RB5-SCCWRP-LC-rev1 Standard Operating Procedures: Extraction and Analysis of a Suite of Pesticide Analytes at Trace Levels in Aqueous Samples and Aqueous Passive Sampler Media by Liquid Chromatography/ Tandem Mass Spectrometry (LC/MS/MS)

Charles S. Wong[1], Danhui Xin[1], Wenjian Lao[1]

[1]Southern California Coastal Water Research Project, Costa Mesa, CA

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1. Scope and Application

1.1

This Standard Operating Procedure (SOP) is for determining a broad suite of pesticide analytes at trace levels in surface water samples by liquid chromatography-tandem mass spectrometry (LC/MS/MS).

1.2

This Method is validated for the measurement of pesticide analytes extracted from environmental surface waters by Hydrophilic-Lipophilic Balanced (HLB) Solid Phase Extraction (SPE) cartridges (Oasis HLB 6 cc Vac Cartridge, 500 mg sorbent) and from Chemcatcher passive sampler sequestration media (Attract SPE Disk with HLB sorbent, 47 mm diameter) deployed in surface waters.

The 32 pesticide analytes that have been evaluated with this Method are in Table 1, with calibration data (Tables 4). Some precision and accuracy data for the aqueous matrix are provided in Tables 5A-C and 5X and Tables 9A-C and 9X, and that data for passive sampler sequestration media are provided in Tables 6A-C and 6X, and Tables 10A-C and 10X. This Method may also be expanded to other pesticide analytes, provided that the laboratory demonstrates and documents performance (refer to Section 11).

1.3

This Method is intended for measuring a wide range of analytes and therefore is not specifically optimized for any specific analytes. The detection limits and quantitation levels in this method are generally dependent on the level of interferences rather than on instrumental limitations. Method Detection Limits (MDLs) in the presence of typical interferences from surface water and the Chemcatcher media are present in Tables 7-8, respectively.

1.4

This Method is intended for use by analysts appropriately trained and experienced in LC/MS/MS or under the close supervision of such qualified persons. Each laboratory that uses this SOP must demonstrate the ability to generate acceptable results using the procedure in Section 9.

1.5

This Method is performance-based, in that the SOP may be modified to improve performance (e.g., to overcome interferences or improve the accuracy or precision of the results) provided that all performance requirements in this SOP are met.

1.6

The SOP was developed at the Southern California Coastal Water Research Project (SCCWRP). It is based on the existing methods of Hladik and Calhoun (2012), Hladik and McWayne (2012), and Sanders et al. (2018) for analyte extraction, Sanders et al. (2018) for choosing isotopically labeled standards of analytes, Hladik and Calhoun (2012) for instrumental analysis, and Vermeirssen et al. (2012) and De Parsia et al. (2018-2019) for generating spiked samples on Chemcatcher disks (References 1-5).

1.7

The method has been evaluated by 3 laboratories following initial single-laboratory development. Based on the results of multi-laboratory validation, quality assurance/quality control (QA/QC) requirements have been updated in this version. Instrumental conditions and performance data from individual laboratories, as well as summaries of results across all participating laboratories, are present in Tables 2-10.

2. DEFINITIONS (IN ALPHABETICAL ORDER)

Analyte

A pesticide or pesticide degradate tested for by this Method. The analytes are listed in Table 1.

Calibration standard

A solution prepared from a secondary standard and/or stock solution and used to calibrate the response of the LC/MS/MS instrument.

Continuous Calibration Verification (CCV)

The calibration verification standard solutions that are used to monitor the method stability in comparison to the initial calibration curve.

CFR

Code of Federal Regulations.

Confirmation Ion

For the purpose of this Method, the confirmation ion is produced by collisionally activated dissociation of a precursor ion to produce distinctive ions of smaller m/z value than the precursor, and is used to confirm the identity of the analyte.

Instrumental Detection Limit (IDL)

The minimum concentration of an analyte that can be identified, but not necessarily quantified, under the stated conditions of a test. IDLs are listed in Table 3.

Internal Standard (IS)

An analyte, not present natively in a sample, used as a reference for quantitation of other analytes used for standards and for quantitation of naturally occurring (native) analytes in a sample.

Internal standard quantitation

A means of determining the concentration of a native analyte or standard analyte by reference to another analyte.

Initial Demonstration of Capability (IDC)

An IDC is performed prior to the first time this Method is used and any time the Method or instrumentation is modified.

Initial Precision and Recovery standard (IPR)

A clean matrix (i.e., reagent water for an aqueous matrix, Attract SPE disk for the Chemcatcher matrix) spiked with the method analytes and labeled compounds and analyzed to establish the initial ability of the laboratory to generate acceptable precision and recovery. An IPR is performed prior to the first time this Method is used, including by a new analyst, and any time the Method or instrumentation is modified.

Laboratory Control Sample (LCS)

An aliquot of reagent water (for aqueous matrices) or passive sampler sequestration media (for Chemcatcher matrices) to which known quantities of the method analytes and labeled compounds are added. The results of the LCS verify method performance in the absence of sample matrix interference. Performance results are listed in Tables 5A-D for individual laboratories and Table 5X across laboratories for the aqueous matrix, and Tables 6A-C for individual laboratories and Table 6X across laboratories for the Chemcatcher matrix, as examples and guidance.

Limit of Quantification (LOQ)

The smallest concentration that produces a quantitative result with known and recorded precision and bias. The LOQ shall be set at or above the concentration of the lowest initial calibration standard.

Matrix Spike (MS)

An aliquot of field samples fortified with a known concentration of target compounds, prior to sample preparation and extraction, and analyzed to measure the effect of matrix interferences. Not to be confused with “mass spectrometer”, which is spelled out or defined differently (e.g., as for tandem mass spectrometry, MS/MS) in this document.

Method blank

An aliquot of reagent water for the aqueous matrix, or cleaned and unexposed Attract SPE disk for the Chemcatcher matrix, that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and recovery standards that are used with samples. The method blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

Method Detection Limit (MDL)

The minimum measured concentration of a substance that can be reported with 99% confidence that the measured analyte concentration is indistinguishable from method blank results (see 40 CFR 136, appendix B). MDLs determined during Multi-Laboratory evaluation are listed in Tables 7-8.

MS/MS

Tandem mass spectrometry, tandem mass spectrometer, or tandem mass spectrometry, the process of separating precursor ions by *m/z* into one or more product ions of smaller *m/z*.

Multiple Reaction Monitoring (MRM)

Also known as selected reaction monitoring (SRM). A type of mass spectrometry where a parent mass of the compound is fragmented through MS/MS and then specifically monitored for a single fragment ion.

Must

This action, activity, or procedural step is required.

m/z

mass-to-charge ratio.

Ongoing Precision and Recovery standard (OPR)

A method blank (i.e., reagent water for an aqueous matrix, Attract SPE disk for the Chemcatcher matrix) spiked with known quantities of analytes. The OPR is analyzed exactly like a sample. Its purpose is to ensure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery.

Percent recovery (R%)

The recovery percentage for samples.

Precursor ion

Ion produced in the ion source that forms particular product ions or undergoes specified neutral losses during MS/MS analysis.

Production

Ion formed as the product of a reaction involving a particular precursor ion.

Quantification Ion

For the purpose of this Method, the quantification ion is produced by collisionally activated dissociation of a precursor ion to produce distinctive ions of a smaller *m/z* value than the precursor. It is used to quantify (determine the concentration) of the analyte. It is usually, but not always, the most intense of the ions produced by the dissociation of the precursor ion.

Reagent water

Water demonstrated to be free from the analytes of interest and potentially interfering substances at or above the MDL for the analyte.

Relative Standard Deviation (RSD)

The standard deviation (STD) times 100 divided by the mean. Also termed “coefficient of variation”.

Relative Response Factor (RRF)

See Section 10.1.

Retention Time (RT)

The time it takes for an analyte or labeled compound to elute off the LC column.

Signal-to-Noise ratio (S/N)

The height of the signal as measured from the mean of the noise to the peak maximum divided by the width of the noise.

Should

This action, activity, or procedural step is suggested but not required.

Solid-Phase Extraction (SPE)

An extraction technique in which an analyte is extracted from an aqueous sample by passage over or through a material capable of reversibly sorbing the analyte. Also termed liquid-solid extraction.

Solvent blank

An appropriate solvent is injected to determine if there is a carryover of target analytes between sample injections (See Sections 7.3.3 and 9.4.1.4).

Stock solution

A solution containing an analyte that is prepared using a reference material traceable to the Environmental Protection Agency (EPA), the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

3. INTERFERENCES

This Method is intended for measuring a wide range of analytes. General sample extraction techniques are provided in this Method. Interferences co-extracted from the samples will vary considerably from matrix to matrix. Sources of interference in this Method can be grouped into three broad categories as follows:

First, contaminated solvents, reagents, or sample collecting and processing hardware.

Second, contaminated instrumental components (e.g., mobile phase, LC/MS interface, column).

Third, compounds extracted from the sample matrix to which the detector will respond.

This Section discusses common issues with interferences and potential solutions.

3.1

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts, elevated baselines, and/or lock-mass suppression causing misinterpretation of chromatograms. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Where possible, reagents are cleaned by extraction or solvent rinse.

3.2

Proper cleaning of glassware is extremely important because interferences from glassware may contaminate the samples.

3.2.1

Wash glassware with a detergent solution as soon after use as is practical. Glassware with removable parts, particularly separatory funnels with fluoropolymer stopcocks, must be disassembled prior to detergent washing.

