NOAA Technical Memorandum NMFS-NWFSC-147

Quality Assurance Plan for Analyses of Environmental Samples

for Polycyclic Aromatic Hydrocarbons, Persistent Organic Pollutants, Dioctyl Sulfosuccinate, Estrogenic Compounds, Steroids, Hydroxylated Polycyclic Aromatic Hydrocarbons, Stable Isotope Ratios, and Lipid Classes

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U.S. DEPARTMENT OF COMMERCE
National Oceanic and Atmospheric Administration
National Marine Fisheries Service
Northwest Fisheries Science Center

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Abbreviations

$\delta^{13}C$	the difference in ratio of carbon isotope ^{13}C to carbon isotope ^{12}C in a sample relative to that in the Pee Dee Belemnite standard, in units of per mil (‰), i.e., $\delta^{13}C = \{[(^{13}C_{sample}/^{12}C_{sample})/(^{13}C_{standard}/^{12}C_{standard})] - 1\}$
$\delta^{15}N$	the difference in ratio of nitrogen isotope ^{15}N to nitrogen isotope ^{14}N in a sample relative to atmospheric nitrogen (used as standard), in units of per mil (‰), i.e., $\delta^{15}N = \{[(^{15}N_{sample}/^{14}N_{sample})/(^{15}N_{standard}/^{14}N_{standard})] - 1\}$
CFR	Code of Federal Regulations
CO_2	carbon dioxide
COC	chain of custody
CCV	continuing calibration verification
DDD	dichlorodiphenyldichloroethylene
DDE	dichlorodiphenyldichloroethane
DDT	dichlorodiphenyltrichloroethane
DQO	data quality objectives
DOSS	dioctyl sulfosuccinate
EA/IRMS	elemental analysis/isotope ratio mass spectrometry
EAP	Ecosystem Analysis Program (NWFSC)
ECP	Environmental Chemistry Program (NWFSC)
EPA	Environmental Protection Agency
GC/MS	gas chromatography/quadrupole mass spectrometry
GLP	good laboratory practices
IAEA	International Atomic Energy Agency
IRM	internal reference material
LC-MS/MS	liquid chromatography/triple-quadrupole mass spectrometry
LOQ	limit of quantitation
mV	millivolt
N_2	nitrogen
NIST	National Institute of Standards and Technology
NMFS	National Marine Fisheries Service (NOAA)
NOAA	National Oceanic and Atmospheric Administration
NWFSC	Northwest Fisheries Science Center (NMFS)
OHPAH	hydroxylated polycyclic aromatic hydrocarbon
PAH	polycyclic aromatic hydrocarbon
PBDE	polybrominated diphenyl ether
PCB	polychlorinated biphenyl
POP	persistent organic pollutant
QA	quality assurance
QAP	quality assurance plan
RSD	relative standard deviation
SRM	Standard Reference Material
SOP	standard operating procedure
TLC/FID	thin-layer chromatography/flame ionization detection
USGS	United States Geological Survey
Wt%C	percent carbon by weight
Wt%N	percent nitrogen by weight

Executive Summary

This technical memorandum serves as the Quality Assurance Plan (QAP) for analyses of biota, water, and sediment samples for selected contaminants and biological compounds by the Environmental Chemistry Program (ECP) within the Environmental and Fisheries Sciences Division, in collaboration with the Ecosystem Analysis Program (EAP) within the Fish Ecology Division, at the Northwest Fisheries Science Center (NWFSC). This QAP describes NWFSC's quality objectives, as well as policies implemented for achieving the objectives and procedures for assessing the completeness of the objectives. It also provides guidelines for monitoring and documenting the quality of analyses so that a desired level of performance can be demonstrated and maintained. These guidelines are based on protocols established previously for specific projects under the National Oceanic and Atmospheric Administration (NOAA) and the Environmental Protection Agency (EPA), and have been adapted to new types of analyses and current technologies. This document updates and supersedes NOAA Technical Memorandum NMFS-NWFSC-77 (Sloan et al. 2006).

Acknowledgments

We thank past Environmental Chemistry Program chemists for their expert contributions, in particular Donald W. Brown and Margaret M. Krahn. We would also like to thank John R. Kucklick of the National Institute of Standards and Technology for his thoughtful and timely review of this document.

1. Introduction

The Environmental Chemistry Program (ECP) within the Environmental and Fisheries Sciences Division, in collaboration with the Ecosystem Analysis Program (EAP) within the Fish Ecology Division, at the Northwest Fisheries Science Center has developed a Quality Assurance Plan (QAP) for analyses of environmental and experimental samples for selected contaminants and biological compounds. Many of the requirements described in the QAP, this technical memorandum, are based on protocols that were originally developed for programs under the National Oceanic and Atmospheric Administration (NOAA; National Status and Trends Program and Natural Resource Damage Assessment) and the Environmental Protection Agency (EPA; Puget Sound Estuary Program and Environmental Monitoring and Assessment Program—Estuaries). ECP continues to measure low-level (i.e., low parts per billion) concentrations of polycyclic aromatic hydrocarbons (PAHs) and persistent organic pollutants (POPs) in biota, water and sediments using gas chromatography/quadrupole mass spectrometry (GC/MS; Sloan et al. 2014), as well as lipid classes using thin-layer chromatography/flame ionization detection (TLC/FID; Ylitalo et al. 2005). ECP and EAP also continue to measure stable isotope ratios using elemental analysis/isotope ratio mass spectrometry (EA/IRMS; Herman et al. 2005, Krahn et al. 2007). More recently, ECP has expanded its studies to include analyses of samples using liquid chromatography/triple-quadrupole mass spectrometry (LC-MS/MS) for other classes of compounds, including dioctyl sulfosuccinate (DOSS; Flurer et al. 2010), estrogenic compounds (da Silva et al. 2013), steroids (Guzman et al. 2015), and hydroxylated polycyclic aromatic hydrocarbons (OHPAHs; Ylitalo et al. 2017).

The requirements specified in this QAP are designed to monitor the performance of the measurement systems to maintain quality, and to document the extent to which the reported data are sufficiently complete, comparable, representative, unbiased, and precise to be suitable for their intended use. This QAP will be adapted to specific projects as needed and will be revised appropriately as changes are made to the NWFSC quality assurance program.

The term "field samples" in this technical memorandum refers to samples collected from the environment or laboratory experiments (e.g., plant or animal tissues, plasma, water, or sediments). "Quality assurance (QA) samples" refers to samples that are analyzed to generate data necessary for evaluating and documenting the performance of the measurement systems. QA samples are analyzed with field samples within a batch (i.e., a group of field samples and QA samples analyzed concurrently) using the same method. The term "samples" refers to field samples and QA samples. The established methods used to measure the various groups of analytes (i.e., PAHs, POPs, DOSS, estrogenic compounds, steroids, stable isotope ratios, or lipids) are documented separately and are available in the form of standard operating procedures (SOPs). In addition, the collection of field samples will be addressed in a separate document (e.g., a sampling plan), when appropriate.

