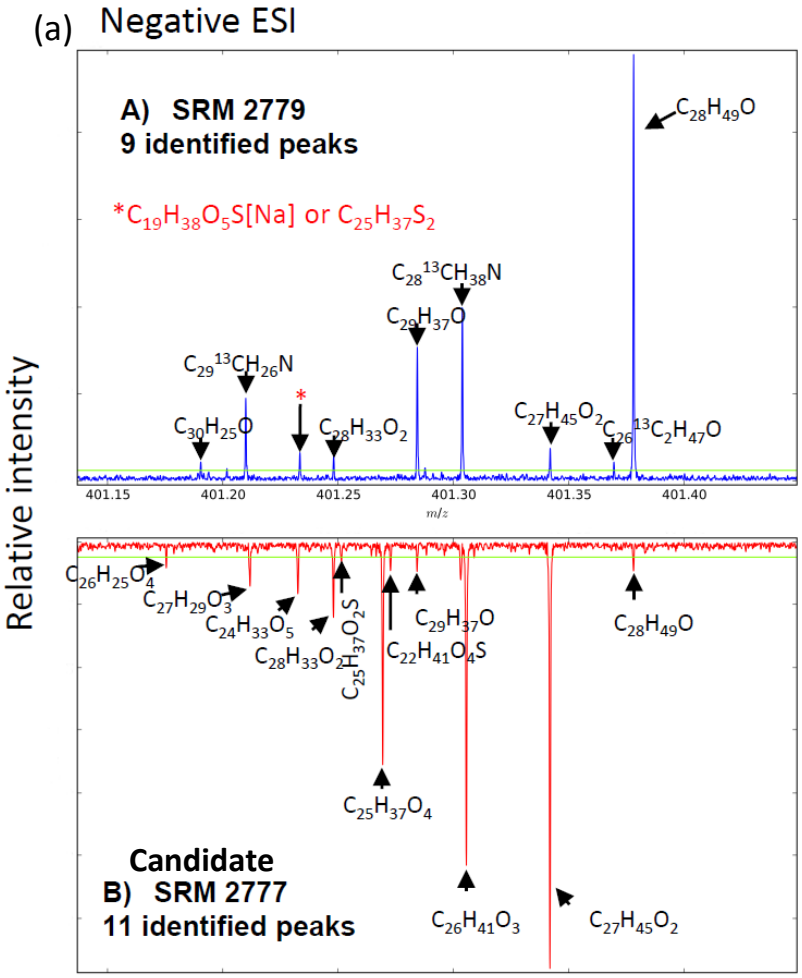


Figure 25a: Mass scale expanded inset at less than one nominal mass for SRM 2779 and candidate SRM 2777 for laboratory FT1.

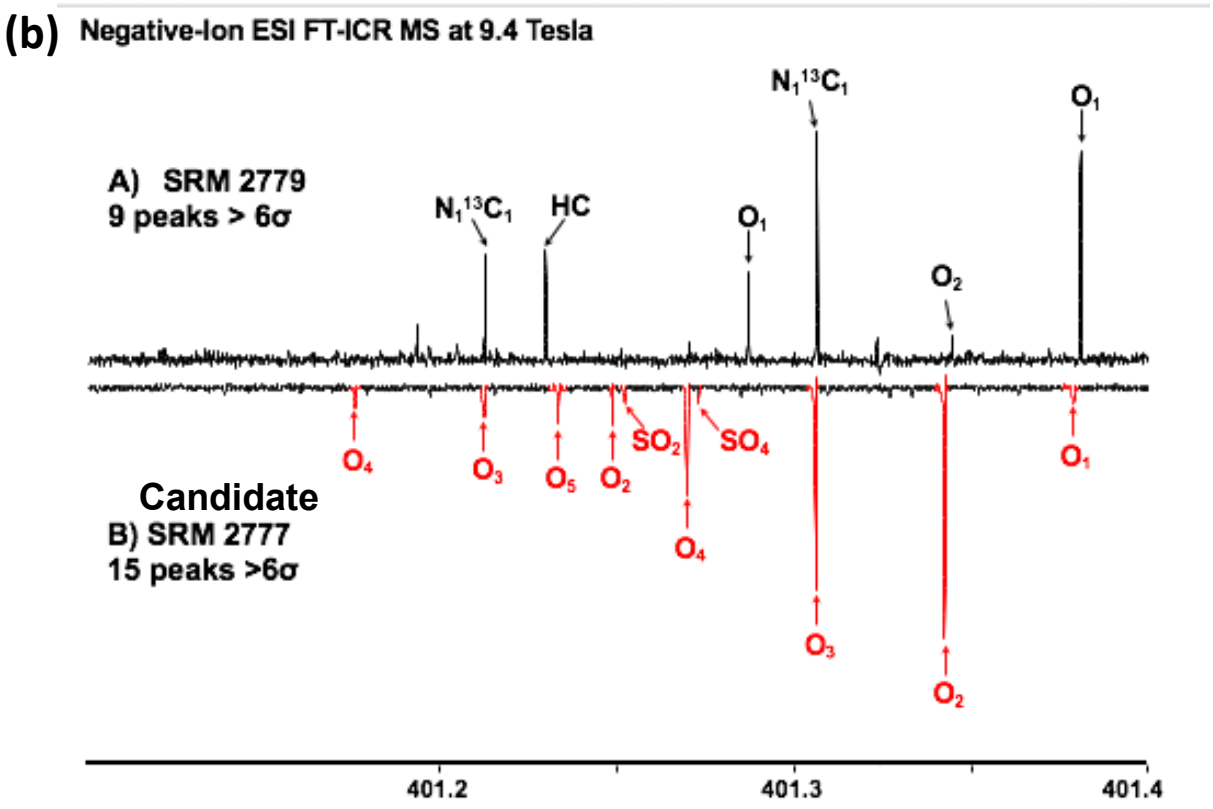


Figure 25b. Mass scale expanded inset at less than one nominal mass for SRM 2779 and candidate SRM 2777 for laboratory FT2.