3.2.2

After detergent washing, rinse glassware immediately, first with tap water, and then with reagent water.

3.2.3

If it is possible, bake glassware at high temperatures (e.g., 500 °C) in a kiln or furnace for 2 to 4 h. The kiln or furnace must be vented to prevent laboratory contamination by pesticide vapors. Volumetric ware must not be baked at high temperatures. Otherwise, rinse glassware with the following series of solvents: methanol, acetone, methylene chloride (dichloromethane, DCM), and hexane, in this order.

3.2.4

After drying and cooling, seal and store glassware in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with solvent-cleaned or ashed aluminum foil.

3.2.5

Vacuum manifolds (including valves and tips) must be rinsed with appropriate organic solvent (e.g., methanol and acetone) before starting a new batch of samples.

3.3

All materials used in the analysis must be demonstrated to be free from interferences by running method blanks (Section 7.3.1) initially. The level of interference must be below the MDL (Tables 7 and 8) before this Method can be performed on actual samples.

3.4

Field and laboratory personnel must be aware that many of the compounds included in this Method are common ingredients in household pesticide products, and exposure to these products should be limited prior to sample collection or sample handling. The potential for contamination bias during sample collection or handling is monitored by the use of field blanks and laboratory method blanks.

3.5

The levels of accuracy and precision that can be achieved with this Method depend on the sample matrix, which may decrease extraction recovery and ionization efficiency for some

compounds. The performance data from multi-laboratory evaluation are provided in Tables 5-6 and 9-10 as examples and guidance.

4. SAFETY

4.1

This Method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of the Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) needs to be made available to all personnel involved in these analyses. The analyst must carefully review the MSDS for all utilized chemicals and reagents and follow all safety recommendations specified in the MSDS.

4.2

The toxicity or carcinogenicity of the chemicals used in this Method has not been precisely determined; however, each compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level.

4.2.1

Some pesticides, most notably 4,4'-DDT, have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standards of pesticides are to be handled only by highly trained personnel thoroughly familiar with handling and cautionary procedures and the associated risks.

4.3

The pure pesticides and samples suspected to contain high concentrations of these compounds are handled using essentially the same techniques employed in handling radioactive or infectious materials. Well-ventilated, controlled access laboratories are required.

4.3.1

All steps that use organic solvents are performed in a well-vented fume hood. Exhaust from solvent evaporation from samples must be vented to a fume hood.

4.3.2 Personal protective equipment (PPE)

Appropriate PPE (gloves, eyewear, etc.) is used during the handling of reagents and chemicals. Use disposable gloves, an apron or lab coat, safety glasses or mask, and a glove box or fume hood. During analytical operations that may give rise to aerosols or dust, wear respirators equipped with activated carbon filters.

4.3.2.1

Nitrile gloves are commonly used to reduce exposure of the hands. When handling samples suspected or known to contain high concentrations of pesticides or DCM, an additional set of gloves can also be worn beneath the nitrile gloves. If DCM comes into contact with the gloves, the outer layer gloves must be removed immediately.

4.3.2.2

Eye protection (preferably full-face shields) must be worn while working with exposed samples or pure analytical standards.

4.3.3 Training

Workers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.

4.3.4 Personal hygiene

Wash hands thoroughly after each operation involving high concentrations of the pesticides, and before breaks (coffee, lunch, and shift).

4.3.5 Decontamination

For glassware, if it can be baked at high temperature (e.g., 500 °C), then follow the glassware cleaning protocol in Section 3.2. For other glassware and tools, wash with detergent water and rinse with deionized water, and then rinse with methanol and acetone. For bench surfaces, clean with a paper towel, then wipe with methanol- and acetone-soaked paper towels.

5. Apparatus and Materials

Note: Brand names, suppliers, and part numbers are for illustration purposes only and no endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here. Meeting the performance requirements of this Method is the responsibility of the laboratory.

5.1 Equipment for glassware cleaning

5.1.1 Laboratory sink

5.1.2 Kiln or muffle furnace

Capable of reaching 500 °C and maintaining 500 °C for 4 hours, with temperature controller and safety switch.

5.1.3 Aluminum foil

Solvents (acetone and DCM) rinsed or baked in a kiln. If baked at 500 °C, heavy-duty aluminum foil is required, as thinner foil will become brittle and unusable.

5.2 Equipment for sample preparation

5.2.1

Laboratory fume hood of sufficient size to contain the sample preparation equipment.

5.2.2 Balances

5.2.2.1 Analytical Capable of weighing 0.1 mg

5.2.2.2 Top-loading Capable of weighing 10 mg

5.3 Filtration apparatus

5.3.1Glass graduated cylinder

5.3.2 Whatman GF/A filter or equivalent

5.3.3 Vacuum pump

5.3.4 Filtration apparatus

5.3.4.1 Stainless-steel vacuum manifold for processing large volume sample

5.3.4.2 Glass filtration funnels

5.3.5 Glass vials (40 mL)

5.4 Sample loading and extraction apparatus

Note: HLB is selected as the sorbent material for this method due to its capacity to capture the suite of analytes listed within this method. Other SPE sorbents may be used, provided that the laboratory establishes the elution conditions and meets the requirements in Section 7.1.3 with that SPE sorbent as an integral part of the analysis.

5.4.1

SPE 12-position vacuum, manifold set (AH0-6023, Phenomenex) (for aqueous samples)

5.4.2

HLB 6cc (500mg) cartridges (Waters, Milford, MA) (for aqueous samples)

5.4.3

Three-station SPE disk manifold (47 mm) (Affinisep, Miami, FL, USA) or equivalent (for Chemcatcher samples)

5.4.4

Attract SPE disks with HLB sorbent (47 mm diameter, SKU# 1144L92) (Thomas Scientific, Swedesboro, NJ, USA) (for Chemcatcher samples)

5.4.5

Pasteur Pyrex borosilicate glass pipettes

5.4.6

Disposable culture tubes 13×100 mm (Fisher 14-961-27)

5.4.7

Autosampler vials, with Teflon-lined screw caps

5.5 Concentration apparatus

5.5.1

TurboVap II concentration station (closed cell concentrator) with concentration tubes, or equivalent

5.5.2 Nitrogen manifold set-up, providing nitrogen stream

5.5.3 Clamp stand

5.6 Liquid chromatograph

Must meet all of the performance specifications in Section 7.

5.6.1 LC instrument

An Agilent 1260 Infinity HPLC system (Santa Clara, CA, USA) coupled with an Agilent 6470 triple quadrupole mass spectrometer or equivalent.

5.6.2 LC column

An Agilent Eclipse Plus C18 column (2.1×50 mm, 1.8 µm dp) or equivalent.

5.7 Data system

Capable of collecting, recording, storing, and processing mass spectrometry data.

5.7.1 Data acquisition

The signal at each specified *m/z* value must be collected repetitively throughout the monitoring period and stored on a mass storage device.

5.7.2 Response factors and multipoint calibrations

The data system must record and maintain lists of response factors and multipoint calibrations.

6. Reagents and Standards

6.1 Reagent water

Millipore water or equivalent (18 MΩ cm)

6.2 Extraction reagents

6.2.1 Acetone

Optima grade or equivalent (A929-4 Fisher)

6.2.2 Methanol

Optima grade or equivalent (A454-4 Fisher)

6.2.3 DCM

Optima grade or equivalent (D151-4 Fisher)

6.2.4 Acetonitrile

HPLC grade or equivalent (A998SK-4, Fisher)

6.2.5 Isopropanol (IPA)

Optima grade or equivalent (A461-1, Fisher)

6.3 Stock solutions

Prepare from materials (labelled or native) of known purity and composition or purchase as solutions or mixtures with certification to their purity, concentration, and authenticity. If the chemical purity is 98% or greater, the weight may be used without correction to calculate the concentration of the standard.

6.4 Calibration standards

Combine and dilute the stock solutions to produce a series of solutions with various concentrations for building calibration curves to quantify the concentration of the analyte.

7. QUALITY CONTROL

7.1

Each laboratory using this Method must operate a QC program. The minimum requirements of this program consist of an IDC and ongoing QC. These QC criteria are discussed in the following sections and are summarized in Tables 11 and 12. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the Method or if corrective actions are needed.

7.1.1

The laboratory must perform an IDC to confirm low system background, demonstrate IPR, determine MDL, and confirm the accuracy of the calibration standards. This demonstration is given in Section 7.2.

7.1.2

The laboratory must meet all ongoing QC requirements given in Section 7.3 for continued performance.

7.1.3

In recognition of advances that are occurring in analytical technology, and to overcome matrix interferences, the laboratory is permitted certain options to improve separations or lower the costs of measurements. These options include alternate extraction, concentration, and cleanup procedures (e.g., with alternate SPE or SPE disk sorbent media), and changes in columns and detectors. If an analytical technique other than the techniques specified in this Method is used, that technique must have a specificity equal to or greater than the specificity of the techniques in this Method for the analytes of interest. Alternate determinative techniques, such as the substitution of spectroscopic or immuno-assay techniques, and changes that degrade method performance, are not allowed.

7.2 Initial Demonstration of Capability (IDC)

An IDC must be performed by the laboratory prior to independently analyzing samples using this Method. The IDC must be repeated if other changes occur (e.g., significant change in procedure, change in personnel). Prior to conducting IDC, the analyst must establish retention times in Section 8.2 and meet the calibration requirements in Section 8.3.

7.2.1 Demonstrate low system background

Analyze a method blank immediately after injecting the highest calibration standard in the selected calibration range. Background concentrations of all analytes must be less than the MDL (Tables 7 and 8). If any pesticide analyte is found in the method blank at concentrations greater than or equal to the MDL, analysis of samples must be halted until the sample batch is re-extracted and the extracts re-analyzed, and the blank associated with the sample batch shows no evidence of contamination at these levels.