2. Project Description

The description of a specific project is to be provided before the analyses begin in order to ensure that the project requirements are known and can be met. The project description may include the following information:

- The principal investigator(s).
- The project's objectives, questions, or issues.
- The type, quantity, and quality of analyses required.
- The sample matrix and the sample mass or volume available for the analyses.
- A time frame for receipt of field samples, analyses, and data delivery.
- How the results must be formatted and reported.
- Who will use the data.
- What decision(s) will be made from the information obtained.

A project proposal that includes the information above in a project description may be used for this purpose.

3. Laboratory Organization and Responsibilities

The analyses for the project will be performed primarily by personnel from the Environmental and Fisheries Sciences Division of the Northwest Fisheries Science Center.

3.1. Project Leader

Gina Ylitalo, ECP manager, is responsible for ensuring that the analytical data quality objectives (DQOs) for the project are met and that staff resources are available to fulfill laboratory analytcal requirements. Her contact information is:

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3.2. Analytical Laboratory Project Managers

Jennie Bolton is responsible for ensuring that the analytical results by GC/MS and TLC/FID meet QA criteria and the stated objectives. Her contact information is:

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Denis da Silva is responsible for ensuring that the analytical results by LC-MS/MS meet QA criteria and the stated objectives. His contact information is:

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Paul Chittaro is responsible for ensuring that the analytical results by EA/IRMS meet QA criteria and the stated objectives. His contact information is:

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4. Sample and Data Handling

Sample handling procedures may depend on the matrix and the analytes of concern. The analytes that can be determined by the ECP laboratory are DOSS and the groups presented in Tables 1–7, and gravimetric percent dry weight or percent lipid weight may be requested for samples analyzed for PAHs or POPs. The analytes within each group are measured concurrently. Sampling procedures, including field sample collection, preservation, storage, and documentation, are addressed in detail elsewhere (e.g., in a sampling and analysis plan). In general, samples and data are handled according to the following steps:

1. Inventory all field samples received.
2. Store the field samples in freezers prior to analyses.
3. Record the field sample identification, information, and storage location in a sample database.
4. Schedule the batches of samples to be analyzed and prepare tracking paperwork.
5. Analyze the batches of samples for the specified analytes.
6. Process the raw sample data and perform calculations to produce formatted data.
7. Review the processed and formatted data.
8. Report the reviewed data.
9. Archive all remaining field sample material in freezers.
10. Archive the raw and processed sample data.

Chain-of-custody (COC) procedures (Section 4.5), if required by the project, will be followed for all field samples throughout the sampling and analytical process.

4.1. Intralaboratory Sample Transfer

The laboratory analysts will maintain a laboratory sample-tracking record, similar to a COC record, that will follow each batch of samples through all stages of laboratory processing. The sample-tracking record will show the date of sample extraction or preparation and sample analysis, as well as the names or initials of individuals responsible for each procedure.

4.2. Sample Archiving

All unanalyzed field samples and unused sample aliquots or extracts will be held by the laboratory in a manner to preserve sample integrity (e.g., at -20°C to -80°C) for up to one year or a specified time period after the data have been validated, as agreed upon by the project leader and the principal investigator(s). All freezers containing samples are monitored for temperature and have an alarm system (also see Section 4.5).

4.3. Laboratory Records

Processed data will be generated and maintained in electronic files with frequent backup and storage onto a hard drive as well as onto tape for offsite storage. Final analytical results will be maintained in electronic database files on a server maintained by IT, with frequent file backups and weekly backups onto tape for offsite storage.

Laboratory log books will be maintained for each of the following:

- Sample preparation.
- Standard preparation.
- Use and maintenance of the accelerated solvent extractors.
- Use and maintenance of the size-exclusion liquid chromatograph.
- Use and maintenance of the GC/MS systems.
- Use and maintenance of the TLC/FID system.
- Use and maintenance of the EA/IRMS system.
- Use and maintenance of the LC-MS/MS systems.

Logbook entries are dated and signed. Filled logbooks are archived.

4.4. Data and Data Documentation

The laboratory will provide data tables and QA documentation suitable for QA assessment. All original data and data documentation developed by the laboratory for a given data package will be kept by the laboratory for at least one year after the data have been validated and reported; and, if requested, the data will be stored in the collection format for up to five years.

4.5. Chain of Custody

When COC records are required, any transfer or movement of samples will use the COC procedures described here. Each field sample will be assigned a unique identification number and will have a separate entry on the COC record. COC records will be completed with indelible ink. A sample is considered "in custody" if any of the following apply:

- It is in the custodian's actual possession or view.
- It is retained in a secured place (under lock) with restricted access.
- It is placed in a container and secured with an official seal such that the sample cannot be reached without breaking the seal.

Field samples are kept in the custody of the designated sampling or field personnel or both until shipment or other transfer. Field samples will be properly packaged for shipment near the sampling area and dispatched to the appropriate party. The original signed and dated COC record will accompany the sample(s); the sample transferor retains a copy of the COC record. All shipments will comply with U.S. Department of Transportation regulations (49 CFR, parts 172 and 173) and, for air shipments, the International Air Transport Association Dangerous Goods Regulations. Immediately upon receipt of shipped samples or subsequently transferred samples, the recipient will review the samples for condition and consistency with the accompanying COC record before signing and dating the COC record. Sample condition(s) will be noted on the original COC sheet at this time. If there are any discrepancies between the COC record and the received sample, the recipient will contact the sample transferor immediately.

5. Assessment of Data Quality

The overall QA objectives are to ensure production of analytical data of known and acceptable quality. The quality of data required is specified in qualitative and quantitative DQOs. These objectives are usually expressed in terms of precision, accuracy, representativeness, completeness, comparability, and sensitivity. Data quality is assessed by applying the specific acceptance criteria to QA elements (Section 6).

5.1. Accuracy

Accuracy is the degree of agreement of a measurement with an accepted (e.g., certified or published) value. Laboratory accuracy will be evaluated through the use of Standard Reference Materials (SRMs), or internal reference materials (IRMs) when available (Section 6.5.3); otherwise, spiked matrix samples will be used to evaluate accuracy (Section 6.5.7). For a particular SRM, accuracy for an analyte will be assessed by comparing the measured value to a value accepted (i.e., certified) by the certifying agency (i.e., the National Institute of Standards and Technology [NIST]). For IRMs, the measured value will be compared to the reference value. For spiked matrix samples, the measured value will be compared to the expected value based on the amount of analyte spiked into the sample prior to extraction.

5.2. Precision

Precision is the variability among individual measurements of the same property under prescribed similar conditions (e.g., replicate measurements of a particular analyte in one sample). Precision is evaluated using laboratory replicates of field samples and SRMs, or IRMs when available (Section 6.5.6). The use of SRMs or IRMs allows for the long-term measurement of precision, whereas replicates of field samples can indicate the precision for the analysis of a particular batch of samples. However, reproducibility, and therefore precision, is also affected by sample collection procedures and matrix variations (e.g., homogeneity). In addition, it is recognized that, typically, precision erodes as the lower limit of detection is approached.

Precision will be expressed as the relative standard deviation (RSD) for three or more repeated measurements. When only two replicate samples are analyzed, precision will be expressed as the percent difference.