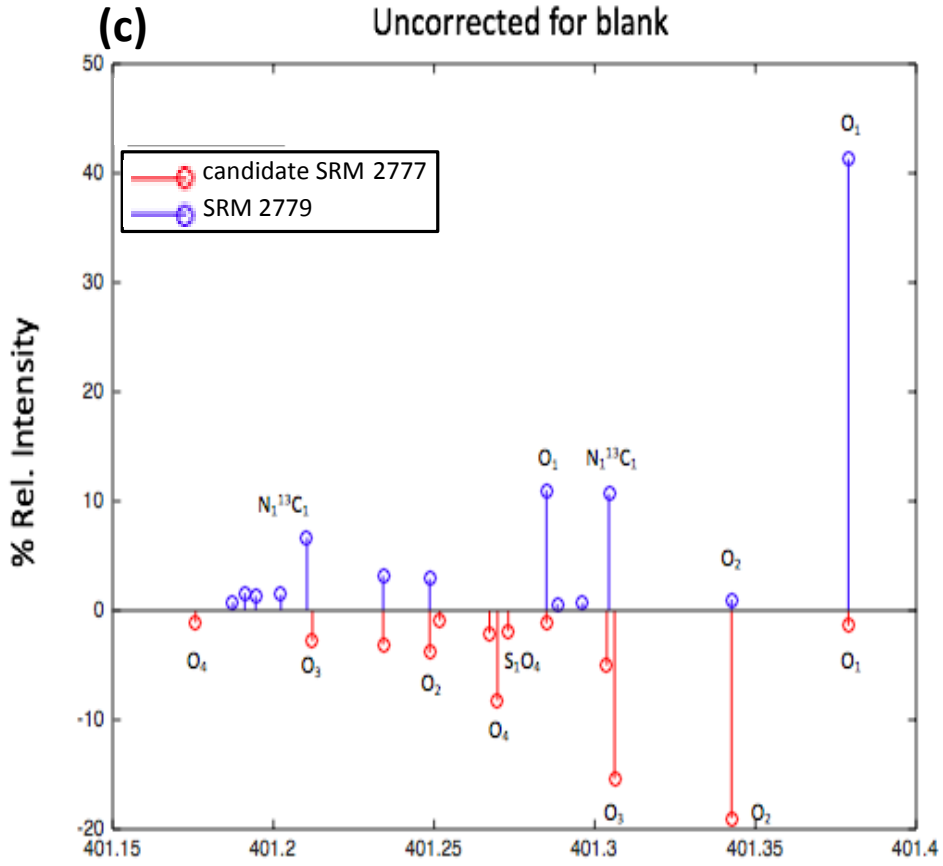


Figure 25c. Mass scale expanded inset at less than one nominal mass for SRM 2779 and candidate SRM 2777 for laboratory FT3.

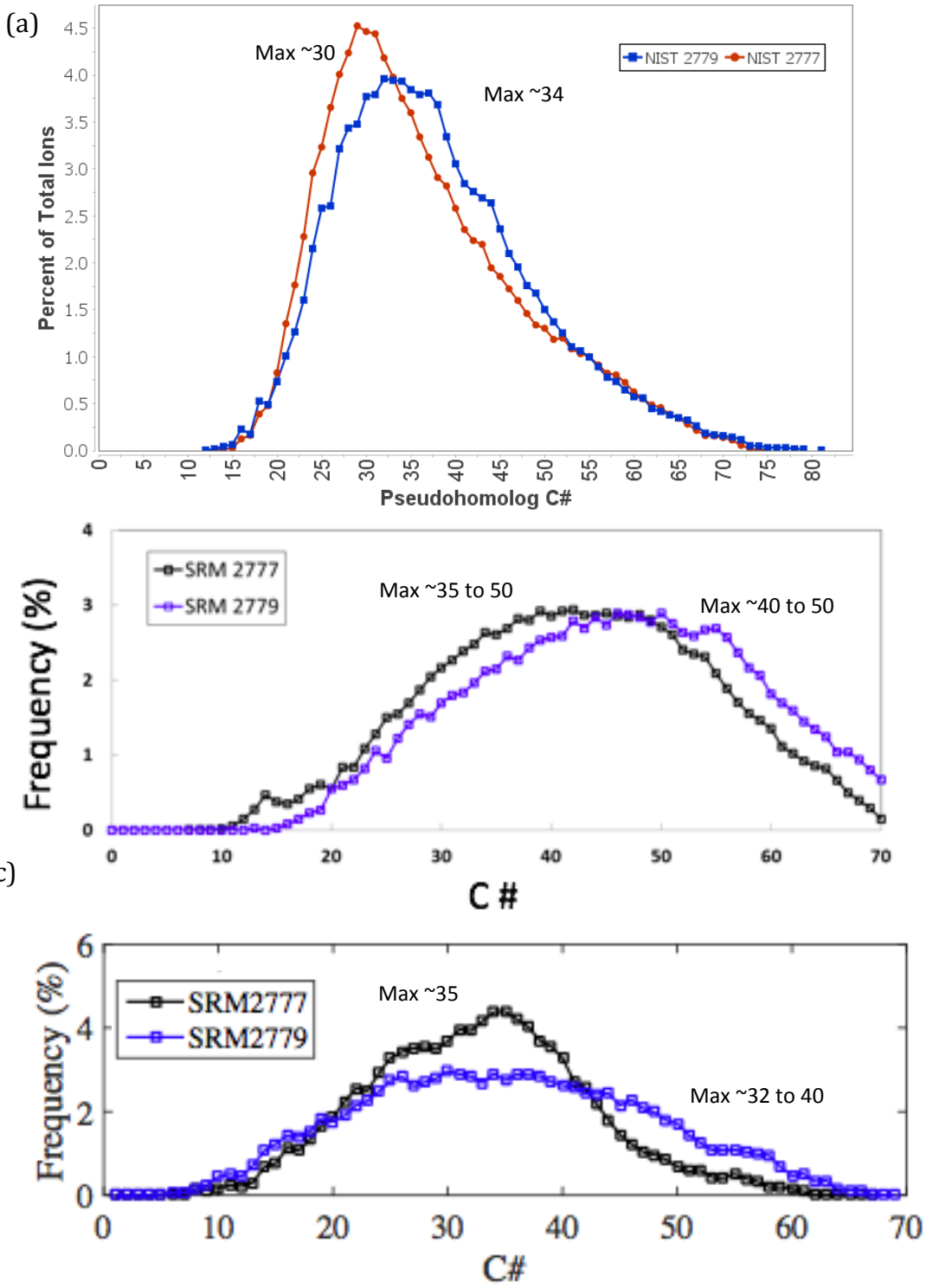
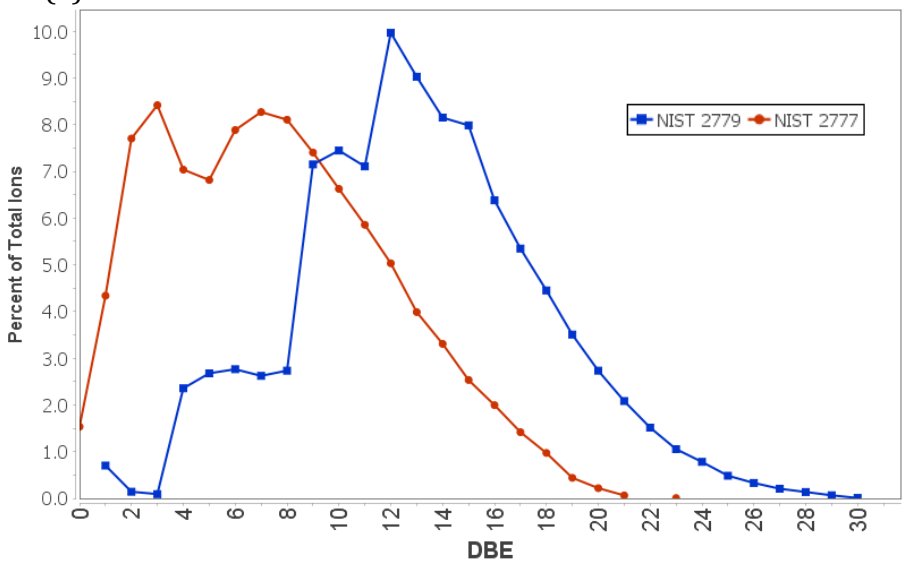
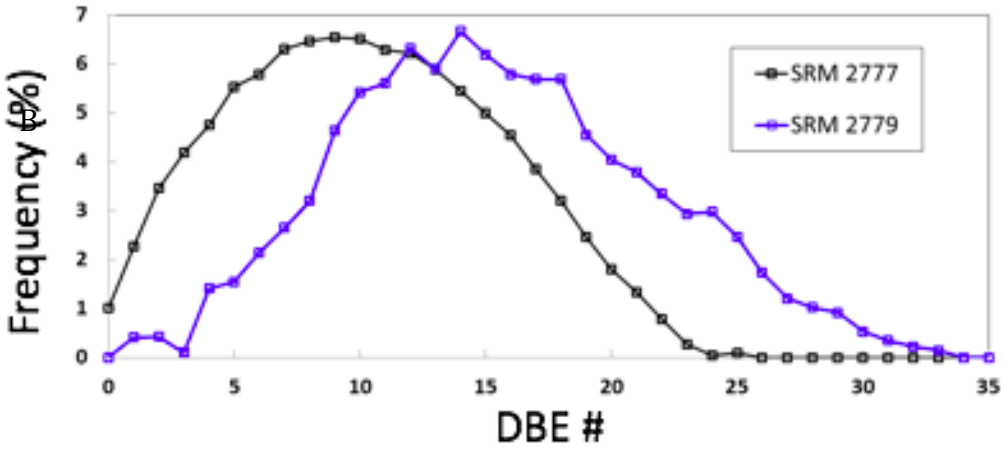


Figure 26: Percentage of total ions or frequency vs. C#. (a) Laboratory FT1, (b) Laboratory FT2, and (c) Laboratory FT3.