7.2.2 Demonstrate precision and recovery

For aqueous samples, at least three IPRs, i.e., 1-L aliquots of reagent water spiked with an appropriate amount of the native and labeled compounds, are used. For passive sampler samples, at least three spiked Chemcatchers are used. All sample processing steps that are to be used for processing samples, including preparation and extraction (Section 9), must be included in this procedure. Compute R% and RSD for each compound using the internal standard. For each pesticide and labeled recovery standard compound, R% must be within a range of 50-150 for both matrices, and RSD must be within ±30% for aqueous samples and

±50**%** for Chemcatcher samples (Tables 5 and 6). Only analytes that meet these criteria shall be included in the laboratory report.

7.2.3 Determine Method Detection Limit (MDL)

The laboratory must establish MDLs for analytes using the MDL procedure at 40 CFR 136, appendix B. Select a spiking level, typically 2-10 times the estimated MDL; the IDL is used as the estimated MDL for this purpose. Process a minimum of seven spiked samples (reagent water and the Attract SPE disk without any pre-exposure) and seven method blank samples through all steps of the method. The samples used for the MDL must be prepared in at least three batches on three separate calendar dates and analyzed on three separate calendar dates. Preparation and analysis may be on the same day.

7.2.3.1

Compute the MDL_s based on the spiked samples as follows:

$$MDL_s = t_{(n-1,1-\alpha=0.99)} \times S_s$$

Where MDL_s = the method detection limit based on spiked samples; $t_{(n\text{-}1,\ 1\text{-}\alpha\ =\ 0.99)}$ = the Student's *t*-value appropriate for a single-tailed 99th percentile t statistic and a standard deviation estimate with n-1 degrees of freedom. $t_{(n\text{-}1,\ 1\text{-}\alpha\ =\ 0.99)}$ =3.143 for seven replicates. S_s = sample standard deviation of the replicate spiked sample analyses.

7.2.3.2

If all of the method blanks for an individual analyte give numerical results, compute the MDL_b based on the method blanks as follows:

$$MDL_b = \bar{X} + t_{(n-1,1-\alpha=0.99)} \times S_b$$

Where MDL_b = the method detection limit based on method blanks. $\bar{X}$ = mean of the method blank results (use zero in place of the mean if the mean is negative). $t_{(n\text{-}1,\ 1\text{-}\alpha\ =\ 0.99)}$ = the Student's *t*-value appropriate for a single-tailed 99th percentile t statistic and a standard deviation estimate with n-1 degrees of freedom. $t_{(n\text{-}1,\ 1\text{-}\alpha\ =\ 0.99)}$ =3.143 for seven replicates. S_s = sample standard deviation of the replicate method blank sample analyses.

7.2.3.3

Select the greater of MDL_s or MDL_b as the MDL. The MDL_s data as MDL are provided in Tables 7 and 8.

7.2.4 Limit of Quantification (LOQ)

The limit of quantification (LOQ) is the smallest concentration that produces a quantitative result with known and recorded precision and bias. In this method, the LOQ is established by each laboratory and must be equal to or greater than the MDL and within the calibration range. For the purpose of this method, the terms “minimum level”, “reporting limit”, “quantification limit”, and “limit of quantification” are used synonymously.

7.3 Ongoing QC requirements

The QC elements listed in this section must be included when processing and analyzing samples.

7.3.1 Method blank

Analyze a method blank per sample batch (20 or fewer field samples). Analyses of method blanks are required to demonstrate no adverse contamination in the sample preparation and analysis procedure. All samples must be associated with an uncontaminated method blank before the results for those samples may be reported or used for permitting or regulatory compliance. Confirm that the method blank is free from contamination by that the concentration of all analytes in the method blank is less than the MDL.

7.3.2 Perform the CCV

The CCV solution, a standard solution of pesticides prepared in a manner similar to the calibration standards (e.g., a midpoint calibration standard), is analyzed at the beginning of each sample batch to monitor the instrument stability in comparison to the initial calibration curve. The CCV solution must be analyzed every 24 h during the sample analysis period. The CCV must be within 70-130% of the expected concentration for each compound, and the retention time (RT) of each analyte must be within ± 0.2 min of the target RT. Samples must be analyzed between acceptable CCV analyses. If a CCV fails the QC criteria, the instrument is recalibrated (See Sections 8.2-8.3) and the affected samples are reanalyzed.

7.3.3 Inject solvent blank

Inject a solvent blank (in this case hexane) after injecting the calibration standards and the CCV solution. Inject a solvent blank every 7 samples or after every suspect dirty sample (at the discretion of the analyst). If analytes are detected in the solvent blank, the source of the carryover is determined, and the sample set is reanalyzed.

7.3.4 LCS

Analyze an LCS per sample batch. The LCS is spiked with similar analytes at the same concentrations as in the MS and is processed identically to the samples. The R% must be within the range of 50-150. When the results of the MS analysis (Section 7.3.7) indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. If, however, any individual R% falls outside the range for recovery, system performance is unacceptable for that compound. Troubleshoot and reestablish IDC (Section 7.2).

7.3.5 Check instrument sensitivity

Check and maintain the LC/MS/MS instrument for high sensitivity following the instrument manufacturer's instructions. Prior to the analysis of any standards and samples, perform mass calibration and sensitivity evaluation using autotune features of the mass spectrometer. Perform a checktune every 24 h during the analysis. Clean the spray chamber in the LC/MS/MS interface every 24 h and after injection of a suspect dirty sample (at the discretion of the analyst). Inject a mid-point calibration standard and a solvent blank to check the instrument performance every 24 h. Instrument sensitivity must be greater than or equal to 50% of the initial calibration level. If the instrumental sensitivity becomes less than 50%, analysis of samples must be halted until the sensitivity of the instrument is resumed.

7.3.6 Recovery standards

The laboratory must spike all samples with labeled recovery standard compounds to monitor method performance. The R% of these labeled compounds must be within the range of 50-150%. If the R% falls outside the range, the sample results are invalid, and the sample batch is re-extracted and the extracts re-analyzed.

7.3.7 MS

Analyze a laboratory MS per sample batch. The R% must be within the range of 50-150. If the R% of MS falls outside of the range, check the R% of the LCS (Section 7.3.4). If the R% of LCS still meets the acceptance criteria, no corrective action is required. Document the matrix spike failure, and flag the associated sample to indicate potential matrix interference.

7.3.8 Matrix spike duplicates (MSD) or laboratory replicate

Analyze a minimum of one MSD or one laboratory replicate per sample batch. The RSD between the replicate samples must be within ±30% for aqueous samples and ±50% for Chemcatcher samples for each analyte included in IDC. If the RSD fails to meet the acceptance criteria, the sample batch is re-extracted and the extracts re-analyzed.

7.3.9 Verification of MDL

If the method is modified in a way that could reasonably affect its sensitivity – such as a change in instrumentation, extraction technique, or quantitation procedure – a new MDL must be established following the initial MDL procedure. Additionally, if method performance data indicate a sustained decline – such as consistently low spike recoveries, declining calibration response, more than 5% of method blanks or spiked samples failing to meet criteria – the MDL must be re-determined. Independently, if the laboratory believes the sensitivity of the method has changed significantly, re-determine MDL. At least once every thirteen months, re-calculate MDL_s and MDL_b from the collected spiked samples and method blank results. If the verified MDL is within 0.5 to 2.0 times the existing MDL, and fewer than 3% of the method blank results (for the individual analyte) have numerical results above the existing MDL, then the existing MDL may optionally be left unchanged. Otherwise, adjust the MDL to the new verification MDL. The range of 0.5 to 2.0 approximates the 95th percentile confidence interval for the initial MDL determination with six degrees of freedom.

7.3.10 OPR

Determine the precision and recovery using at least three OPR standards at least every thirteen months. If the verified precision and recovery are within the range of 50-150% of the existing results, the existing procedure may optionally be left unchanged. Otherwise, analysis of samples must be halted until the precision and recovery are resumed.

8. CALIBRATION AND STANDARDIZATION

8.1 Establish operating conditions

8.1.1 Mass spectrometer instrumental parameters

Optimize the precursor and product ions using a standard solution of the target analytes at high concentration (e.g., 1~4 mg/mL solvent) following the instrument manufacturer's instructions. The optimized operating conditions for the Agilent 6470 triple quadrupole mass spectrometer used in single-laboratory evaluation and followed during multi-laboratory evaluation, operated in positive polarity electrospray ionization (ESI) mode under multiple reaction monitoring (MRM) mode:

- Gas temperature: 350 °C
- Gas flow: 11 L/min
- Nebulizer: 40 psi
- Sheath gas heater: 375 °C
- Sheath gas flow: 11 L/min

- Capillary: 4000 V
- Mass spectrometer 1st quadrupole temperature: 100 °C
- Mass spectrometer 3rd quadrupole temperature: 100 °C

8.1.2 Chromatographic conditions

The method's chromatographic conditions are optimized for compound separation and sensitivity. The chromatographic conditions for this Method using the Agilent 1260 Infinity HPLC system and column used in single laboratory evaluation and followed during multi-laboratory evaluation, are specified below:

- Analytical column: Agilent Eclipse Plus C18 column (2.1×50 mm, 1.8 µm particle size)
- Mobile phases: A: water (5mM formic acid), B: acetonitrile. The LC gradient program is listed in Table 3.
- Flow rate: 0.4 mL/min
- Injection volume: 10 µL.