5.3. Representativeness

Representativeness expresses the degree to which data accurately and precisely represent a defined or particular characteristic of a population, parameter variations at a sampling point, a processed condition, or an environmental condition. Representativeness is a qualitative parameter that depends upon the proper design of the sampling program (as addressed in a sampling plan) and proper laboratory protocol. Evaluation of the data for SRMs, IRMs, replicate field samples, and spiked matrix samples (Sections 6.5.3, 6.5.6, and 6.5.7) may provide an assessment of the representativeness of the analyte measurements for field samples, but not for the representativeness of the field samples for the population, sample site, or environmental condition.

5.4. Comparability

Comparability is a qualitative parameter expressing the confidence with which one data set can be compared to another, as well as the potential for combining the data with those generated outside of the present project. Comparability of the analytical data is established through the use of:

- Program-defined analytical methodology, quantitation limits, reporting units, and quality assurance measurements.
- NIST-traceable (or other) calibration standards and SRMs, when available.
- Participation in interlaboratory comparison exercises (Section 6.3).

5.5. Completeness

Completeness is defined as the percentage of measured data that meet the DQOs as determined by the QA review process. A typical analytical completeness goal for a project is 90% (i.e., no more than 10% of the analytical data will be qualified as unreliable, meaning they do not meet the DQOs). Data qualified as "estimated" as a result of QA criteria not being met will be considered usable.

5.6. Sensitivity

Sensitivity refers to the capability of a method to measure the analytes at low levels. For each method, criteria are established for the minimum concentrations that can be measured with known and acceptable quality (Section 6.4).

6. Quality Assurance Procedures

Prior to the analysis of samples, the laboratory will specify written protocols for the analytical methods to be used and will identify the analytes to be quantified. If a method is significantly modified, the written analytical protocol will be amended. The QA procedures are presented with each analytical method and are applied to each batch. The laboratory must also demonstrate its continued proficiency by participation in refereed intercomparison exercises, as available. The QA procedures and acceptance criteria presented in this document may be specific to the protocols and instrumentation currently in use by ECP and EAP.

6.1. Laboratory Operations

The laboratory will have the appropriate facilities to store and prepare samples and the appropriate instrumentation and staff to provide data of the required quality within the time period indicated. The laboratory is expected to conduct operations using good laboratory practices (GLP), including:

- Performing scheduled maintenance of analytical balances, laboratory equipment, and instrumentation.
- Validating instrument calibration standards.
- Recording pertinent analytical data in logbooks with each entry signed/dated by the analyst.

Personnel should be well versed in GLP, including standard safety procedures. It is the responsibility of the project manager to ensure that all laboratory personnel complete mandatory safety training. The laboratory is responsible for following the NWFSC Chemical Hygiene Plan, in compliance with the Occupational Safety and Health Administration or equivalent state or local regulations. Proper procedures for safe storage, handling, and disposal of chemicals should be followed at all times; each chemical should be treated appropriately based on its potential health hazard. The NWFSC Safety and Environmental Compliance Officer should be consulted as needed.

6.2. Quality Assurance Documentation

All participants in a project must have the current version of the QAP. In addition, the following documents and information must be current and available to all laboratory personnel participating in the processing of samples:

- Laboratory SOPs—the detailed instructions for performing routine laboratory procedures.
- Instrument performance information—for example, information on instrument calibration (Section 6.5.1), range of response, and stability.
- QA information—QA data tables will be developed and maintained throughout the project for all appropriate analyses and measurements, such as results for instrument continuing calibration verification (Section 6.5.2), reference materials (Section 6.5.3), surrogate (internal standard) recovery (Section 6.5.4), method blanks (Section 6.5.5), sample replicates (Section 6.5.6), and spiked matrix samples (Section 6.5.7).

The SOPs used in the analyses of samples depend on the project and the analytes to be determined (e.g., DOSS and the analyte groups listed in Tables 1–7). Documentation of all analytical methods will accompany the analytical results.

6.3. Participation in Intercomparison Exercises

The analytical laboratory is required to participate, whenever possible, in applicable intercomparison exercises managed by the NIST, the International Atomic Energy Agency (IAEA), or other entities that conduct these exercises. A variety of samples, including accuracy-based solutions, sample extracts, and representative matrices (e.g., tissue or sediment samples), are used in these exercises, which may take place once a year. Acceptance criteria are specified by the entity that conducts the exercise. Upon review of the results, if the laboratory fails to achieve acceptable performance, it will be required to undertake appropriate corrective actions. This section applies only to analyses for PAHs (Table 1), POPs (Table 2), and stable isotope ratios (Table 10); it does not apply to analyses for DOSS, estrogenic compounds (Table 3), steroids (Table 4), OHPAHs (Table 5), or lipid classes (Table 7), because formal intercomparison exercises by NIST or IAEA have not been conducted for these analytes.

6.4. Quantitation Range

For each GC/MS method (for PAHs and POPs) and LC-MS/MS method (for DOSS, estrogenic compounds, steroids, and OHPAHs), the lower limit of quantitation (LOQ) for a given analyte in a specific sample is the concentration that would be calculated if that analyte had a detector's response area equal to its area in the lowest-level calibration standard used in the instrument calibration. When an analyte is not detected in a sample or it has a response area that is smaller than its area in the lowest-level calibration standard used, the concentration of the analyte in that sample is reported to be less than the value of its LOQ. The treatment of out-of-range results depends on the project. When an analyte in a sample has a response area that is larger than its area in the highest-level calibration standard used in the calibration, the sample is a) diluted appropriately and then reanalyzed in order for the analyte's area to be within the range of the analyte's areas in the calibration standards, or b) the analyte amount may be calculated using the relative response factor of that analyte (i.e., relative to the surrogate standard's response factor) in the highest-level calibration standard used, and the concentration is footnoted as exceeding the calibration range and is therefore an estimate.

For the EA/IRMS method, the $\delta^{13}C$ and $\delta^{15}N$ values can be affected if the MS responses for the CO_2 and N_2 peaks are too small or too large. For field samples, results are reported if peak amplitudes for N_2 (mass 28 and 29) and CO_2 (mass 44 and 46) are between 500 and 12,000 mV. Samples that do not meet the above criteria are reanalyzed. If peak amplitudes are near their limits, the accuracy of the result is less certain. Sample results are footnoted to be used with caution if the peak amplitudes for N_2 (mass 28 or 29) or CO_2 (mass 44 or 46) are between 9,000 and 12,000 mV or between 500 and 750 mV. The corresponding delta and weight percentage (Wt%) measurements will not be reported if the sample's peak amplitude for mass 28 or mass 29 is >12,000 mV or if its peak amplitude for mass 44 or mass 46 is <500 mV.

For the TLC/FID method (for lipid classes), the lower LOQ for a given analyte in a specific sample is the concentration that would be calculated if that analyte had a detector's response area equal to its area in the lowest-level calibration standard used in the instrument calibration. When an analyte is not detected in a sample or it has a response area that is smaller than its area in the lowest-level calibration standard used, the concentration of the analyte in that sample is considered to be zero when calculating the lipid class proportions and percent lipid. When an analyte in a sample has a response area that is larger than its area in the highest-level calibration standard used in the calibration, the sample is diluted appropriately and then reanalyzed in order for the analyte's area to be within the range of the analyte's areas in the calibration standards.