(a)



(b)



(c)

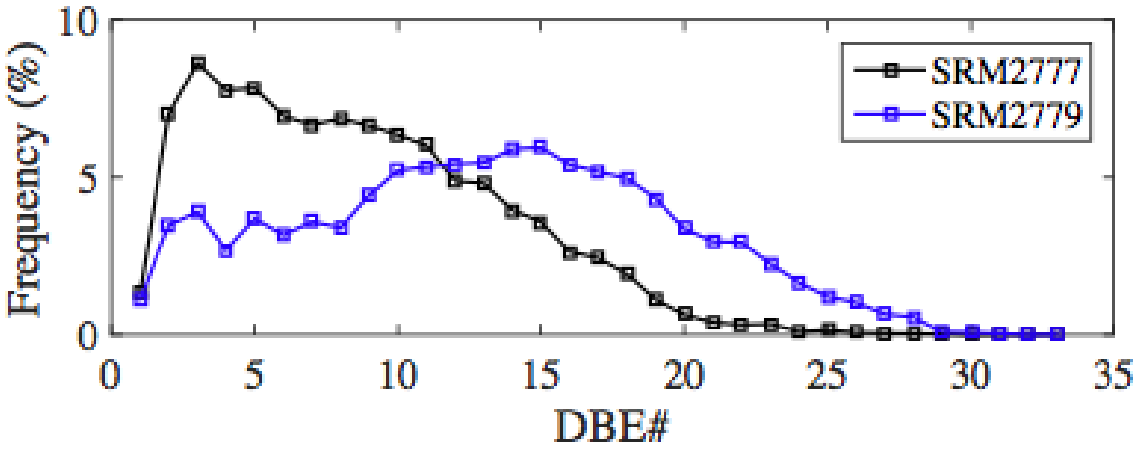


Figure 27: Percentage of total ions or frequency vs. DBE. (a) Laboratory FT1, (b) Laboratory FT2, and (c) Laboratory FT3.

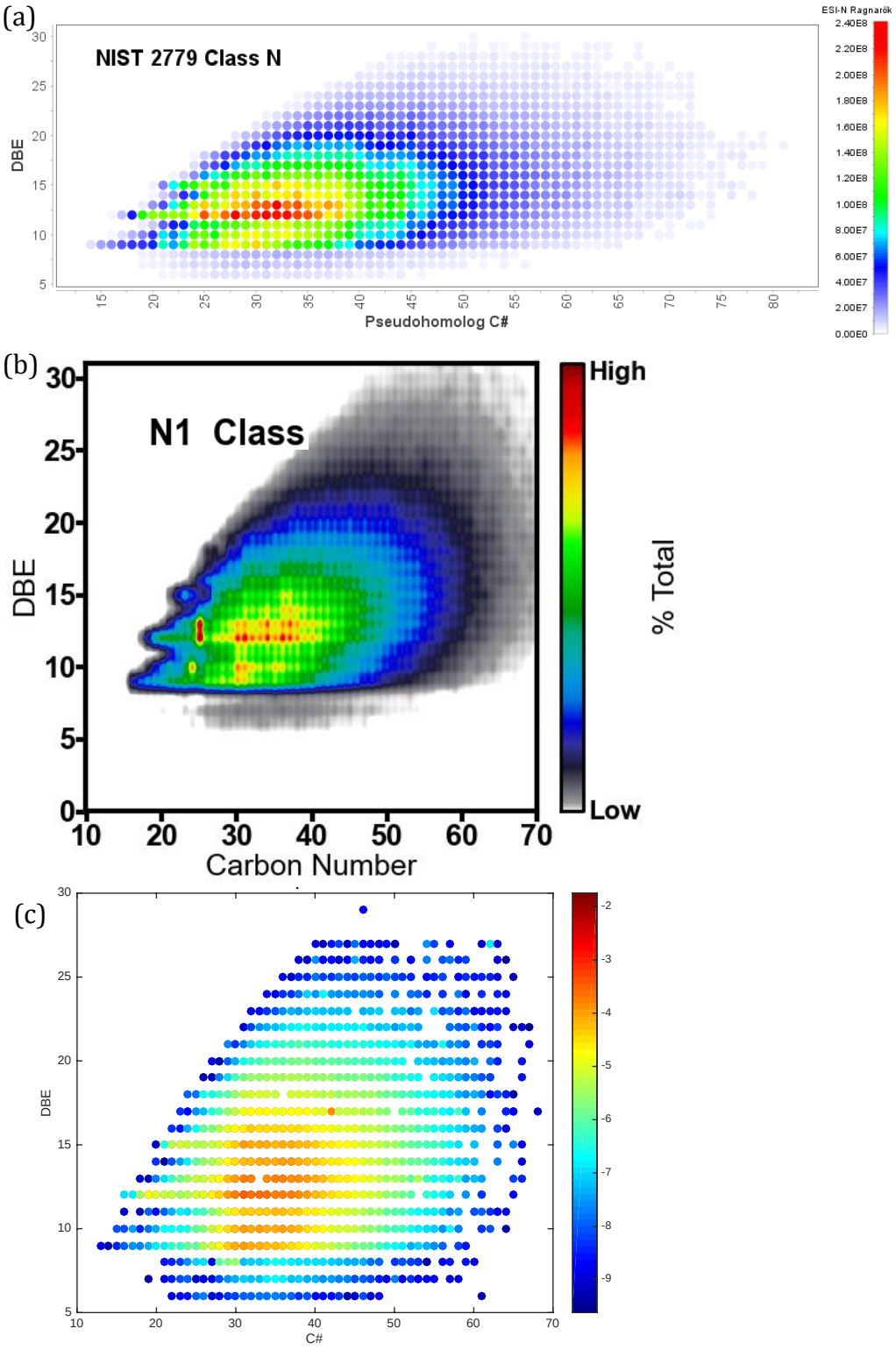


Figure 28. Kendrick plot of class N1 for SRM 2779 in negative ESI. (a) Laboratory FT1, (b) Laboratory FT2, and (c) Laboratory FT3.

Appendix 1

GoMRI Hydrocarbons Analysis QA/QC Workshop
– Experienced Analysts, New Analysts and All Interested Welcome –

Sunday Afternoon, 26th January 2014
5-6:00 PM
Grand Bay Ballroom

Background

Quality matters! Analysis of organic compounds is difficult: There are millions of individual organic compounds, and many of them are labile when exposed, e.g., to molecular oxygen and microbial activity. This applies to both target compounds and standard reference materials (SRMs). There is a particular need for Quality Assurance (QA) and Quality Control (QC) to insure valid data are produced.