8.2 Establish stable RT

Inject a midpoint calibration standard under optimized LC/MS/MS conditions to determine the RTs of each method analyte. The RTs of analytes observed from all participating laboratories during the Multi-Laboratory Method Validation are listed in Table 4. After establishing RTs, ensure that the RT of each analyte is within ± 0.2 min of the target RT in the midpoint calibration standard.

Note: Analyte retention orders determined in this step may differ slightly from that listed in Table 4, but retention times and MS ions are sufficient for laboratories to identify analytes and establish chromatographic methods.

8.3 Initial calibration

Calibration is performed using a series of calibration solutions, with at least five (and up to nine) calibration standards within the quantitation range, with the lowest standard at or below LOQ or the lowest concentration for which quantitative data are to be reported.

Build internal standard calibration curves using instrumental software. The calibration range used from participating laboratories are specified in Table 4 (0.1 to 400 ng/mL or other concentrations as appropriate). The calibration curve is built based on the areas of the characteristic peaks of the same RTs of the corresponding peaks in the calibration standard. The R^2 of the linear calibration curve must be greater than or equal to 0.99. If the R^2 is less than 0.99 for a majority of compounds, inspect the system for problems and re-analyze the calibration

solutions. Alternatively, preparation and analysis of fresh calibration standards or performing a new initial calibration.

8.4 Calibration frequency

Each LC/MS/MS system must be calibrated whenever the laboratory takes an action that changes the chromatographic conditions and experiences a recovery action for low sensitivity.

9. PROCEDURE

9.1

Water sample filtration, loading, and elution (for aqueous samples only. Go to Section 9.2 for Chemcatcher samples.)

9.1.1 Sample filtration

9.1.1.1

Measure the sample volume with a graduated cylinder and record the volume.

9.1.1.2

Place a GF/A 1.6 µm filter on the filtration apparatus.

9.1.1.3

Turn on the vacuum in the filtration system and begin transferring the sample into the filtration funnel. Ensure that the water level of the sample does not exceed one-third of the filtration funnel's capacity (approximately 100-150 mL). Exercise caution when working with samples containing high levels of suspended solids, as the filter may become clogged. In such cases, replace the filter with a new one as needed until the filtration process is complete for the sample.

9.1.1.4

Transfer the filtered sample into a clean glass flask or bottle for loading onto the SPE cartridge.

9.1.2 Conditioning the HLB cartridge

9.1.2.1

Place the Oasis HLB SPE cartridge on a vacuum manifold and place the waste vessel container under the manifold.

9.1.2.2

Pre-condition the SPE cartridge by sequentially adding DCM (10 mL), followed by acetone (10 mL), and reagent water (10 mL). Add the first solvent into the barrel (6 mL) of the HLB cartridge. Turn on the vacuum pump, maintaining a pressure of 5~10 psi. Open the manifold flow control valve. Once a small amount of solvent passes through the cartridge, turn off the vacuum pump, and allow the solvent in the cartridge barrel to be pulled through the cartridge by gravity. This technique prevents the solvent from passing through the column too quickly. Turn the vacuum pump on and off to control the flow, continuing to add all three solvents (10 mL each) sequentially to the cartridge barrel until conditioning is complete. Allow the sorbent to soak with each solution for approximately 30 s.

9.1.2.3

Once pre-conditioning begins, ensure that the cartridge does not dry out until loading the water sample.

9.1.3 Sample loading

9.1.3.1 Cleaning the sample transfer tubing

Clean the sample transfer tubing, typically made of polypropylene or Teflon, both before and after loading the sample.

Begin by cleaning the external surface of the sample transfer tubing using soapy water, followed by sequential rinses with reagent water, methanol, acetone, DCM, hexane, and acetone.

For internal cleaning, place a used SPE cartridge on the vacuum manifold, insert the adapter, and submerge the opposite end of the cartridge into a solvent container until it reaches the bottom. Turn on the vacuum and unlatch the manifold flow control valve, enabling the solvent to pass through the sample transfer tubing at an approximate flow rate of 10 mL/min. Clean the sample transfer tubing in the order of soapy water, followed by sequential rinses with reagent water, methanol, acetone, DCM, and hexane. Before transitioning to reagent water, rinse the external portion of the sample transfer tubing submerged in soapy water with reagent water. No such rinsing is required before switching to the subsequent solvents in the cleaning sequence.

9.1.3.2 Spiking Recovery Standard (RS) solution

Spike a predetermined amount of RS solution into the water sample. To keep the recovery standard concentration within environmentally relevant ranges, ensure that the recovery standard concentration in the extracted sample is lower or equal to the concentration of the midpoint of the calibration curve assuming 100% recovery. For LC/MS/MS analysis, use

atrazine-$^{13}C_3$ and imidacloprid-d_6 (or other labeled compounds as appropriate) as the RSs. After analysis, the laboratory should confirm and adjust the spiked concentration, if necessary, to ensure that the spiked recovery standard concentration is environmentally relevant.

9.1.3.3

Set up an SPE loading system by assembling a stainless-steel vacuum manifold, a vacuum pump, and a dedicated wastewater container for handling large-volume samples.

9.1.3.4

Position the conditioned HLB SPE cartridge onto the stainless-steel vacuum manifold with the flow control valve remaining closed. Insert the SPE cartridge adapter into the cartridge and submerge the opposite end of the cartridge into a solvent container until it reaches the bottom. Turn the vacuum on and gradually open the flow control valve to direct the sample into the SPE cartridge, maintaining control over the flow rate through the SPE cartridge at approximately 10 mL/min.

Note: Loading the aqueous phase onto SPE cartridges, even after filtering, could be slow if colloidal material in the matrix clogged the pore spaces of the cartridges sufficiently.

9.1.3.5

Once the sample is loaded, leave the vacuum pump running for up to 15 min to dry the sorbent.

9.1.3.6

Wrap the cartridge in aluminum foil and store it at -20 °C until extraction. Some of this method's analytes are stable on HLB SPE cartridges for at least 20 months (Reference 6); however, not all analytes have been evaluated.

9.1.4 Elution of analytes from SPE cartridge

9.1.4.1

Detach the cover assembly of the SPE manifold, remove the waste container from the chamber, and place the collection rack assembly into the chamber. Arrange the disposable 10 mL collection glass tubes on the rack and cover the chamber with the assembly. Ensure that the delivery tips are properly inserted into all the collection tubes.

9.1.4.2

Insert the tip of the loaded SPE cartridge into the Luer stopcock valve on the manifold. If the cartridge, wrapped in aluminum foil, was stored in the freezer after sample loading, allow it to reach room temperature before placing it on the manifold.

9.1.4.3

Elute the loaded SPE cartridge by passing a solvent mixture of acetone/DCM (10 mL, 1:1 by volume) through it at a controlled flow rate of 1 mL/min. Since a commonly used collection glass tube has a capacity of 10 mL, divide the eluting solution into two portions (5 mL each) to add to the cartridge, preventing overflow. Combine the two extract portions in a Turbovap concentrator tube. Additionally, rinse the collection tube with the acetone/DCM solvent mixture, directing the rinsate into the concentrator tube. The extract should be processed (see Section 9.3) immediately after the elution. If it is not possible, the concentrator tube may be covered with aluminum foil to prevent contamination and to keep it from drying out and stored at −20 °C for a maximum of 72 h until processing.

9.2

HLB disk (Chemcatcher passive sampler sequestration media) sample cleaning, conditioning, and extraction (go to Section 9.1 for aqueous samples)

9.2.1 Cleaning and conditioning

9.2.1.1

Set up an HLB disk loading system by assembling an SPE disk manifold (47 mm), a vacuum pump, and a dedicated wastewater container for handling large-volume samples.

9.2.1.2

Assemble the support base, an HLB disk, and a funnel on the manifold. The solvents for cleaning and conditioning include acetone (10 mL), isopropyl alcohol (IPA, 10 mL), methanol (10 mL), and reagent water (20 mL). Add each solvent sequentially into the funnel, turn on the vacuum pump, and gently open the manifold flow control valve to allow the solvent to pass through the disk. Control the flow to let the solvent soak into the disk for 1 min before being drawn through. Repeat this procedure for each solvent, preventing the disk from drying between conditioning steps.

Note: This method is usable irrespective of the number of stations on the disk manifold (Section 5.4.3); however, having fewer stations requires more cleaning between samples.

9.2.1.3

Keep the conditioned disk in reagent water in a closed container and store it at 4 °C until deployment for passive sampling or use for matrix spiking. Analytes sequestered to similar passive samplers have been shown to be stable for up to 6 years at -20 °C (Reference 7); however, Chemcatcher disks were not evaluated, nor were all analytes of this Method.

9.2.2 Elution of analytes from HLB disk

Insert a collection vial (40 mL) into the SPE disk manifold.

Assemble the SPE apparatus and place the HLB disk on the support base. If the disk was stored in the fridge, allow it to reach room temperature before placing it on the manifold.

Elute the HLB disk by passing a solvent mixture of methanol/acetonitrile (10 mL, 1:1 by volume) through it. Control the flow to allow the solvent to soak into the disk for 1 min before being drawn through.

Remove the filtration support, take the collection vial out of the manifold, cover the vial, and store it at −20 °C until further processing (see Section 9.3).

9.3 Concentration of the extract

9.3.1

Evaporate the solvent volume of extracts from Sections 9.1 and 9.2 to approximately 1 mL on the Turbovap using a gentle stream of nitrogen. Add acetonitrile (~5 mL) three times during the concentration for solvent exchange. Ensure that the extract does not dry out.