6.5. Quality Assurance Criteria for the Analytical Measurements

QA elements (e.g., Sections 6.5.1–6.5.7) are included in the analyses of every batch of samples. Acceptance criteria and required minimum frequency of analysis for each QA element are summarized in Tables 8–11. Laboratory personnel review the results for the various QA elements immediately following the analysis of each sample batch. These results are then used to determine when acceptance criteria have not been met and which corrective actions are required before analyses may proceed.

6.5.1. Instrument Calibration

Calibration for each method is established before or during sample analyses at the frequencies specified in Tables 8–11, and calibration documentation is archived with the sample data.

The GC/MS methods require at least five concentration levels of analyte calibration standards for analyte quantitation using point-to point calibration. Each surrogate standard in the calibration standards must have an RSD of its response factors (response area divided by the concentration) that is ≤15%.

The LC-MS/MS methods require at least five concentration levels of analyte calibration standards for analyte quantitation using a Wagner regression curve. The measured concentrations of each analyte in each calibration standard (measured using the calibration curve) must be 70–130% of the actual concentration.

The TLC/FID methods require at least three analyses of each of six concentration levels of analyte calibration standards for analyte quantitation using point-to point calibration based on the average response area of the three or more analyses for each concentration level. Each analyte must have an r^2 value of at least 0.95 for its averaged areas in the middle four concentration levels of calibration standards.

The EA/IRMS method requires at least two delta levels of calibration standards (histidine and aspartic acid, prepared in-house) for analyte ratio measurements. The $\delta^{15}N$ and $\delta^{13}C$ values for the calibration standards are assigned using primary standard materials from IAEA (IAEA CH-7) and the United States Geological Survey (USGS 40 and USGS 41a). $\delta^{15}N$ and $\delta^{13}C$ must be calculated using linear calibration and at least five replicate analyses of each calibration standard,

including at least one of each at the beginning and end of the batch after extreme points, if any, are identified and excluded during the continuing calibration verification (Section 6.5.2). The $\delta^{15}N$ results and $\delta^{13}C$ results for the included replicate analyses of the calibration standards versus the respective assigned δ values must have a correlation of $r > 0.9900$; if this criterion is not met, then the samples in the batch must be reanalyzed.

6.5.2. Continuing Calibration Verification

Continuing calibration verification (CCV) standards will be analyzed at the frequencies specified in Tables 8–11, and CCV documentation is archived with the sample data.

For the GC/MS methods, the CCV standards' RSDs of each analyte's responses relative to the surrogate standard's responses must be ≤15%.

For the LC-MS/MS methods, the CCV standards' RSDs of each analyte's responses relative to the surrogate standard's responses must be ≤20%.

For the TLC/FID method, the measured values for the CCV standards must be plus or minus 25% of the expected values.

For the EA/IRMS method, the CCV standards' $\delta^{15}N$ and $\delta^{13}C$ values are evaluated using the applicable four steps as follows:

1. The amplitudes of N_2 (mass 28 and 29) peaks must be between 500 and 12,000 mV and the amplitudes of CO_2 (mass 44 and 46) peaks must be between 500 and 12,000 mV; otherwise, that analysis of the standard is excluded from the data set and not further evaluated. At least one analysis of each standard must remain at the beginning and end of the batch.
2. The standard deviation of δ values in the replicate analyses of each standard must be ≤0.25 per mil (‰) for $\delta^{15}N$ and ≤0.35‰ for $\delta^{13}C$; otherwise, extreme points will be identified and removed (see Step 3).
3. An extreme point is defined as the CCV standard with the greatest difference in $\delta^{15}N$ and $\delta^{13}C$ from the median of all replicate CCV standards. Extreme points are identified and excluded in a stepwise process until the standard deviations meet the criteria in Step 2.
4. No more than 20% of $\delta^{15}N$ or $\delta^{13}C$ values in the replicates of each CCV standard can be excluded due to extreme values. At least one analysis of each standard must remain at the beginning and end of the batch.

If CCV results for the GC/MS, LC-MS/MS, TLC/FID, or EA/IRMS methods do not meet their respective acceptance criteria, then the entire batch of samples and calibration standards must be reanalyzed by that method.

6.5.3. Reference Materials

At least one appropriate SRM from the NIST, if available, is analyzed with every batch of field samples for quality assurance. The SRM is chosen based on the analytes that are certified in the SRM and to best match the sample matrices. If an appropriate SRM is not available, an IRM with in-house assigned values or a spiked matrix sample (Section 6.5.7) is analyzed with every batch of field samples. The data resulting from the analyses of SRMs are reported in the same manner as field samples (Section 7.1) and are used to document the estimated accuracy of the associated field sample data.

The laboratory's performance for PAHs or POPs in sediment, tissue, or plasma by the GC/MS method is considered acceptable if ≥70% of reported analytes having certified values in the SRM are within their control limits (Equations 1 and 2).

$$\text{Upper control limit} = 1.3 \times (\text{certified concentration} + \text{uncertainty value for 95\% confidence}) \quad (1)$$

$$\text{Lower control limit} = 0.7 \times (\text{certified concentration} - \text{uncertainty value for 95\% confidence}) \quad (2)$$

If gravimetric percent lipid values are requested for tissue samples that are analyzed for PAHs or POPs, then the percent lipid measured in the SRM for the batch must also be within its control limits (Equations 1 and 2).

The laboratory's performance for OHPAHs by the LC-MS/MS method is considered acceptable if ≥70% of reported analytes having certified values in the SRM are within their control limits (Equations 3 and 4).

$$\text{Upper control limit} = 1.3 \times (\text{certified concentration} + \text{uncertainty value for 95\% confidence}) \quad (3)$$

$$\text{Lower control limit} = 0.7 \times (\text{certified concentration} - \text{uncertainty value for 95\% confidence}) \quad (4)$$

For all GC/MS and LC-MS/MS methods with available NIST SRMs, acceptance criteria do not apply to analytes that have concentrations below their lower LOQ when their lower LOQ is above the lower control limit, or to analytes that coelute with interfering compounds.

There is no SRM certified for DOSS. However, an oyster IRM was prepared in-house and analyzed repeatedly for the concentration of DOSS. The assigned reference value for DOSS in this IRM is the mean of the results of the replicate analyses. The laboratory's performance for DOSS by the LC/MS-MS method is considered acceptable if the DOSS concentration in the IRM is within the control limits (Equations 5 and 6).

$$\text{Upper control limit} = 1.3 \times (\text{reference value} + \text{uncertainty value for 95\% confidence}) \quad (5)$$

$$\text{Lower control limit} = 0.7 \times (\text{reference value} - \text{uncertainty value for 95\% confidence}) \quad (6)$$

Analyses for estrogenic compounds or steroids do not have an SRM available; thus, spiked matrix samples are analyzed for monitoring the data quality (Section 6.5.7).