GoMRI research involves hydrocarbon analysis of unweathered and weathered oil, sediments, and biological tissues by a number of laboratories. This is a unique chance for a concerted QA/QC effort in hydrocarbon analysis. GoMRI management is willing to support such an effort, but the initiative and execution should be developed by GoMRI researchers.

This workshop seeks to

- encourage existing QA/QC programs in hydrocarbon analysis,
- motivate those who have thought about QA/QC in hydrocarbon analysis but set it aside for (alleged) lack of previous experience, time, capacity or other reasons,
- support those who can be convinced that QA/QC in hydrocarbon analysis is important but do not yet know how to exercise it.

DRAFT Agenda

1) Welcome – Chuck Wilson, CSO GoMRI, 5 min.

2) Early history of QA/QC procedures and interlaboratory intercomparison exercises for hydrocarbon analysis – John Farrington, Jürgen Rullkötter 10 min.

3) NOAA National Status & Trends and other recent programs – Terry Wade, 10 min.

4) Relevant SRMs (NIST), potential activities for the future – Steve Wise, Chris Reddy, 10 min.

Open Discussion – Chuck Wilson, moderator.

Appendix 2

GoMRI Hydrocarbons Analysis QA/QC Workshop

Sponsored by the Gulf of Mexico Research Initiative Research Board
Westin Galleria-Houston, Galleria III
February 16, 2015 1:00 – 6:00 pm

In response to discussions at the Hydrocarbon Chemistry QAQC meeting during the 2014 Gulf of Mexico Oil Spill and Ecosystem Science Conference, the Gulf of Mexico Research Initiative (GoMRI) Research Board engaged the National Institute of Standards and Technology to help it conduct an intercomparison of methods and results and to better refine and improve reference analytes and levels. Intercomparison exercises have become an excellent tool for assessing the comparability of analytical measurements. In addition, they also provide an opportunity for researchers to compare their methods and approaches as well as report on novel or typically untargeted analytes that may eventually become more standard because of their importance to tracking spilled oil, and understanding fates and effects of spilled oil. For example, recent studies have identified in weathered samples an increase in oxygen in the oil residues on bulk sample, class of chemicals, and molecular levels using non-traditional techniques.

To address the need for hydrocarbon chemistry calibration, the GoMRI Research Board undertook the Hydrocarbon Intercalibration Experiment (HIE), realizing it is the responsibility of the scientific community involved in hydrocarbon analysis to continue to assure that everyone is doing the best science possible. The HIE was an effort by the GoMRI Research Board to further enable the best science.

The HIE supported multiple science teams in exploring various aspects of oil chemistry. The large network of chemistry laboratories involved in GoMRI research afforded the GoMRI Research Board the opportunity to partner with the National Institute of Standards and Technology and organize an across laboratory comparison using common reference material. This workshop will present the analytical results from this experiment. The overall results and trends of analysis will be presented and discussed. Areas of consistencies and differences will be considered, and QAQC recommendations for publications resulting from the study and associated best practices will be highlighted. Non-participants of the HIE are welcome and encouraged to attend along with study participants.

Appendix 2

Agenda

1:00 pm **Welcome/Introduction**

Dr. Margaret Leinen – Vice Chair, GoMRI Research Board

1:10 pm **Opening Comments**

Dr. Steve Wise - Senior Analytical Chemist, National Institute of Standards and Technology

1:30 pm **Presentation of Initial Results**

Dr. Chris Reddy - Senior Scientist of Marine Chemistry and Geochemistry at Woods Hole Oceanographic Institution and Director of the Coastal Ocean Institute

3:00 pm **Break (15 minutes)**

3:15 pm **HIE Participant Discussion (challenges, lessons learned)**

Buffy Meyer – Graduate Student, Louisiana State University
Dr. Ryan Rodgers – Director of Future Fuels Institute, National High Magnetic Field Laboratory, Florida State University
Dr. Charles Miller – Professor, Tulane University

4:15 pm **How will NIST use these results? (Dr. Steve Wise)**

4:30 pm **SRM in Daily Analysis**

Dr. Terry Wade – Research Scientist and Deputy Director, Geochemical and Environmental Research Group, Texas A&M University

5:00 pm **Open Discussion, facilitated by Drs. Brewer, Farrington, and Rullkötter**

Dr. Peter Brewer - GoMRI Research Board; Senior Scientist, Monterey Bay Aquarium Research Institute
Dr. John Farrington - GoMRI Research Board; Dean Emeritus, Woods Hole Oceanographic Institution
Dr. Jürgen Rullkötter – GoMRI Research Board; Professor of Organic Geochemistry (retired), University of Oldenburg, Germany

5:45 pm **Concluding Remarks (Dr. John Farrington, GoMRI Research Board)**

Appendix 3

Hydrocarbon Intercalibration Experiment (HIE)

Samples: Candidate SRM 2777 Weathered Gulf of Mexico Oil and SRM 2779 Gulf of Mexico Crude Oil

Please fill in all blanks; Use requested units of concentration; Report results as if 3 figures were significant

DO NOT INSERT ROWS OR COLUMNS WITHIN THIS TABLE. DO NOT MOVE CELLS.

- If ne cessary, add additional data/information at the end of the reults table.
- U se one of the following if no concentration is reported for an analyte:

  N A = Not analyzed/determined; <"conc" = <detection limit conc.; Other = other, explain in a note at end of table

  (D L = "below detection limit" may be used, but <"conc", e.g., <8, is preferable.)

  D o not use parentheses or negative numbers to indicate "less than detection limit".

Reporting Date (m/d/y): 2/10/15
Laboratory: Reddy Lab, WHOI
Submitted by: Chris Reddy

BRIEF DESCRIPTION OF PROCEDURES USED:

Approximate amount of sample analyzed:

Candidate SRM 2777 1.067 g SRM 2779 0.119 g

Sample cleanup and/or separation method: None

Analytical method used (e.g., GC/MS): GC/MS

	Analyt. Instr.	Column Phase	Col. Length, m	Col. i.d., mm	Col. film thickness, µm	mode of injection (split/splitless/on-column)
PAH	Agilent 6890A GC/5973N MS	DB-XLB	60	0.25	0.25	splitless
Alkylated PAH	Agilent 6890A GC/5973N MS	DB-XLB	60	0.25	0.25	splitless
Alkanes	Agilent 6890A GC/5973N MS	DB-XLB	60	0.25	0.25	splitless
Biomarkers	Agilent 6890A GC/5973N MS	DB-XLB	60	0.25	0.25	splitless

Method of quantitation (IS = internal standard, ES = external standard):

PAH IS
Alkylated PAH IS
Alkanes IS
Biomarkers IS

IF internal standard method was used, please complete the following section:

Identity of internal standards/surrogates used that were:

Added PRIOR to extraction of sample: No extraction performed

PAH naphthalene-d8, fluorene-d10, dibenzothiophene-d8, phenanthrene-d10, o-terphenyl, fluoranthene-d10, pyrene-d10, chrysene-d12, benzo[a]pyrene-d12
Alkylated PAH _____
Alkanes nC20-d42, nC16-d34
Biomarkers _____

Added after extraction/cleanup and JUST PRIOR to chromatographic analysis:

PAH No extraction performed
Alkylated PAH No extraction performed
Alkanes No extraction performed
Biomarkers No extraction performed

Any others? Added at what point in analyses:

PAH _____
Alkylated PAH _____
Alkanes _____
Biomarkers _____

IS/surrogate standards used for quantitation calculations were:

X those added prior to extraction

_____ those added after extraction/cleanup and just prior to chromatographic analysis *No extraction performed

If t he IS/surrogates added after extraction/cleanup extraction were used for quantitation, w ere results corrected for percent recovery? No

If ye s, include the associated percent recovery acceptance ranges in the results table below.