Note: Concentration of eluted extracts to 1 mL final volume for instrumental analysis could also be slow.

9.3.2

Further concentrate the extract to less than 0.5 mL. Transfer the concentrated extract into an autosampler vial using a glass disposable pipette. Rinse the concentrator tube three times with small amounts of acetonitrile and transfer the rinsate into the autosampler vial. If the solution volume exceeds 1 mL, reduce it by blowing down the nitrogen to below 1 mL. (The 1 mL volume can be estimated by comparing it with a vial containing a known 1 mL solution.)

9.3.3

Spike the IS solution into the extract. To keep the IS concentration within environmentally relevant ranges, ensure that the IS concentration in the extracted sample is lower or equal to the concentration of the midpoint of the calibration curve assuming 100% recovery. For LC/MS/MS analysis, use thiacloprid-d_4, and myclobutanil-d_4 (or other labeled compounds as appropriate). After analysis, the laboratory should confirm and adjust the spiked concentration, if necessary, to ensure that the spiked recovery standard concentration is environmentally relevant.

9.3.4

Add acetonitrile into the vial to bring the final volume to 1 mL.

9.3.5

Filter the extract through a 0.2 µm syringe filter and transfer it to a new autosampler vial.

9.3.6

Store the extracts in a freezer at −20 °C.

9.4 Instrumental analysis

9.4.1

Analyze the samples on an LC/MS/MS system. Calibration and standardization must be performed and verified prior to analysis of the samples as noted in Section 8.

9.4.1.1

Load the calibration standard solutions (including CCVs), the solvent blank (reagent water), the QA/QC samples including LCS samples, MS/MSD samples, and actual samples on the autosampler of the LC instrument.

9.4.1.2

Analyze a solvent blank and a mid-point calibration standard solution (i.e., the CCV) to check the system as noted in Sections 7.3.3 and 7.3.2.

9.4.1.3

Inject the calibration solutions from low to high concentrations. Build and evaluate initial calibration curves for the pesticides and the recovery standards as noted in Sections 8.2 and 8.3.

9.4.1.4

Inject at least one solvent blank (at the discretion of the analyst) after injection of the calibration solutions to avoid any carryover contamination.

9.4.1.5

Inject QA/QC samples, including LCS, MS, MSD or laboratory replicate samples, prior to injection of sample extracts. Inject the clean solvent intermittently during injection sequences for QA/QC samples, and between each dirty sample extract (at the discretion of the analyst) as noted in Section 7.3.3.

9.4.2 Continuing calibration verification

Inject a midpoint concentration of calibration standard (e.g., 50 ng/mL for LC/MS/MS) to verify initial calibration and RT stability every 24 hours during the analytical sequence for sample extracts.

10. CALCULATIONS AND REPORTING

10.1 Quantitation based on internal calibration curve

10.1.1

Quantitation is based on the areas of the characteristic peaks as compared to the areas of the corresponding peaks at the same RTs in the calibration standard, using internal calibration procedures.

10.1.2

Once a target compound has been identified based on the RT, quantification ion and confirmation ion, the quantitation of the compound is based on the integrated abundance of the quantification ion from the extracted ion chromatogram.

Table 4 lists example RTs for the target analytes. The RTs listed in Table 4 are provided for illustrative purposes only. Each laboratory must determine RTs and RT windows for its specific application of the method.

10.1.3

Use the integration produced by the software to determine if the integration is correct because the software should produce more consistent integrations. However, manual integrations may be necessary when the software does not produce proper integration results due to improper baseline selection, missing peaks, coelution, partial integration of peaks, etc. The analyst is responsible for ensuring that the integration is correct whether performed by the software or done manually.

10.1.4

Multi-point (5 to 9 points) calibration curves are constructed by using linear regression from the calibration standards. The selection of standards depends on sample concentrations and instrument performance. The correlation coefficient for each standard curve has to be greater

than or equal to 0.99 to be accepted. The RRF for each compound is calculated from the calibration curve.

10.1.4.1 RRF calculation

Calculate the RRF for each selected compound relative to one of the internal standards as follows:

$$RRF = \frac{C_i \times A_c}{C_c \times A_i}$$

where C_c = concentration of the selected compound, in nanograms per milliliter; A_i = peak area of the quantitation ion for the internal standard; C_i = concentration of the internal standard, in nanograms per milliliter; and A_c = peak area of the quantitation ion for the selected compound.

10.1.5

The concentration (ng/mL) of the compound in the extract is calculated from the RRF by the quantitative analysis software as follows:

$$C_{ex} = \frac{C_i \times A_{ex}}{RRF \times A_i}$$

where C_{ex} = the concentration (ng/mL) of the compound in the extract. A_{ex} = peak area of the quantitation ion for the selected compound in the extract.

10.2

Using the concentration in the extract determined above, compute the percent recovery of the recovery standards using the following equation:

$$Recovery\ (\%) = \frac{C_{ex} \times V_{ex}(ng)}{expected\ mass\ (ng)} \times 100$$

where V_{ex} = the extract volume (mL).

10.2.1

The concentration of a native pesticide in the aqueous phase of the sample is computed using the concentration of the compound in the extract and the volume of water extracted (V_s, L), as follows:

$$concentration\ in\ aqueous\ phase\ \left(\frac{ng}{L}\right) = \frac{C_{ex} \times V_{ex}}{V_s}$$

The concentration of a native pesticide in a passive sampler is reported as ng/Chemcatcher.

10.3

If any pesticide exceeds the calibration range of the system, dilute the sample extract by the factor necessary to bring the concentration within the calibration range, and add an additional internal standard solution to the diluted extract to maintain the same concentration as in the calibration standards (e.g., 50 ng/mL or other concentrations as appropriate), and analyze an aliquot of this diluted extract. The pesticide concentration in the extract must be back-calculated from the diluted extract to facilitate the calculation of the concentration in the aqueous phase.

10.4 Reporting of data results

10.4.1

Report the result for each pesticide in each sample, method blank, and matrix spikes at or above the LOQ to 3 significant figures, in the concentration of the original matrix (i.e., ng/L for aqueous samples, ng/Chemcatcher for passive samplers). Report the result below the LOQ in each sample as <LOQ.

10.4.2

Report the percent recovery of the recovery standards (RS).

11. METHOD PERFORMANCE

Performance data and related information from the Multi-Laboratory Validation Study are provided in this SOP only for example and guidance. These data do not represent the required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. Performance data must not be used as absolute QC acceptance criteria for the purposes of laboratory QC or accreditation.

NOTE: The laboratory should establish an in-house target analyte list for the application of this method. Some analytes shown in multi-laboratory evaluation to be problematic across participating laboratories, due to poor and/or variable recoveries, are flonicamid (LC analyte

#1), thiamethoxam (LC analyte #4), sulfoxaflor (LC analyte #5), and tolfenpyrad (LC analyte #35). The laboratory should use this information to prioritize optimization of analytes to be measured by this method.

11.1

Table 1 lists the analytes evaluated for this Method, along with their CAS Numbers, chemical classes, and pesticide types. Internal and recovery standards are included.

11.2

Table 2 provides information on the LC/MS/MS instruments used by participating laboratories, including details about the LC/MS/MS systems, columns, and operating conditions.

11.3

Table 3 lists representative RTs, precursor ions, fragmentor voltage, product ions, collosion energies, calibration ranges, and IDLs for the analytes.

11.4

Table 4 lists concentrations of solutions of a selected analyte purchased from an alternate vendor at the specified levels, and measured against the calibration solutions obtained from a common vendor and used by all participating laboratories.

11.5

Tables 5A-C contain performance data of individual laboratories for analytes on spiked reagent water (aqueous LCS). Table 5X contains performance data summarized across all laboratories for the aqueous LCS. Data is provided for guidance purposes.

11.6

Tables 6A-C contain performance data of individual laboratories for analytes on spiked blank Chemcatcher disk samples (Chemcatcher passive sampler LCS). Table 6X contains performance data summarized across all laboratories for Chemcatcher LCS. Data is provided for guidance purposes.

11.7

Tables 7-8 contains Method Detection Limit (MDL) information for individual laboratories for the aqueous and Chemcatcher matrices. Data is provided for guidance purposes.

11.8

Table 9 contains performance data on matrix spikes (1L river water) from individual laboratories. Data is provided for guidance purposes.

11.9

Table 10 contains performance data for matrix spikes (Chemcatcher disks) exposed to river water in the laboratory for 14 d. Data is provided for guidance purposes.

12. Pollution Prevention and Waste Management

12.1 Pollution Prevention

12.1.1

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory operations. Whenever feasible, laboratory personnel should use pollution prevention techniques to address waste generation. When waste cannot be reduced at the source, recycling is the next best option.

12.1.2

The pesticides in this method are used in extremely small amounts and pose little threat to the environment when managed properly. Standards should be prepared in volumes consistent with laboratory use to minimize the disposal of excess volumes of expired standards.

12.1.3

For information about pollution prevention applied to laboratories and research institutions, consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Governmental Relations and Science Policy, 1155 16th Street NW, Washington DC 20036, 202/872-4477.

12.2 Waste Management

12.2.1

The laboratory is responsible for complying with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, for protecting the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. An overview of requirements can be found in the *Environmental Management Guide for Small Laboratories* (EPA 233-B-98-001).

12.2.1.1

All liquid waste produced during the extraction is considered “organic waste” and must be placed in thick-walled carboys and disposed of according to local regulations.