There is no tissue SRM certified for ratios of stable isotopes of carbon and nitrogen. However, NIST SRM 1946 (fish muscle tissue) is used as an IRM. The assigned reference values for $\delta^{15}N$, $\delta^{13}C$, Wt%N, and Wt%C for SRM 1946 are the mean of repeated in-house analyses of this IRM for stable isotopes of carbon and nitrogen. The laboratory's performance for the EA/IRMS method is considered acceptable if a minimum of three samples of IRM per batch meet four criteria as follows:

1. For each IRM sample, the amplitudes of N_2 (mass 28 and 29) and CO_2 (mass 44 and 46) peaks must be between 500 and 12,000 mV; otherwise, that sample of the IRM is excluded from the data set and not further evaluated.
2. The mean of the $\delta^{15}N$ values and the mean of the $\delta^{13}C$ values must be within their respective control limits (Equations 7–10).
3. The standard deviation of the $\delta^{15}N$ values must be ≤0.3‰ and the standard deviation of the $\delta^{13}C$ values must be ≤0.2‰.
4. The mean of the Wt%N values and the mean of the Wt%C values must be within their control limits (Equations 11 and 12).

$$\delta^{15}N \text{ upper control limit} = \text{reference value} + 0.3‰ \quad (7)$$

$$\delta^{15}N \text{ lower control limit} = \text{reference value} - 0.3‰ \quad (8)$$

$$\delta^{13}C \text{ upper control limit} = \text{reference value} + 0.2‰ \quad (9)$$

$$\delta^{13}C \text{ lower control limit} = \text{reference value} - 0.2‰ \quad (10)$$

$$\text{Wt\% upper control limit} = (1.05 \times \text{Wt\% reference value}) \quad (11)$$

$$\text{Wt\% lower control limit} = (0.95 \times \text{Wt\% reference value}) \quad (12)$$

If both $\delta^{15}N$ and $\delta^{13}C$ meet the acceptance criteria but a Wt% does not, then the $\delta^{15}N$ and $\delta^{13}C$ are reported for all sample types in the batch but Wt% and C/N ratio are not.

Gravimetric percent lipid values of NIST tissue SRMs must be within 35% of either end of the 95% confidence interval of the certified value. None of the NIST tissue SRMs (SRM 1974c, 1945, 1947) are certified for lipid classes.

If the SRM or IRM results for a method do not meet the acceptance criteria, then the results for the entire batch of samples analyzed by that method are to be considered suspect. The source of the error must be identified and corrected, and the samples may need to be reanalyzed or the data qualified, depending on the project requirements.

6.5.4. Surrogate (Internal Standard) Recovery

All samples analyzed by GC/MS or LC-MS/MS will be spiked with appropriate extraction surrogates (internal standards) as described in the laboratory SOPs. The measured percent recovery of the surrogates must be 60–130%. If a percent recovery does not meet the specified criteria, the sample will be re-extracted and reanalyzed, if possible (i.e., is a sufficient amount of sample is still available); otherwise, the corresponding data will be qualified as being an estimate.

6.5.5. Method Blanks

Method blanks (also known as reagent blanks) are laboratory-derived samples that are subjected to the same analytical protocols as are the field samples.

For the GC/MS and LC-MS/MS methods, no more than 10% of the analytes in the suite of analytes (excluding naphthalene or alkylated naphthalenes for PAHs) may exceed 2 × lower LOQ in a method blank. Field samples are not corrected for analytes found in the blank.

For the EA/IRMS analyses, the method blanks are tin cups with no sample added, which are analyzed in the same manner as the environmental samples. These blanks are used to correct the $\delta^{15}N$ and $\delta^{13}C$ sample values for traces of nitrogen or carbon materials in the tin cups, and are not a measure of contamination that occurred during sample processing. The N_2 mass 28 and CO_2 mass 44 peak amplitudes for all of the method blanks must be <50 mV, or the source of contamination must be determined and corrective action taken.

For the TLC/FID method, no lipid classes may be detected in a method blank.

Failure to meet acceptance criteria for a method blank requires definitive corrective action to identify and eliminate the source(s) of contamination, then re-extraction and reanalysis of the batch of samples, if possible (i.e., if a sufficient amount of sample is still available).

6.5.6. Sample Replicates

Field samples will be analyzed in replicate (i.e., duplicate or triplicate) at the specified frequency to help ascertain whether samples are analytically homogeneous and to indicate whether other problems with reproducibility occurred during analysis. The reproducibility of SRM results can indicate the precision for all of the same analyses in the project.

For analyses by GC/MS or LC-MS/MS, the RSDs of analyte concentrations must be ≤15% for triplicates, or percent differences must be ≤30% for duplicates, for ≥90% of the analytes in the group that have concentrations above their lower LOQ. For analyses by GC/MS, this applies to only those analytes that have concentrations ≥1 ng/g.

For EA/IRMS analyses, replicate samples of the IRM are analyzed between every 15 or fewer field samples, with a minimum of three per batch, to show the performance of the EA/IRMS system (Section 6.5.3). Duplicate or triplicate field samples are suggested for approximately every 10 field samples, but are not used for QA. There are no acceptance criteria for replicate field samples because many explanations exist for widely varying values (e.g., problems with the sample processing or the homogeneity of the starting sample) that are often outside the control of the analytical laboratory. However, within-sample variability of the results for replicate field samples may be useful to the researcher.

For lipid classes by TLC/FID, the RSDs of the concentrations of lipid classes must be ≤25% for triplicates, or percent differences must be ≤50% for duplicates.

For analyses by GC/MS, LC-MS/MS, or TLC/FID, if the replicate sample results exceed the control limit criteria, then the data for the replicate samples will be footnoted (Section 6.6).

6.5.7. Spiked Matrix Samples

A spiked matrix sample is a sample of clean matrix (previously shown to be free of analytes) that is spiked with specified amounts of analytes prior to extraction, according to the method's SOP. The matrix is chosen to best match the sample matrices.

At least one spiked matrix sample is analyzed for quality assurance with every batch of water samples that is analyzed for PAHs or POPs and with every batch of field samples that is analyzed for DOSS, estrogenic compounds, or steroids. The data resulting from the analyses of spiked matrix samples are reported as the percent recovery of the amount spiked. The measured percent recovery of the spiked analytes must be 60–130%. If the spiked matrix sample results exceed the control limit criteria, then the entire batch of samples is to be considered suspect. The source of the error must be identified and corrected, and the batch of samples may need to be reanalyzed, depending on the project requirements and if possible (i.e., if a sufficient amount of sample is still available); otherwise, the corresponding data will be qualified as being an estimate.

6.6. Laboratory Qualification of Data

Sample results that did not meet the QA acceptance criteria or that presented analytical difficulties are footnoted so that the data user is aware of the potential limitations of the data. These footnotes are summarized and presented in text (e.g., a report or case narrative) accompanying the data.

7. Data Reduction

Data reduction is the process whereby raw data (analytical measurements) are converted or reduced to usable results that are reported in the format specified for the project, including QA data. Primary data reduction is the responsibility of the analyst(s) conducting the analytical measurements, and is subject to further review by laboratory staff, the project leader, and the project manager(s).

Primary data reduction requires accounting for specific sample preparations, sample volume or weight analyzed, and any concentrations or dilutions required. All data reduction procedures are described in the laboratory's SOPs.