Calibration Curve

	Number of Calibration Levels		Any non-conformances with calibrations?
	Points	Conc. Range	If yes, please discuss
PAH	6	45.5-0.2 mg/kg	_____
Alkylated PAH	6	45.5-0.2 mg/kg	_____
Alkanes	6	37-0.6 mg/kg	_____
Biomarkers	6	8.9-0.004 mg/kg	_____

If analyte was quantitated using a "reprentative compound", e.g. quantitated against an isomer, parent compound, or s ingle alkylated compound for a group of hom ologs c ompound for a group of hom ologs, list the compound used in the results table below.

Please note any differences in procedures used for SRM 2779 analyses from those for Candidate SRM 2777 described above:
SRM 2779 was diluted with isooctane prior to the addition of internal standards, whereas SRM 2777 was not diluted.

Appendix 3

Analytical method used for elemental analysis: _____

RESULTS:

PAH ANALYSES	Candidate SRM 2777 Sample 1	Candidate SRM 2777 Sample 2	Candidate SRM 2777 Sample 3	SRM 2779 Sample 1	SRM 2779 Sample 2	SRM 2779 Sample 3	
Analyst (Initials)	RFS	RFS	RFS	RFS	RFS	RFS	
Date(s) of measurements (m/d/y)	2/7/15	2/7/15	2/7/15	2/7/15	2/7/15	2/7/15	
Sample ampoule number	box 2, ampuole 84	box 2, ampuole 84	box 2, ampuole 84				
	Candidate SRM 2777 Sample 1	Candidate SRM 2777 Sample 2	Candidate SRM 2777 Sample 3	SRM 2779 Sample 1	SRM 2779 Sample 2	SRM 2779 Sample 3	IS/surrogate used for qunatitation
	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	
naphthalene	<0.20	<0.20	<0.20	956	899	863	o-terphenyl
biphenyl	<0.20	<0.20	<0.20	183	173	166	o-terphenyl
acenaphthene	<0.20	<0.20	<0.20	43.0	37.9	39.7	o-terphenyl
acenaphthylene	<0.20	<0.20	<0.20	11.5	10.9	10.3	o-terphenyl
fluorene	<0.20	<0.20	<0.20	156	150	142	o-terphenyl
phenanthrene	0.53	0.55	0.55	288	270	261	o-terphenyl
anthracene	<0.20	<0.20	<0.20	6.55	5.69	5.78	o-terphenyl
fluoranthene	0.21	0.21	0.20	5.02	4.68	4.51	o-terphenyl
pyrene	0.43	0.43	0.42	13.9	12.9	12.0	o-terphenyl
benzo[b]fluorene	NA	NA	NA	NA	NA	NA	NA
benz[a]anthracene	<0.20	<0.20	<0.20	6.91	6.83	6.75	o-terphenyl
chrysene	1.98	1.97	1.89	28.5	26.6	25.5	o-terphenyl
triphenylene	3.21	3.14	2.95	26.4	24.8	23.8	o-terphenyl
chrysene+triphenylene*	NA	NA	NA	NA	NA	NA	NA
benzo[*b*]fluoranthene	0.50	0.48	0.45	5.66	5.06	4.78	o-terphenyl
benzo[*j*]fluoranthene	NA	NA	NA	NA	NA	NA	NA
benzo[*k*]fluoranthene	<0.20	<0.20	<0.20	3.54	3.20	3.19	o-terphenyl
benzo[a]fluoranthene	NA	NA	NA	NA	NA	NA	NA
benzo[e]pyrene	0.81	0.76	0.70	12.6	11.6	11.0	o-terphenyl
benzo[a]pyrene	<0.20	<0.20	<0.20	4.20	3.95	3.65	o-terphenyl
perylene	<0.20	<0.20	<0.20	1.30	1.23	1.12	o-terphenyl
indeno[1,2,3-cd]pyrene	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	o-terphenyl
benzo[ghi]perylene	<0.20	<0.20	<0.20	2.31	1.96	1.79	o-terphenyl
dibenz[a,h]anthracene	<0.20	<0.20	<0.20	1.24	1.21	1.10	o-terphenyl
cis/trans-decalin	NA	NA	NA	NA	NA	NA	NA
dibenzofuran	<0.20	<0.20	<0.20	26.4	25.1	23.9	o-terphenyl
retene	NA	NA	NA	NA	NA	NA	NA
benzothiophene	NA	NA	NA	NA	NA	NA	NA
dibenzothiophene	0.34	0.35	0.34	50.8	47.8	46.1	o-terphenyl
Naphthobenzothiophene	NA	NA	NA	NA	NA	NA	NA

Report on Toxicity

Charles Miller
Tulane University
New Orleans, LA 70112

Aryl hydrocarbon receptor activation by HIE samples

I set up experiments to examine dimethylsulfoxide (DMSO) and aqueous extracts of fresh (HIE sample SRM 2779) and weathered crude (HIE sample SRM 2777) for human aryl hydrocarbon receptor (AhR) activity. This AhR bioassay has been described previously and has been used by a number of investigators (Fox *et al.* 2008).

A fresh culture of the AhR reporter yeast strain (YCM3) was prepared at a 1:50 dilution in synthetic galactose medium lacking tryptophan as described previously. 200 µl cultures were set up in 96 wells and then treated with 2 µl of each sample (performed in triplicate). A series of dilutions was made for each oil sample. The first dilution was made by taking 100 µl oil sample and mixing it into 900 µl pure water or dimethylsulfoxide (DMSO) on a vortex at the "high" setting for approximately 2 minutes. Dilutions (starting with the highest 3-fold dilution into water or DMSO) result in final dilutions to the cells at doses of 1xE-3, 3.3xE-4, 1xE-4, 3.3xE-5, 1xE-5, 3.3xE-6, 1xE-6, and 3.3xE-7 of each original oil sample. These dilutions assume that the oil completely mixed with the solvent, which is clearly not the case. Only a tiny amount of the oil mixed with the solvent and rapidly formed a separated layer at the top of the tube shortly after vortexing was completed. Some oil material did enter the DMSO and water because the solutions took on a faint brown color after vortexing. The amount of oil that entered the solutions is estimated to be 5% or less of the input oil.

The well-known AhR ligand β-naphthoflavone was used as a positive control at a maximally activating concentration of 1 µmol/L. Negative controls contained solvent alone.

Cultures were treated and incubated at 30^{o} C at ~ 4:30 pm and harvested for assessment (lacZ reporter assays) after 18 h.

The highest dose of the DMSO soluble fractions of oil retarded growth and/or killed some of the yeast cells (cytotoxicity), causing about a 3- to 4-fold decrease in culture density at the highest treatment. (Figure A1). The oil components that partitioned into water were not toxic at the concentrations tested.