12.2.1.2

The solid-waste stream produced during sample analysis comprises SPE cartridges, extracted Chemcatcher passive samplers, and assorted disposable glassware (such as glass pipettes and vials). Once the solid-waste items have been dried in a hood (that is, until no organic solvent remains), they can be disposed of according to local policy.

12.2.2

For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel and Less is Better-Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

13. REFERENCES

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14. TABLES AND VALIDATION DATA

The Tables listed below include performance results from three laboratories (designated as Laboratories A-C), including those from the Single-Laboratory Method Validation where the SOP was developed.

Table 1. Analyte list with Chemical Abstracts Service (CAS) numbers, chemical classes, and pesticide types, arranged by increasing Retention Time (RT) observed in the Single Laboratory Validation.

#	Analyte[1]	CAS	Chemical Class	Pesticide Type
1	Flonicamid	158062-67-0	Pyridinecarboxamide	Insecticide
2	Dinotefuron	165252-70-0	Neonicotinoid	Insecticide
3	Thiabendazole	148-79-8	Benzimidazole	Fungicide
4	Thiamethoxam	153719-23-4	Neonicotinoid	Insecticide
5	Sulfoxaflor	946578-00-3	Sulfoximine	Insecticide
6	Clothianidin	210880-92-5	Neonicotinoid	Insecticide
7	Imidacloprid-d_6 (RS)	-	Neonicotinoid	Insecticide
8	Imidacloprid	138261-41-3	Neonicotinoid	Insecticide
9	Acetamiprid	135410-20-7	Neonicotinoid	Insecticide
10	Tricyclazole	41814-78-2	Triazole	Fungicide
11	Thiacloprid-d_4 (IS)	-	Neonicotinoid	Insecticide
12	Thiacloprid	111988-49-9	Neonicotinoid	Insecticide
13	DCPMU	3567-62-2	Phenylurea	Herbicide
14	Cymoxanil	57966-95-7	Acetamide	Fungicide
15	Ethaboxam	162650-77-3	Benzamide	Fungicide
16	Imidacloprid Urea	120868-66-8	Neonicotinoid	Insecticide
17	Atrazine-$^{13}C_3$ (RS)	1912-24-9	Triazine	Herbicide
18	Carboxin	5234-68-4	Triazine	Herbicide
19	Cyantraniliprole	736994-63-1	Anthranilic Diamide	Insecticide
20	DCPU	2/8/2327	Phenylurea	Herbicide
21	Penoxsulam	219714-96-2	Triazolopyrimidine	Herbicide
22	Chlorantraniliprole	500008-45-7	Anthranilic Diamide	Insecticide
23	Fluridone	59756-60-4	Pyridine	Insecticide
24	Desthio-Prothioconazole	178928-70-6	Triazole	Fungicide
25	Myclobutanil-d_4 (IS)	88671-89-0	Triazole	Fungicide
26	Mandipropamide	374726-62-2	Carboxylic Acid Amide	Fungicide
27	Ibuprofen-d_5 (IS)	15687-27-1	Nonsteroidal Anti-inflammatory Drug (NSAID)	-

#	Analyte[1]	CAS	Chemical Class	Pesticide Type
28	Methoxyfenozide	161050-58-4	Diacylhydrazine	Insecticide
29	Oxathiapiprolin	1003318-67-9	Piperidinyl-thiazole-isoxazoline	Fungicide
30	Tebufenozide	112410-23-8	Diacylhydrazine	Insecticide
31	Oryzalin	19044-88-3	Dinitroaniline	Herbicide
32	Cyzaofamid	120116-88-3	Imidazole	Fungicide
33	Diuron	330-54-1	Phenylurea	Herbicide
34	Penthiopyrad	183675-82-3	Carboxamide	Fungicide
35	Tolfenpyrad	129558-76-5	Pyrazole	Insecticide

[1] Atrazine-$^{13}C_3$ and imidacloprid-d_6 were used as Recovery Standards (RS), and thiacloprid-d_4, myclobutanil-d_4, and ibuprofen-d_5 were used as Internal Standards (IS).

Table 2_i. Liquid Chromatography-Tandem Mass Spectrometry (LC/MS/MS) instrumentation and operating conditions across participating laboratories

Laboratory	A	B	C
Manufacturer	Agilent	Agilent	Agilent
HPLC/MS/MS model	1260 Infinity HPLC system coupled with an Agilent 6470 triple quadrupole mass spectrometer	1260 Infinity II HPLC coupled with an Agilent 6495 triple quadrupole mass spectrometer	1290 Infinity HPLC system coupled with an Agilent 6495B triple quadrupole mass spectrometer
Column model	Agilent Eclipse Plus C18 column	Agilent Zorbax Eclipse Plus C18	Phenomenex C18 column
Column dimensions	50 × 2.1 mm, 1.8 µm	100 × 2.1 mm, 1.8 µm	50 x 2.1mm, 1.6 µm
Mobile phase	A: water (5mM FA), B: acetonitrile	A: water (5mM FA), B: acetonitrile	A: 95% Aqueous, 5% acetonitrile, B: acetonitrile
Ionization mode	Electrospray (Positive mode)	Electrospray (Positive mode)	Electrospray (Positive mode)
Data analysis software	MassHunter. E. 08.00	MassHunter	MassHunter

Table 2_ii. Liquid Chromatography-Tandem Mass Spectrometry (LC/MS/MS) mobile phase timetables across participating laboratories

-	**Laboratory A and B**			**Laboratory C**		
#	Time (min)	A: water, 5 mM formic acid	B: acetonitrile	Time (min)	A: 95% aqueous, 5% acetonitrile	B: acetonitrile
1	2.00	97.00%	3.00%	1.00	95.00%	5.00%
2	4.00	50.00%	50.00%	4.50	0.00%	100.00%
3	6.00	50.00%	50.00%	6.00	0.00%	100.00%
4	8.00	5.00%	95.00%			
5	10.00	5.00%	95.00%			
6	10.01	97.00%	3.00%			
7	15.00	97.00%	3.00%			

Table 3. Instrumental parameters for the calibration of Liquid Chromatography-Tandem Mass Spectrometry (LC/MS/MS) method. The ionization mode is positive Electrospray Ionization (ESI). The lower limit of the calibration range represents the Instrumental Detection Limit (IDL) of the LC/MS/MS method for each analyte, with concentrations expressed as ng/mL extract from each laboratory. Analytes that did not elute in the same order as those from Laboratory A are highlighted in yellow and marked with an asterisk.

-	-	Laboratory A								Laboratory B								Laboratory C							
#	Analyte	Pre Ion[1] (*m/z*)	Frag Voltage[2] (V)	Prod Ion 1 (*m/z*)[3]	Prod Ion 2 (*m/z*)	Collision Energy 1 (V)	Collision Energy 2 (V)	RT (min)	Calibration Range (ng/mL)	Pre Ion (*m/z*)	Frag Voltage (V)	Prod Ion 1 (*m/z*)	Prod Ion 2 (*m/z*)	Collision Energy 1 (V)	Collision Energy 2 (V)	RT (min)	Calibration Range (ng/mL)	Pre Ion (*m/z*)	Frag Voltage (V)	Prod Ion 1 (*m/z*)	Prod Ion 2 (*m/z*)	Collision Energy 1 (V)	Collision Energy 2 (V)	RT (min)	Calibration Range (ng/mL)
1	Flonicamid	230.1	124	148	146	29	37	5.152	10 - 400	230.1	166	213.1	194.1	5	10	9.51	7.38 -99.5	230.1	380	148	146	32	40	2.371	5 - 400
2	Dinotefuron	203.1	86	157.1	132	5	37	5.23	0.1 - 400	203.1	166	87.1	132	15	37	7.24*	16438	203.1	380	157.1	129	4	20	1.507*	0.1 - 200
3	Thiabendazole	202	124	175	131	29	37	5.231	10 - 400	202	166	175	131	29	37	7.24	0.34 -39.8	202	380	175	131	28	44	2.804	0.1 - 200
4	Thiamethoxam	292	86	211	131.9	9	21	5.448	10 - 400	292	166	205.9	132.9	1	16	5.28*	13.9 -99.3	292	380	211	131.9	12	24	2.566*	0.1 - 200
5	Sulfoxaflor	278.1	86	257.5	237	5		5.595	50 - 400	278.1	166	174	105	5	10	7.54	0.43 -36.5	278.1	380	174	154	8	36	3.127	0.1 - 400
6	Clothianidin	250	86	169	131.9	9	17	5.662	0.1 - 400	250	166	169	131.9	9	17	7.13*	0.79 -41.1	250	380	169	131.9	8	16	2.735*	0.1 - 400
7	Imidacloprid-d_6 (RS)	260.1	86	213	179	13	17	5.746	-	-	-	-	-	-	-	-	-	260	380	179	-	24	-	2.798	-
8	Imidacloprid	256.1	86	209	175	13	21	5.756	5 - 400	256.1	166	209	175	13	21	7.04*	1.44 -33.9	256.1	380	209	175	12	24	2.808	0.1 - 200
9	Acetamiprid	223.1	86	126	107	21	37	5.868	0.1 - 400	223.1	166	126	107	21	37	7.39	0.56 -41.1	223.1	380	126	56	20	44	2.894	0.1 - 200
10	Tricyclazole	190	124	136	109	33	41	5.913	0.1 - 400	190	166	136	109	33	41	7.24*	0.57 -44.5	190	380	136	109	28	40	2.917	0.1 - 200
11	Thiacloprid-d_4 (IS)	257.7	86	127	100	25	57	6.088	-	-	-	-	-	-	-	-	-	257.7	380	127	-	24	-	3.09	-
12	Thiacloprid	253	86	211.7	126	5	21	6.105	0.1 - 400	253	166	186	126	11	20	7.51	0.48 -38.4	253	380	126	90	24	0	3.091	0.1 - 400
13	DCPMU	219	83	161.9	127	13	33	6.533	0.1 - 400	219	166	161.9	127	13	33	8.17	0.67 -40.6	219	380	161.9	127	16	28	3.407	0.1 - 400
14	Cymoxanil	199.1	200	182	154	9	13	6.54	0.1 - 400	199.1	166	128.1	154	5	13	7.38*	11.1 -102	199.1	380	128	44	4	44	2.982*	0.1 - 400
15	Ethaboxam	321.1	124	155	127	29	53	6.597	0.1 - 400	321.1	166	155	127	29	53	8.62	1.61 -43.7	321.1	380	155	127	32	52	3.547	0.1 - 200
16	Imidacloprid Urea	224.1	86	203.7	107	1	33	6.609	0.1 - 400	212.1	166	128	126	22	30	6.69*	1.26 -38.2	212	380	128	126	16	24	2.607*	0.1 - 200
17	Atrazine-$^{13}C_3$ (RS)	219.7	124	178	104	17	29	6.618	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
18	Carboxin	236.1	86	143	132	13	29	6.702	0.1 - 400	236.1	166	143	132	13	29	8.73	0.76 -41.1	236.1	380	143	132	12	24	3.512	0.1 - 100
19	Cyantraniliprole	473	127	283.9	176.9	13	49	6.8	0.1 - 400	473	166	283.9	176.9	13	49	8.79	0.38 -41.6	473	380	283.9	176.9	28	56	3.544	0.1 - 200
20	DCPU	205	86	132	127	37	29	6.812	0.1 - 400	205	166	132	127	37	29	7.74*	0.96 -40.8	205	380	132	127	40	28	3.256*	0.1 - 400
21	Penoxsulam	484.1	124	195	194.1	29	41	7.072	0.1 - 400	484.1	166	195	194.1	29	41	7.29*	0.7 -43.5	484.1	380	195	194.1	32	48	3.611	0.1 - 200