7.1. Reported Results

In general, results are reported as follows:

- For PAHs and POPs, analyte concentrations in sediments are reported as ng/g dry weight, in tissues or plasma as ng/g wet weight, and in water as ng/mL. Gravimetric percent dry weights or percent lipid weights of samples are determined and reported for tissue analyses, if requested.
- For DOSS, analyte concentrations in tissues are reported as ng/g wet weight.
- For estrogenic compounds, steroids, and OHPAHs, analyte concentrations in biological fluids are reported as ng/mL and in tissues as ng/g wet weight.
- For stable isotope ratios, $\delta^{15}N$ and $\delta^{13}C$ values are reported as ‰, where δ^{13} is the difference in ratio of carbon isotope ^{13}C to carbon isotope ^{12}C in a sample relative to that in the Pee Dee Belemnite standard, and $\delta^{15}N$ is the difference in ratio of nitrogen isotope ^{15}N to nitrogen isotope ^{14}N in a sample relative to atmospheric nitrogen used as the standard (Equations 13 and 14).

$$\delta^{13}C = \{[(^{13}C_{sample}/^{12}C_{sample})/(^{13}C_{standard}/^{12}C_{standard})] - 1\} \quad (13)$$

$$\delta^{15}N = \{[(^{15}N_{sample}/^{14}N_{sample})/(^{15}N_{standard}/^{14}N_{standard})] - 1\} \quad (14)$$

- For stable isotope ratios, Wt%N, Wt%C, and C/N ratios are also reported.
- For lipid classes, the data for each lipid class are reported as percent of total lipid.
- Results are reported to two (or, if requested, three) significant figures for analyses by GC/MS or LC-MS/MS; to two figures following the decimal point for $\delta^{15}N$ and $\delta^{13}C$ values; to one figure following the decimal point for Wt%N, Wt%C, C/N ratios, and lipid classes; and to one figure following the decimal point for percent lipid if the value is >1%, or to two figures following the decimal if the value is <1%.
- For analyses by GC/MS or LC-MS/MS, the analyte concentrations are calculated based on the surrogate standard(s) spiked into the sample prior to extraction.
- For analyses by GC/MS or LC-MS/MS, the percent recovery of each surrogate standard is reported.

- Results for analytes in method blanks are reported on the same basis as those for the samples being analyzed. The mean of the sample weights or volumes for the field samples comprising a batch, as well as the mean of the percent dry weights for sediments, is used in the calculations for the method blank.
- For analyses by GC/MS or LC-MS/MS, the lower LOQ preceded by "<" is reported instead of a concentration when an analyte is below the quantitation range. For summed groups of analytes derived by summing concentrations of individually quantified analytes, "< LOQ" is reported if every analyte in the summed group is below its individual lower LOQ.
- For stable isotope ratios, if a sample's peak amplitudes for N_2 (mass 28 or 29) or CO_2 (mass 44 or 46) are between 9,000 and 12,000 mV, then the data are flagged to be used with caution; if any are >12,000 mV, then the corresponding data are not reported. Also, if a sample's peak amplitudes for N_2 (mass 28 or 29) or CO_2 (mass 44 or 46) are between 500 and 750 mV, then the data are flagged to be used with caution; if any are <500 mV or >12,000 mV, then the corresponding data are not reported.
- If a lipid class is not detected in a sample, a value of zero is reported for the proportion of that lipid class.
- Data generated from the analysis of blank samples are not used for correction of analyte results in samples, except for the EA/IRMS analyses.
- Replicate sample data are summarized as the mean plus or minus RSD.

7.2. Data Review

Data review is an internal process during which the data are reviewed and evaluated by laboratory personnel. This review is undertaken by analysts who are responsible for ensuring that the analytical data are correct and complete, the appropriate SOPs have been followed, and the QA results meet the acceptance criteria. It is the project manager's responsibility to ensure that all analyses performed by the laboratory are correct, complete, and meet project DQOs. The project leader has final review authority.

7.3. Laboratory Data Deliverables

The laboratory reports any difficulties encountered during sample preparation and analysis (e.g., in a case narrative), as well as any limitations to the use of the data. In addition, the following specific information will be provided as requested:

- A COC/sample receipt checklist.
- Procedure modifications.
- Calibration summaries (initial calibration data and/or continuing calibration data).
- Data tables for field samples.
- QA data (surrogate recoveries, method blanks, SRMs or IRMs, spiked matrix samples, and/or replicate field samples), as applicable,.
- Any corrective actions that were necessary.

8. Corrective Action/Procedure Alteration

The laboratory is required to adhere to the SOPs specified for the project unless procedure alterations are necessary to correct unforeseen analytical problems. Laboratory personnel are alerted that corrective action is necessary when QA data do not meet the acceptance criteria.

Because most of the corrective actions are handled at the laboratory level, it is the immediate responsibility of the analyst to identify and correct the situation before continuing with sample analysis. If the problem persists or cannot be identified, the matter is referred to the project leader or project manager for further investigation. Once resolved, a narrative must be prepared and submitted with the relevant data package, describing 1) the problem, 2) the steps taken to identify and correct the problem, and 3) the action taken to remedy the problem in the relevant sample batches. If the action involves a change from the accepted SOP, the SOP must be revised as appropriate.

Tables

Table 1. Individual polycyclic aromatic hydrocarbons (PAHs) determined by gas chromatography/ quadrupole mass spectrometry.

Low-molecular-weight PAHs	
Acenaphthene	1-Methyl-7-isopropyl phenanthrene (retene)
Acenaphthylene	1-Methylnaphthalene
Anthracene	2-Methylnaphthalene
Benzo[*b*]naphtho[2,1-*d*]thiophene	1-Methylphenanthrene
Dibenzothiophene	Naphthalene
2,6-Dimethylnaphthalene	Phenanthrene
1,7-Dimethylphenanthrene	2,3,5-Trimethylnaphthalene
Fluorene	
High-molecular-weight PAHs	
Benz[*a*]anthracene	Chrysene + Triphenylene
Benzo[*b*]fluoranthene	Dibenz[*a*,*h*]anthracene + Dibenz[*a*,*c*]anthracene
Benzo[*j*]fluoranthene + Benzo[*k*]fluoranthene	Fluoranthene
Benzo[*ghi*]perylene	Indeno[1,2,3-*cd*]pyrene
Benzo[*a*]pyrene	Perylene
Benzo[*e*]pyrene	Pyrene

Table 2. Persistent organic pollutants (POPs) determined by gas chromatography/quadrupole mass spectrometry.

Dichlorodiphenyldichloroethylenes (DDDs), dichlorodiphenyldichloroethanes (DDEs), dichlorodiphenyltrichloroethanes (DDTs), and other organochlorine pesticides and metabolites or by-products			
2,4'-DDD	Aldrin	Heptachlor epoxide	Mirex
4,4'-DDD	*cis*-Chlordane	Hexachlorobenzene	*cis*-Nonachlor
2,4'-DDE	*trans*-Chlordane	α-Hexachlorocyclohexane	*trans*-Nonachlor
4,4'-DDE	Dieldrin	β-Hexachlorocyclohexane	Nonachlor III[a]
2,4'-DDT	Endosulfan I	γ-Hexachlorocyclohexane (Lindane)	Oxychlordane
4,4'-DDT	Heptachlor		
Polychlorinated biphenyl (PCB) congeners[b]			
PCB 11[a,d]	PCB 82	PCB 153 + PCB 132[c]	PCB 195
PCB 17	PCB 87	PCB 156	PCB 196[a,d]
PCB 18	PCB 95	PCB 158	PCB 199
PCB 28	PCB 99	PCB 170	PCB 200[a,d]
PCB 31	PCB 101 + PCB 90[c]	PCB 171	PCB 201[a,d]
PCB 33	PCB 105	PCB 177	PCB 202[a,d]
PCB 44	PCB 110	PCB 180	PCB 205
PCB 49	PCB 118	PCB 183	PCB 206
PCB 52	PCB 128	PCB 187 + PCB 159 + PCB 182[c]	PCB 207[a,d]
PCB 66	PCB 138 + PCB 163 + PCB 164[c]	PCB 191	PCB 208
PCB 70	PCB 149	PCB 194	PCB 209
PCB 74	PCB 151		
Polybrominated diphenyl ether (PBDE) congeners[a,e]			
PBDE 28	PBDE 66	PBDE 100	PBDE 155
PBDE 47	PBDE 85	PBDE 153	PBDE 183
PBDE 49	PBDE 99	PBDE 154	

[a] Analytes that do not have Continuing Calibration QA criteria.