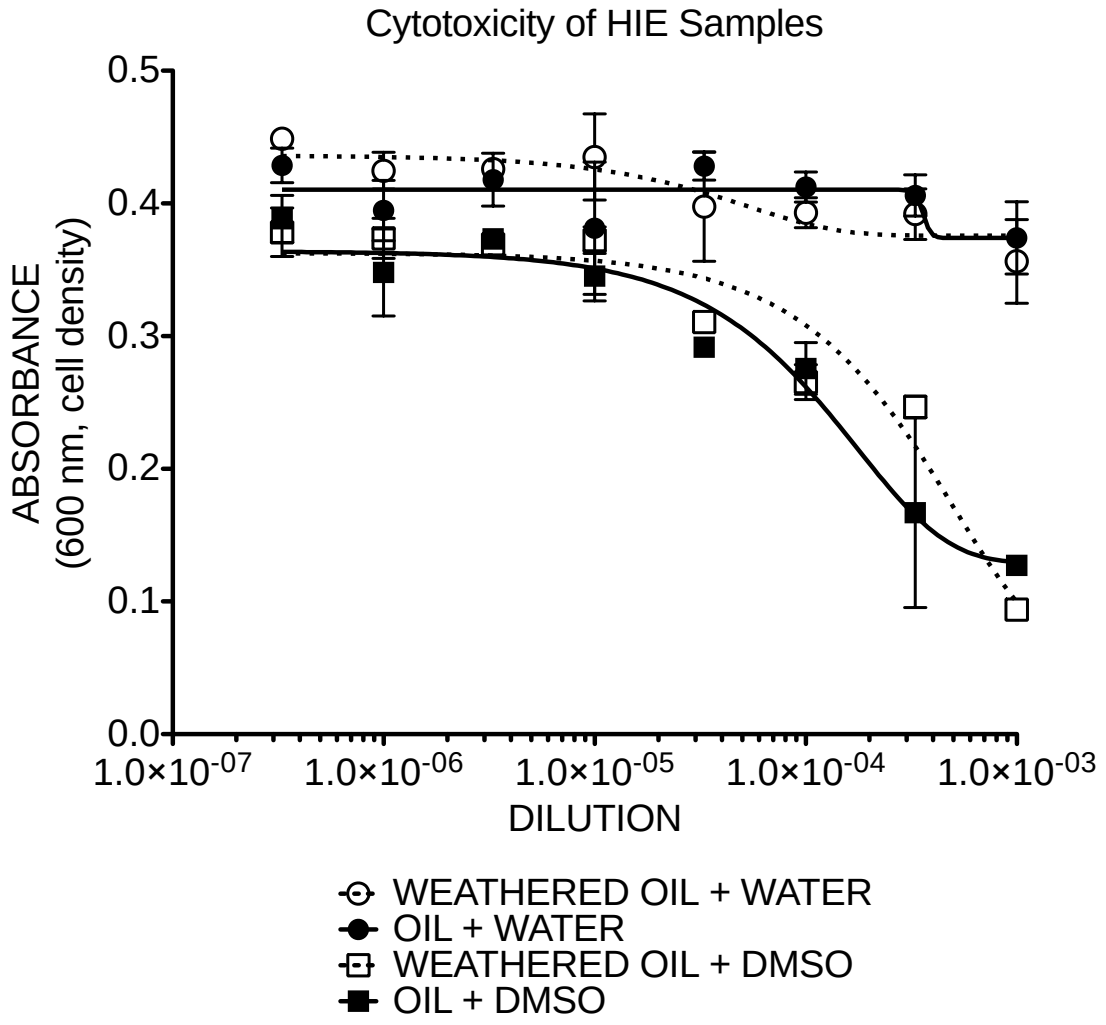
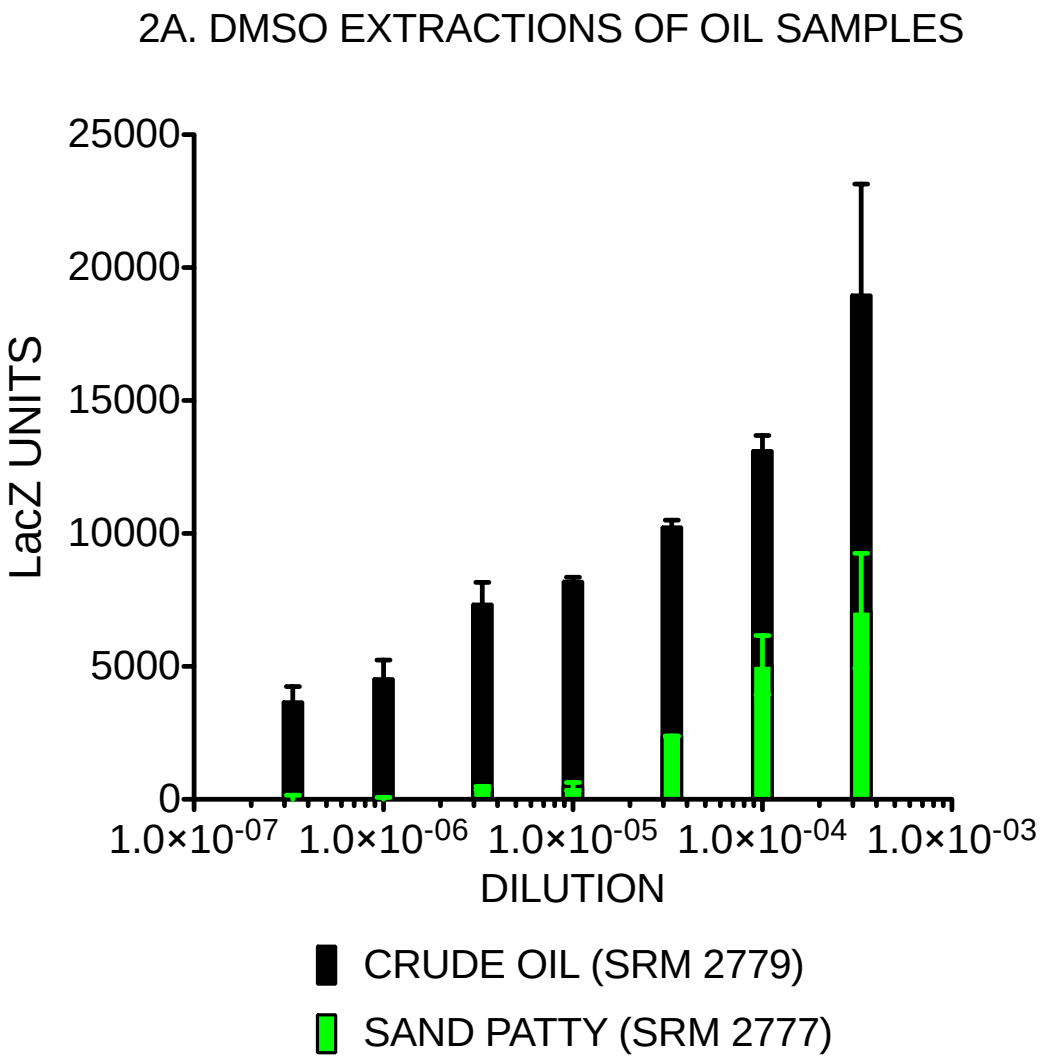


Figure A1. Cytotoxicity of HIE Samples to YCM3 Yeast Strain. Growth inhibition and/or cell killing, as measured by reduced absorbance (reflecting cell density), was assessed after 18 h exposure. The samples dissolved in DMSO were significantly more affected by the oil samples than were those dissolved in water ($p<0.05$ using ANOVA with Tukey's multi-comparison test.) Non-linear curve fitting and statistics were performed using Prism software version 5.0 (Graphpad Software, Inc.). Error bars represents ± one standard deviation.