-	-	Laboratory A								Laboratory B								Laboratory C							
#	Analyte	Pre Ion[1] (*m/z*)	Frag Voltage[2] (V)	Prod Ion 1 (*m/z*)[3]	Prod Ion 2 (*m/z*)	Collision Energy 1 (V)	Collision Energy 2 (V)	RT (min)	Calibration Range (ng/mL)	Pre Ion (*m/z*)	Frag Voltage (V)	Prod Ion 1 (*m/z*)	Prod Ion 2 (*m/z*)	Collision Energy 1 (V)	Collision Energy 2 (V)	RT (min)	Calibration Range (ng/mL)	Pre Ion (*m/z*)	Frag Voltage (V)	Prod Ion 1 (*m/z*)	Prod Ion 2 (*m/z*)	Collision Energy 1 (V)	Collision Energy 2 (V)	RT (min)	Calibration Range (ng/mL)
22	Chlorantraniliprole	482	86	283.9	112	9	89	7.191	0.1 - 400	482	166	283.9	112	9	59	8.79	0.54 -41.5	482	380	283.9	112	12	72	3.708	0.1 - 400
23	Fluridone	330.1	162	309	259	41	57	7.432	10 - 400	330.1	166	309	259	41	57	9.61	0.67 -36.1	330.1	380	309	259	40	56	3.789	0.1 - 100
24	Desthio-Prothioconazole	312.1	124	125	115	33	73	7.722	0.1 - 400	312.1	166	125	115	33	124	9.94	10.4 -102	312.1	380	125	115	44	76	3.859	0.1 - 200
25	Myclobutanil-d_4 (IS)	293.8	124	129.9	129	33	37	7.842	-	-	-	-	-	-	-	-	-	293	380	70	-	-	-	3.879	-
26	Mandipropamide	412.1	86	328.1	125	13	41	8.248	0.1 - 400	412.1	166	328.1	125	13	41	10.18	0.77 -42.8	412.1	380	328.1	125	12	36	3.931	0.1 - 400
27	Ibuprofen-d_5 (IS)	210.2	86	189.5	164	1	5	8.433	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
28	Methoxyfenozide	369.2	124	313.1	149	5	13	8.436	0.1 - 400	369.2	166	313.1	149	5	13	10.44	0.71 -40.6	369.2	380	149	313.1	16	4	4.019	0.1 - 20
29	Oxathiapiprolin	540.2	162	162	139	49	45	8.784	0.1 - 400	540.2	166	162	139	49	45	10.54	0.82 -38.5	540.2	380	139	162	76	52	4.044	0.1 - 400
30	Tebufenozide	353.2	200	351.2	-	1	-	8.965	5 - 400	353.2	166	169.3	147.1	6	15	12.29	19.1 -106.6	353.2	380	297	351.2	4	60	4.153	0.1 - 100
31	Oryzalin	347.1	124	335.1	223.7	1	17	8.974	0.1 - 400	347.1	166	305.1	43.1	10	20	11.12*	0.54 -37.6	347.1	380	305	288	12	20	4.069*	0.1 - 400
32	Cyzaofamid	325.1	86	261	108	5	13	9.127	0.1 - 400	325.1	166	261	108	5	13	10.9*	0.55 -41	325.1	380	261	108	4	12	4.193	0.1 - 200
33	Diuron	233	86	212.4	191.8	1	5	9.173	50 - 400	233	166	72	46.1	20	15	8.61*	1.42 -43	235	380	72	233/72	24	28	3.532*	0.1 - 400
34	Penthiopyrad	360.1	86	276	176.9	13	41	9.178	0.1 - 400	360.1	166	276	176.9	13	41	10.98	0.86 -47.7	360.1	380	276	176.9	12	36	4.217	0.1 - 200
35	Tolfenpyrad	384.2	162	154	117	45	37	9.731	0.1 - 400	384.2	166	154	117	45	37	11.64	0.85 -37.1	384.2	380	154	117	48	36	4.478	0.1 - 200

[1] Precursor ion; [2] Fragmentor voltage; [2] Product ion

Table 4C. Measured concentration of a standard analyte from a second source for calibration verification in laboratory C.

Analyte	0.1 ng/mL	1 ng/mL	10 ng/mL	100 ng/mL	Solvent	Source vendor
Imidacloprid	0.1903	1.1296	11.463	96.6224	Neat solid	CAYMAN

Table 5A. Recoveries of analytes in 1 L reagent water Laboratory Control Samples (LCSs), arranged by analyte number (Table 1) with Recovery Standards (RS) at the end of the Table, following Solid Phase Extraction (SPE) with Hydrophilic-Lipophilic Balance (HLB) cartridge (6cc, 500 mg sorbent). Performance data from Laboratory A, with high and low spiking levels of 100 ng/L and 20 ng/L, respectively. Mean and Relative Standard Deviation (RSD) values outside of Quality Assurance/Quality Control (QA/QC) requirements (Mean>150% or <50%, RSD>30%) are highlighted in red and an asterisk.

#	Analyte	High1	High2	High3	High Mean	High RSD	Low1	Low2	Low3	Low Mean	Low RSD
1	Flonicamid	-	-	-	-	-	-	-	-	-	-
2	Dinotefuron	90%	90%	89%	90%	1%	2%	2%	2%	2%*	0%
3	Thiabendazole	0%	0%	0%	0%*	-	3%	2%	2%	2%*	25%
4	Thiamethoxam	0%	0%	0%	0%*	-	213%	100%	198%	170%*	36%*
5	Sulfoxaflor	32%	56%	48%	45%*	27%	95%	102%	38%	78%	45%*
6	Clothianidin	53%	67%	37%	52%	29%	69%	60%	69%	66%	8%
8	Imidacloprid	60%	60%	43%	54%	18%	88%	85%	79%	84%	5%
9	Acetamiprid	58%	61%	47%	55%	13%	94%	97%	93%	95%	2%
10	Tricyclazole	52%	56%	44%	51%	12%	94%	106%	95%	98%	7%
12	Thiacloprid	161%	171%	72%	135%	40%*	104%	103%	106%	104%	1%
13	DCPMU	103%	116%	75%	98%	21%	100%	98%	101%	100%	2%
14	Cymoxanil	85%	88%	77%	83%	7%	98%	94%	103%	98%	5%
15	Ethaboxam	84%	88%	78%	83%	6%	70%	90%	80%	80%	12%
16	Imidacloprid Urea	65%	72%	57%	65%	12%	83%	91%	102%	92%	10%
18	Carboxin	61%	65%	39%	55%	25%	31%	55%	47%	44%*	28%
19	Cyantraniliprole	82%	92%	64%	79%	18%	81%	107%	87%	92%	15%
20	DCPU	85%	94%	71%	83%	14%	104%	102%	109%	105%	3%
21	Penoxsulam	90%	90%	63%	81%	19%	80%	99%	88%	89%	11%
22	Chlorantraniliprole	79%	78%	66%	74%	10%	83%	100%	87%	90%	10%
23	Fluridone	76%	81%	70%	76%	7%	68%	97%	82%	82%	18%
24	Desthio-Prothioconazole	75%	80%	65%	73%	10%	76%	104%	88%	89%	16%
26	Mandipropamide	83%	84%	66%	78%	13%	84%	103%	91%	93%	10%
27	Ibuprofen-d_5	108%	114%	109%	110%	3%	58%	81%	65%	68%	17%
28	Methoxyfenozide	76%	77%	60%	71%	13%	61%	101%	84%	82%	24%
29	Oxathiapiprolin	74%	75%	60%	70%	12%	94%	76%	36%	69%	43%*
30	Tebufenozide	19%	52%	0%	24%*	111%*	105%	113%	109%	109%	4%
31	Oryzalin	84%	105%	84%	91%	13%	126%	94%	115%	112%	15%
32	Cyzaofamid	74%	77%	70%	74%	5%	107%	91%	56%	85%	31%*
33	Diuron	121%	110%	100%	110%	10%	76%	85%	244%	135%	70%*
34	Penthiopyrad	87%	90%	72%	83%	12%	87%	74%	37%	66%	39%*
35	Tolfenpyrad	29%	30%	24%	28%*	12%	42%	26%	13%	27%*	54%*
7	Imidacloprid-d_6 (RS)	62%	64%	45%	57%	18%	73%	71%	87%	77%	11%
17	Atrazine-$^{13}C_3$ (RS)	72%	77%	61%	70%	12%	117%	112%	117%	115%	3%