[b] Congeners are numbered as in Ballschmiter et al. (1992).

[c] Coeluting congeners are listed together, and their combined concentrations are measured and reported.

[d] Congeners that are measured and reported only upon request.

[e] PBDE congeners are numbered as for PCBs in Ballschmiter et al. (1992).

Table 3. Estrogenic compounds determined by liquid chromatography/triple-quadrupole mass spectrometry.

Estrogenic compounds	
Bisphenol-A	Estriol
Bisphenol-AF	17α-Ethinyl estradiol
Bisphenol-F	Sum of Octylphenols
Bisphenol-S	Sum of Nonylphenols
17β-Estradiol	

Table 4. Steroids determined by liquid chromatography/triple-quadrupole mass spectrometry.

Progestagens	
17α,20β-Dihydoxyprogesterone	Progesterone
17-Hydroxypregnenolone	17,20β,21-Trihydroxyprogesterone
17α-Hydroxyprogesterone	
Androgens	
4-Androstenedione	11-Ketoandrostendione
5α-Dihydrotestosterone	11-Ketotestosterone
11-Hydroxyandrostenedione	Testosterone
11β-Hydroxytestosterone	
Estrogens	
Estradiol	Estrone
Glucocorticoids	
Cortisol	11-Desoxycortisol

Table 5. Hydroxylated polycyclic aromatic hydrocarbons (OHPAHs) determined by liquid chromatography/triple-quadrupole mass spectrometry.

OHPAHs
2-ring
4,4-Dihydroxybiphenyl
1-Hydroxynaphthalene
2-Hydroxynaphthalene
6-Methyl-2-hydroxynaphthalene
1-Methyl-2-hydroxynaphthalene + 1-Methyl-2-hydroxynaphthalene[a]
3-ring
3-Hydroxyfluorene
2-Hydroxyfluorene
2-Hydroxydibenzothiophene
3-Hydroxyphenanthrene + 2-Hydroxyphenanthrene[a]
4-Hydroxyphenanthrene
1-Hydroxyphenanthrene
9-Hydroxyphenanthrene
trans-9,10-dihydroxy-9,10-dihydrophenanthrene
trans-1,2-dihydroxy-1,2-dihydrophenanthrene
1,8-bis(hydroxymethyl)anthracene
2-hydroxy-9,10-anthraquinone
1,5-dihydroxy-1,2-dihydro-9,10-anthraquinone
4-ring
trans-2,3-dihydroxy-2,3-dihydrofluoranthene
trans-5,6-dihydroxy-5,6-dihydrochrysene
trans-3,4-dihydroxy-3,4-dihydrochrysene
trans-1,2-dihydroxy-1,2-dihydrochrysene
cis-5,6-dihydroxy-5,6-dihydrobenz[*a*]anthracene
trans-8,9-dihydroxy-8,9-dihydrobenz[*a*]anthracene
5-ring
cis-4,5-dihydroxy-4,5-dihydrobenzo[*a*]pyrene
cis-7,8-dihydroxy-7,8-dihydrobenzo[*a*]pyrene

[a] Coeluting isomers are listed together, and their combined concentrations are measured and reported.

Table 6. Stable isotope ratios determined by elemental analysis/isotope ratio mass spectrometry.

Delta (δ) values	
$\delta^{13}C$	$\delta^{15}N$
Other ratios	
Carbon/nitrogen ratio (C/N ratio)	Percent nitrogen by weight (Wt%N)
Percent carbon by weight (Wt%C)	

Table 7. Lipid class proportions and percent lipid determined by thin-layer chromatography/flame ionization detection.

Lipid classes	
Cholesterol/sterols	Sterol esters/wax esters
Free fatty acids	Triglycerides
Phospholipids/other polar lipids	

Table 8. Minimum analytical quality assurance criteria for polycyclic aromatic hydrocarbons (PAHs) and/or persistent organic pollutants (POPs) by gas chromatography/quadrupole mass spectrometry.

Quality assurance element	Minimum frequency	Acceptance criteria
Instrument calibration	Each calibration standard is analyzed once every batch of samples, or once every two batches in one continuous analytical sequence.	Analyte concentrations must be calculated using point-to-point calibration with at least five concentration levels of calibration standards. Each surrogate standard in the calibration standards must have an RSD of its response factors (response area divided by the concentration) that is ≤15%.
Continuing calibration verification	One at start and end of every analytical sequence and between every 10 or fewer field samples.	The RSD of each analyte's responses relative to the internal standard must be ≤15% for the repetitions. This criterion does not apply to Nonachlor III, PBDEs, or PCBs 11, 196, 200, 201, 202, or 207.
Reference materials: NIST SRM 1944—sediment, NIST SRM 1941b—sediment, NIST SRM 1974c—mussel tissue (PAHs), NIST SRM 1945—whale blubber, NIST SRM 1947—fish tissue (POPs), NIST SRM 1958—human serum (POPs)	One appropriate SRM with every batch of 20 or fewer tissue or sediment field samples.	Concentrations of ≥70% of individual analytes, as well as the gravimetric percent lipid, if requested, must be within 30% of either end of the 95% confidence interval of the certified values. These criteria do not apply to analytes with concentrations below their lower LOQ when the lower LOQ is within or greater than the 95% confidence interval, nor to those analytes known to have coeluting compounds.
Spiked matrix	One with every batch of 20 or fewer water field samples.	The recoveries of spiked analytes must be 60–130%.
Method blank	One with every batch of 20 or fewer field samples.	No more than 10% of the analytes' concentrations can exceed 2 × lower LOQ in a method blank.
Sample replicates (i.e., duplicates or triplicates)	One with every 26 or fewer field samples, as amount of available sample allows.	The RSDs of analyte concentrations must be ≤15% for triplicates, or percent differences must be ≤30% for duplicates, for ≥90% of the analytes that have concentrations >1 ng/g.
Surrogates (internal standards)	Every sample.	The surrogate recoveries must be 60–130%.
Interlaboratory comparison	At least one per year, if available.	In conjunction with NIST or IAEA.

Table 9. Minimum analytical quality assurance criteria for dioctyl sulfosuccinate (DOSS), estrogenic compounds, steroids, and/or hydroxylated polycyclic aromatic hydrocarbons (OHPAHs) by liquid chromatography/triple-quadrupole mass spectrometry.