The lacZ gene reporter assays that accompanied the cytotoxicity assays revealed that all four oil fractions had compounds that activated the AhR pathway in the YCM3 yeast strain. The fresh crude oil sample that was extracted with DMSO was the most potent inducer in the study (Figure A2A and A2B). The DMSO extract of the neat crude oil sample (SRM2997) was approximately 100 times more effective than the other extracts, indicating that it contains a greater concentration of ligands, more potent ligands, or a combination thereof. The other extracts (DMSO extract of weathered sand patty, SRM 2777) and the aqueous extracts of SRM 2997 and 2777 were similar in the ability to

activate AhR signaling in the bioassay. Note the change in scale on the Y-axis between Figures A2A and A2B.



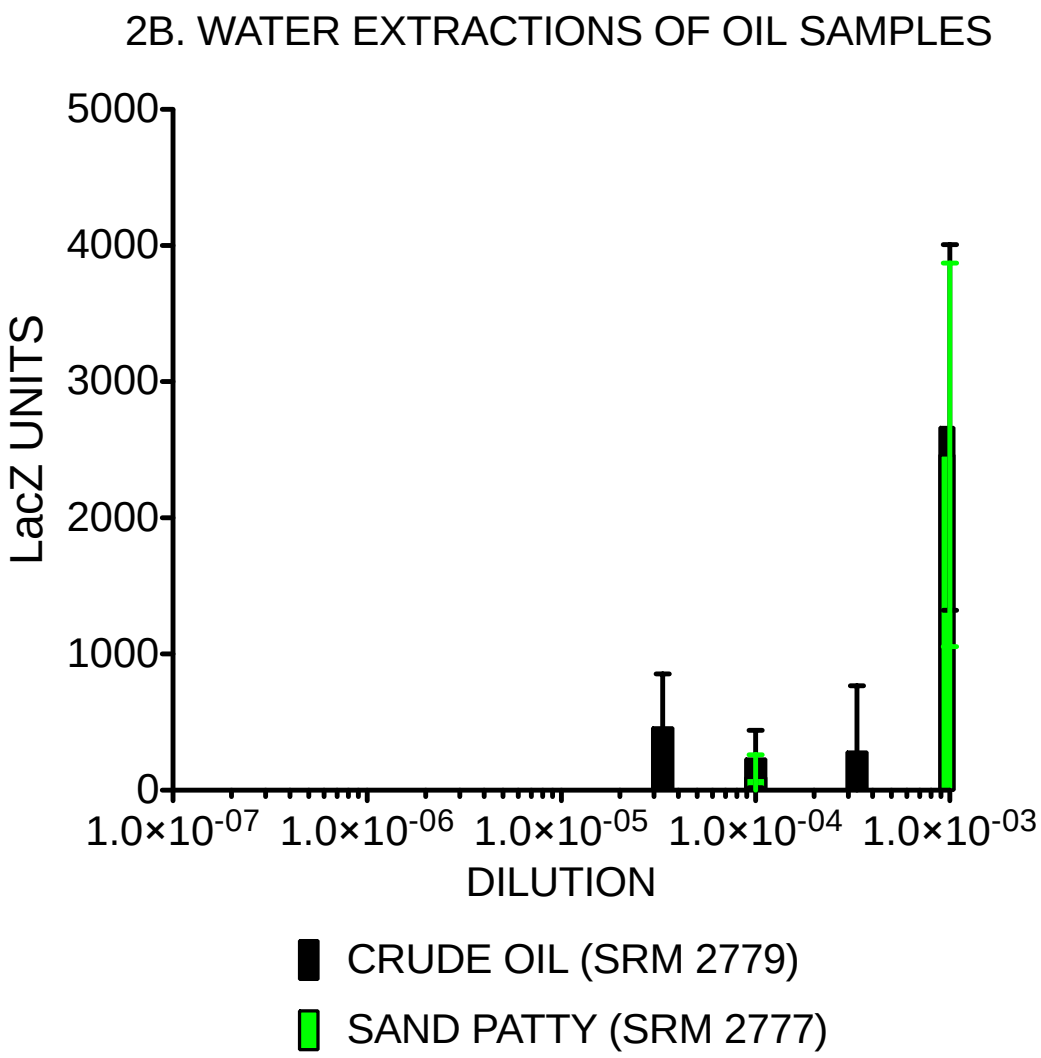


Figure A2. Bar graphs reflect induction of AhR directed expression of the lacZ reporter gene in response to the oil fractions. In 2A, the DMSO signaling dose-responses of the diluted fractions are compared, with the fresh crude fraction depicted in black and the aged crude (from a sand patty) shown in green bars (error bars indicate standard deviation). The graph in 2B shows AhR driven lacZ reporter gene expression for diluted aqueous extracts of the fresh and aged crude samples.

Conclusions: Both fresh and aged crude contain a compound, or more likely, compounds, that activate AhR signaling. AhR signaling is key to the toxic actions of chemicals such as TCDD (dioxin) and multi-ringed PAHs such as benzo[α]pyrene, so these results could be significant in that regard. The cytotoxic activity detected in the samples (Fig. 1) did not strictly correlate with the ability to activate AhR signaling (Fig. 2), suggesting that different chemicals are responsible for these two effects. The bioactive compound(s) was most apparent in the DMSO extract of the fresh crude sample (SRM2779). The ability to detect AhR signaling was diminished after time and /or weathering since the DMSO extract of sample 2777 had muck less activity. The aqueous extracts of samples 2779 and

2777 yielded similar (lower) levels of bioactivity in the AhR signaling bioassays. Perhaps only a small subset of the AhR ligand(s) in these samples is water-soluble. These results might have implications for ecotoxicity since the ligand activated AhR appeared, evolutionarily speaking, with the fishes and other vertebrates. AhR-active compounds in the aqueous phase could cause toxicity to vertebrates that encounter this contaminated environmental medium.

Issues in working with these samples: The volatile components of SRM 2779 and candidate SRM 2777 are an issue. I observed reductions in the apparent volumes of the samples over time (e.g., I am losing volatiles over time after opening the samples). There was a prominent loss of volume (toluene loss) for candidate 2777. This loss of volume will alter the concentrations and composition of the oil components. As noted above, the "dilutions" shown in the graphs are large overestimates of the actual oil components added into the assays. This is because the oil samples did not dissolve well in DMSO or in water. This is why I presented the data as dilutions rather than ug/L or some other quantitative units. In short, I do not actually know how much oil I was adding into the assays, but I was able to detect relatively strong AhR signaling. This means that some compounds were getting into the DMSO and into the water. The compound(s) subsequently reached the interior of the yeast cell to activate AhR signaling. It will be interesting to learn the identity of the bioactive compound(s) that is detected in this bioassay – especially the one(s) that is water-soluble.

Reference

Fox, J.E., Burrow, M.E., McLachlan J.A., Miller, C.A. (2008) Detecting ligands and dissecting nuclear receptor-signaling pathways using recombinant strains of the yeast *Saccharomyces cerevisiae.* Nature Protocols, 3, 637-645.

Appendix 5

Report on interfacial tension

Stephanie M. Kirby, Shelley L. Anna, and Lynn M. Walker
Department of Chemical Engineering, Center for Complex Fluids Engineering, Carnegie Mellon University, Pittsburgh, PA 15213

Abstract
A microtensiometer is used to measure the dynamic interfacial tension of two samples, SRM 2779 and Candidate SRM 2777 (Box 5, Ampule 10), against simulated sea water and deionized water. Measurements are taken at room temperature. The interfacial tension values of SRM 2779 are 10-15mN/m higher than the values of candidate SRM 2777 throughout the measurement. Equilibrium interfacial tension values could not reliably be obtained due to continued decreases in the interfacial tension values even at long experimental times.