Quality assurance element	Minimum frequency	Acceptance criteria
Instrument calibration	Each calibration standard is analyzed at the start and end of every batch of samples.	Analyte concentrations must be calculated using a Wagner calibration curve with at least five concentration levels of calibration standards. Concentrations of analytes in the calibration standards as measured using the calibration curve must be 70–130% of the actual concentration.
Continuing calibration verification	One at start and end of every analytical sequence and between every 15 or fewer field samples.	The RSD of each analyte's responses relative to the internal standard must be ≤20% for the repetitions.
Reference material: NIST SRM 3672—smokers' urine (OHPAHs)	One with every batch of 20 or fewer field samples analyzed for OHPAHs.	The concentrations ≥70% of individual OHPAHs must be within 15% of either end of the 95% confidence interval range of the reference values. These criteria do not apply to analytes with concentrations below their lower LOQ when the lower LOQ is within or greater than the 95% confidence interval.
Reference material: IRM—oyster (DOSS; prepared in-house)	One with every batch of 20 or fewer field samples analyzed for DOSS.	The concentration of DOSS must be within 30% of either end of the 95% confidence interval range of the reference values.
Spiked matrix (estrogenic compounds, steroids)	One with every batch of 20 or fewer field samples for estrogenic compounds or steroids.	The recoveries of spiked analytes must be 60–130%.
Method blank	One with every batch of 20 or fewer field samples.	No more than 10% of the analytes' concentrations can exceed 2 × lower LOQ in a method blank.
Sample replicates (i.e., duplicates or triplicates)	One with every 26 or fewer field samples, as amount of available sample allows.	The RSDs of analyte concentrations must be ≤15% for triplicates, or percent differences must be ≤30% for duplicates, for ≥90% of the analytes that have concentrations >LOQ.
Surrogates (internal standards)	Every sample.	The surrogate recoveries must be 60–130%.
Interlaboratory comparison	No intercomparison studies are available at present.	

Table 10. Minimum analytical quality assurance criteria for stable isotope ratios by elemental analysis/isotope ratio mass spectrometry.

Quality assurance element	Minimum frequency	Acceptance criteria
Instrument calibration	At least two of each calibration standard at the beginning and end of every batch and between every 10 or fewer field samples.	$\delta^{15}N$ and $\delta^{13}C$ must be calculated using linear calibration with two δ levels of calibration standards (histidine and aspartic acid, with δ values assigned using primary standards IAEA CH-7, USGS 40, and USGS 41a) and at least five replicate analyses of each calibration standard, including at least one of each at the beginning and end of the batch after outliers, if any, are identified and excluded during the continuing calibration verification. The $\delta^{15}N$ results and $\delta^{13}C$ results for the included replicate analyses of the calibration standards versus the respective assigned δ values for the calibration standards must have a correlation of $r > 0.9900$.
Continuing calibration verification	At least two of each calibration standard at the beginning and end of every batch and between every 10 or fewer field samples (same standards as those used for instrument calibration).	A four-step process is used, as applicable, to evaluate CCV standards: 1. The peak amplitudes of N_2 (mass 28 and 29) and CO_2 (mass 44 and 46) must be between 500 and 12,000 mV; otherwise, that analysis of the standard is excluded from the data set and not further evaluated. At least one analysis of each standard must remain at the beginning and end of the batch. 2. The standard deviation of δ values in the replicate analyses of each standard must be ≤0.25‰ for $\delta^{15}N$ and ≤0.35‰ for $\delta^{13}C$; otherwise, extreme points will be identified and removed (see Step 3). 3. An extreme point is defined as the replicate of the CCV standards with the greatest difference in $\delta^{15}N$ or $\delta^{13}C$ from the median of all replicate CCV standards. Expreme points are identified and excluded in a stepwise process until the standard deviations meet the criteria in Step 2. 4. No more than 20% of $\delta^{15}N$ or $\delta^{13}C$ values in the replicates of each CCV standard can be excluded due to extreme values. At least one analysis of each standard must remain at the beginning and end of the batch.

Table 10 (continued). Minimum analytical quality assurance criteria for stable isotope ratios by elemental analysis/isotope ratio mass spectrometry.

Quality assurance element	Minimum frequency	Acceptance criteria
Reference material: NIST SRM 1946—fish muscle tissue, used as an IRM	One between every 15 or fewer field samples, with a minimum of three samples of IRM per batch meeting the acceptance criteria.	A four-step process is used to evaluate the IRM samples in the batch: 1. For each IRM, the peak amplitudes of N_2 (mass 28 and 29) and CO_2 (mass 44 and 46) must be between 500 and 12,000 mV; otherwise, that sample of the IRM is excluded from the data set and not further evaluated. 2. The mean of the $\delta^{15}N$ values must be within ±0.3‰ of the $\delta^{15}N$ in-house reference value, and the mean of the $\delta^{13}C$ values must be within ±0.2‰ of the $\delta^{13}C$ in-house reference value. 3. The standard deviation of the $\delta^{15}N$ values must be ≤0.3‰, and the standard deviation of the $\delta^{13}C$ values must be ≤0.2‰. 4. The mean of the Wt%N values and the mean of the Wt%C values must be within ±5% of the Wt%N and Wt%C reference values, respectively. If both $\delta^{15}N$ and $\delta^{13}C$ meet the acceptance criteria but a Wt% does not, then the $\delta^{15}N$ and $\delta^{13}C$ are reported for all sample types in the batch, but Wt% and C/N ratio are not.
Method blank	Three at the beginning of every batch.	The N_2 mass 28 and CO_2 mass 44 peak amplitudes for all of the method blanks must be <50 mV.

Table 11. Minimum analytical quality assurance criteria for lipid class proportions by thin-layer chromatography/flame ionization detection.

Quality assurance element	Minimum frequency	Acceptance criteria
Instrument calibration	Every four to six weeks.	The concentrations of lipid classes must be calculated using point-to-point calibration with at least three analyses of six concentration levels of calibration standards. Each analyte must have an r^2 value of at least 0.95 for its response areas in the middle four concentration levels of calibration standards.
Continuing calibration verification	One standard between every four field samples.	The measured concentrations of lipid classes in the continuing calibration standards must be ±25% of the expected concentrations.
Reference materials: NIST SRM 1974c—mussel tissue, NIST SRM 1945—whale blubber, NIST SRM 1947—fish tissue	One appropriate SRM with every batch of 20 or fewer tissue field samples.	The gravimetric percent lipid value of each tissue SRM must be within 35% of either end of the 95% confidence interval of the certified value. There are no certified values for lipid classes in NIST SRMs 1974c, 1945, or 1947.
Method blank	One extraction method blank with every batch of 10–14 field samples.	Each lipid class must not be detected in a method blank or solvent blank.
Sample replicates (i.e., duplicates or triplicates)	One with every 26 or fewer field samples, as amount of available sample allows.	The RSDs of the concentrations of lipid classes must be ≤25% for triplicates, or percent differences must be ≤50% for duplicates.
Interlaboratory comparison	Infrequent intercomparison studies are available at present.	As defined by NIST, or through informal participation with comparable government or university laboratories, or both.

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