Methodology
A microtensiometer is used to measure the dynamic interfacial tension of the oil/deionized water and oil/simulated sea water interfaces[1]. The microtensiometer consists of an Omegadyne PX409-001GV pressure transducer in line with a capillary filled with the oil sample, held at a constant pressure by a pressure head. A 3D-printed thermoplastic cell has been designed to hold the capillary, which is submerged in an aqueous solution reservoir, and imaged on a Nikon T-300 inverted light microscope. The oil forms a spherical cap at the tip of the capillary. The radius of the cap is measured in real time with the pressure jump across the interface to determine the instantaneous interfacial tension, $\gamma(t)$, from the Laplace equation for a spherical cap

$$\gamma(t) = (P_1(t) - P_2)\frac{R(t)}{2} \quad \gamma(t) = (P_1(t) - P_2)\frac{R(t)}{2}$$

where P_1 is the pressure inside the oil cap, P_2 is the hydrostatic pressure of the aqueous solution at the capillary, and R is the measured interface radius.

The capillaries are purchased from World Precision Instruments, Inc. (Sarasota, FL) with dimensions of i.d.=0.75mm, o.d.=1mm, and L=150mm, and are pulled to a tip radius of 44μm using custom settings on a PMP-100 capillary puller (Micro Data Instrument Inc., South Plainfield, NJ). To ensure that the three phase contact line remains pinned at the tip of the capillary, the interiors of the capillaries are acid washed and coated with hydrophobic Dynasylan® SIVOCLEAR (Evonik Industries, Essen, Germany). Capillaries are rinsed with deionized water and acetone and are baked at 60 ^{o}C for 30 min prior to use.

Deionized water (DI) is prepared with a Barnstead Ultrapure water purification system to 18.2MΩ·cm resistivity. Simulated sea water (SSW) is prepared with DI water and added salts of sodium chloride at 430mM, magnesium chloride at 50mM, and sodium sulfate at 35mM.

Results
Figure A4 shows the dynamic interfacial tension of SRM 2779 and candidate SRM 2777 in simulated sea water. The interfacial tension for both samples decreases over time. The equilibrium interfacial tension value of candidate SRM 2777 approaches (13.2 ± 0.5) mN/m at long times. The equilibrium interfacial tension value of SRM 2779 could not be reliably obtained due to long equilibration times.

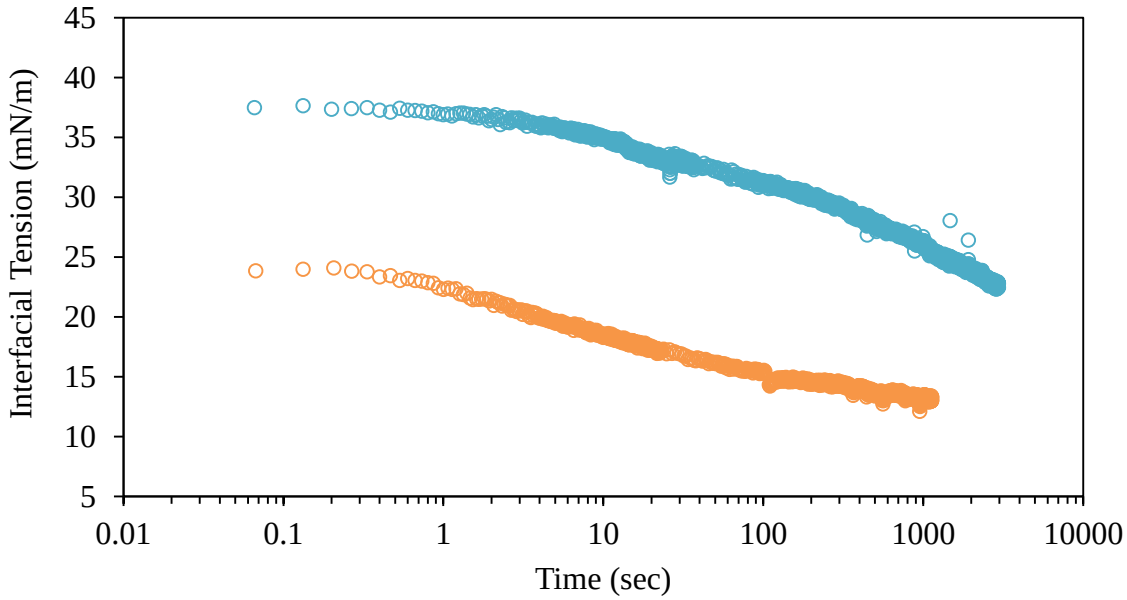


Figure A4: Dynamic interfacial tension of SRM 2779 (blue) and candidate SRM 2777 (green) in simulated sea water at 23.7ºC.

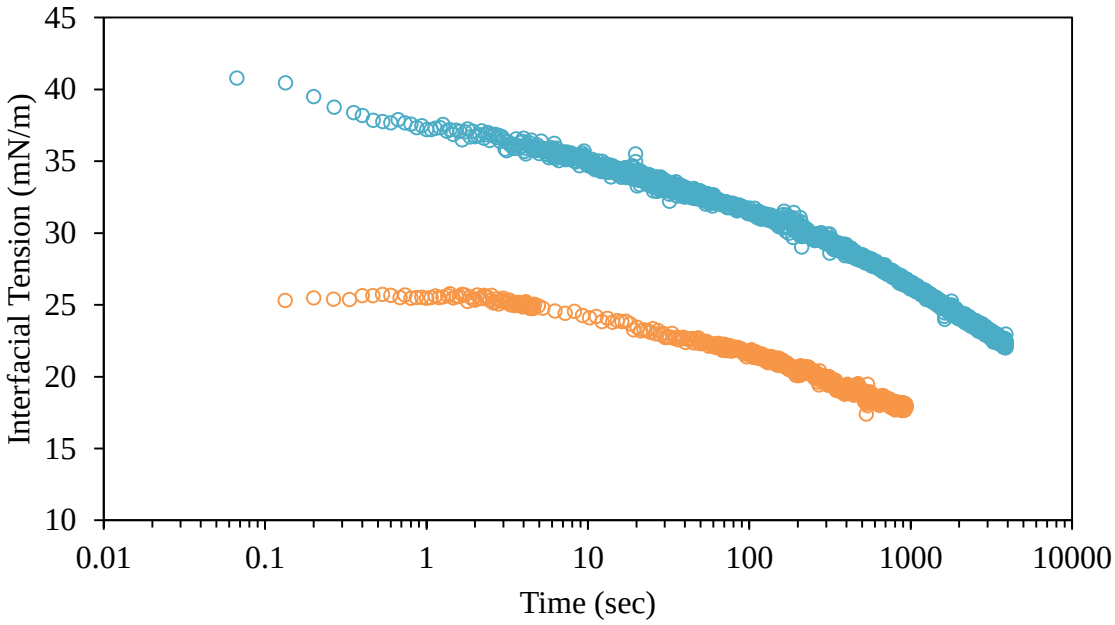


Figure A5: Dynamic interfacial tension of SRM 2779 (blue) and candidate SRM 2777 (green) in deionized water at 23.7ºC.

Figure A5 shows the dynamic interfacial tension of SRM 2779 and SRM 2777 in deionized water. As in simulated sea water, the interfacial tension for both samples decreases over time. Equilibrium interfacial tension values could not be determined.

Reference

Alvarez, N.J., Walker, L.M., Anna, S.L. (2010) A Microtensiometer to Probe the Effect of Radius of Curvature on Surfactant Transport to a Spherical Interface. Langmuir 26, 13310–13319.