Table 5B. Recoveries of analytes in 1 L reagent water Laboratory Control Samples (LCSs), arranged by analyte number (Table 1), following Solid Phase Extraction (SPE) with Hydrophilic-Lipophilic Balance (HLB) cartridge (6cc, 500 mg sorbent). Performance data from Laboratory B, with high spiking levels of 50 ng/L. Mean and Relative Standard Deviation (RSD) values outside of Quality Assurance/Quality Control (QA/QC) requirements (Mean>150% or <50%, RSD>30%) are highlighted in red and an asterisk.

#	Analyte	High1	High2	High3	High4	High Mean	High RSD
1	Flonicamid	14%	13%	14%	15%	14%*	6%
2	Dinotefuron	69%	70%	64%	65%	67%	4%
3	Thiabendazole	102%	103%	101%	101%	102%	1%
4	Thiamethoxam	-	-	-	-	-	-
5	Sulfoxaflor	52%	47%	49%	50%	50%*	4%
6	Clothianidin	22%	17%	21%	20%	20%*	11%
8	Imidacloprid	54%	50%	43%	55%	51%	11%
9	Acetamiprid	81%	83%	80%	90%	84%	5%
10	Tricyclazole	100%	97%	106%	110%	103%	6%
12	Thiacloprid	84%	83%	76%	81%	81%	4%
13	DCPMU	100%	111%	93%	101%	101%	7%
14	Cymoxanil	1%	1%	3%	3%	2%*	58%*
15	Ethaboxam	5%	4%	3%	6%	5%*	29%
16	Imidacloprid Urea	4%	4%	3%	3%	4%*	16%
18	Carboxin	105%	98%	100%	106%	102%	4%
19	Cyantraniliprole	15%	15%	14%	18%	16%*	11%
20	DCPU	101%	112%	99%	95%	102%	7%
21	Penoxsulam	27%	26%	28%	31%	28%*	8%
22	Chlorantraniliprole	21%	22%	22%	23%	22%*	4%
23	Fluridone	48%	45%	48%	50%	48%*	4%
24	Desthio-Prothioconazole	64%	64%	63%	59%	63%	4%
26	Mandipropamide	28%	27%	27%	29%	28%*	3%
27	Ibuprofen-d_5	-	-	-	-	-	-
28	Methoxyfenozide	34%	33%	38%	38%	36%*	7%
29	Oxathiapiprolin	38%	35%	38%	35%	37%*	5%
30	Tebufenozide	-	-	-	-	-	-
31	Oryzalin	50%	41%	41%	51%	46%*	12%
32	Cyzaofamid	49%	38%	50%	44%	45%*	12%
33	Diuron	98%	87%	94%	89%	92%	5%
34	Penthiopyrad	38%	39%	42%	35%	39%*	7%
35	Tolfenpyrad	27%	30%	28%	26%	28%*	6%

Table 5C. Recoveries of analytes in 1 L reagent water Laboratory Control Samples (LCSs), arranged by analyte number (Table 1), following Solid Phase Extraction (SPE) with Hydrophilic-Lipophilic Balance (HLB) cartridge (6cc, 500 mg sorbent). Performance data from Laboratory C, with low spiking levels of 5 ng/L. Mean and Relative Standard Deviation (RSD) values outside of Quality Assurance/Quality Control (QA/QC) requirements (Mean>150% or <50%, RSD>30%) are highlighted in red and an asterisk.

#	Analyte	Low1	Low2	Low3	Low4	Low5	Low6	Low7	Low Mean	Low RSD
1	Flonicamid	52%	65%	132%	80%	70%	106%	100%	86%	32%*
2	Dinotefuron	96%	95%	80%	92%	97%	100%	96%	94%	7%
3	Thiabendazole	51%	52%	53%	57%	56%	65%	67%	57%	11%
4	Thiamethoxam	88%	88%	84%	94%	97%	98%	97%	92%	6%
5	Sulfoxaflor	85%	89%	78%	100%	97%	88%	89%	89%	8%
6	Clothianidin	89%	102%	94%	103%	113%	90%	96%	98%	9%
8	Imidacloprid	83%	81%	87%	94%	90%	98%	98%	90%	8%
9	Acetamiprid	92%	101%	85%	99%	88%	113%	105%	98%	10%
10	Tricyclazole	96%	90%	90%	90%	81%	84%	86%	88%	6%
12	Thiacloprid	67%	66%	70%	74%	84%	83%	72%	74%	10%
13	DCPMU	71%	68%	70%	70%	81%	75%	70%	72%	6%
14	Cymoxanil	72%	58%	57%	89%	59%	81%	89%	72%	20%
15	Ethaboxam	128%	133%	229%	208%	279%	442%	434%	265%*	49%*
16	Imidacloprid Urea	68%	67%	63%	77%	72%	110%	108%	81%	25%
18	Carboxin	60%	67%	78%	93%	105%	52%	49%	72%	29%
19	Cyantraniliprole	78%	76%	43%	59%	35%	83%	74%	64%	29%
20	DCPU	74%	78%	65%	57%	69%	61%	56%	66%	13%
21	Penoxsulam	88%	86%	72%	88%	88%	96%	87%	86%	8%
22	Chlorantraniliprole	83%	86%	100%	122%	115%	90%	92%	98%	15%
23	Fluridone	95%	82%	71%	68%	82%	81%	68%	78%	13%
24	Desthio-Prothioconazole	68%	62%	48%	57%	56%	74%	56%	60%	14%
26	Mandipropamide	82%	104%	82%	70%	74%	103%	75%	84%	16%
27	Ibuprofen-d_5	-	-	-	-	-	-	-	-	-
28	Methoxyfenozide	89%	85%	68%	59%	68%	86%	83%	77%	15%
29	Oxathiapiprolin	122%	125%	84%	81%	87%	135%	106%	106%	21%
30	Tebufenozide	90%	95%	90%	95%	103%	80%	72%	89%	12%
31	Oryzalin	90%	119%	176%	128%	87%	112%	119%	119%	25%
32	Cyzaofamid	76%	63%	97%	84%	92%	86%	86%	83%	13%
33	Diuron	82%	78%	86%	77%	84%	101%	77%	84%	10%
34	Penthiopyrad	85%	75%	65%	66%	66%	80%	71%	73%	11%
35	Tolfenpyrad	87%	89%	87%	84%	91%	76%	74%	84%	8%

Table 5X. Recoveries of analytes in 1 L reagent water Laboratory Control Samples (LCSs), arranged by analyte number (Table 1) with Recovery Standards (RS) at the end of the Table, following Solid Phase Extraction (SPE) with Hydrophilic-Lipophilic Balance (HLB) cartridge (6cc, 500 mg sorbent). Summary of performance data from all laboratories, with high and low spiking levels of 50-100 ng/L and 5-20 ng/L, respectively. Mean and Relative Standard Deviation (RSD) values outside of Quality Assurance/Quality Control (QA/QC) requirements (Mean>150% or <50%, RSD>30%) are highlighted in red and an asterisk.

#	Analyte	Total High Mean	Total High RSD	Total Low Mean	Total Low RSD
1	Flonicamid	8%*	94%*	61%	78%*
2	Dinotefuron	77%	16%	66%	67%*
3	Thiabendazole	58%	94%*	41%*	66%*
4	Thiamethoxam	0%*	-	116%	41%*
5	Sulfoxaflor	48%*	16%	86%	21%
6	Clothianidin	34%*	57%*	89%	19%
8	Imidacloprid	52%	14%	88%	8%
9	Acetamiprid	71%	22%	97%	9%
10	Tricyclazole	81%	35%*	91%	8%
12	Thiacloprid	104%	41%*	83%	19%
13	DCPMU	100%	13%	80%	17%
14	Cymoxanil	37%*	118%*	80%	22%
15	Ethaboxam	38%*	110%*	209%*	66%*
16	Imidacloprid Urea	30%*	111%*	84%	21%
18	Carboxin	82%	33%*	64%	35%
19	Cyantraniliprole	43%*	82%*	72%	29%
20	DCPU	94%	14%	78%	26%
21	Penoxsulam	51%	59%*	87%	9%
22	Chlorantraniliprole	44%*	64%*	96%	14%
23	Fluridone	60%	26%	79%	14%
24	Desthio-Prothioconazole	67%	11%	69%	25%
26	Mandipropamide	49%*	56%*	87%	15%
27	Ibuprofen-d_5	110%	3%	68%	17%
28	Methoxyfenozide	51%	39%*	78%	17%
29	Oxathiapiprolin	51%	36%*	95%	31%*
30	Tebufenozide	10%*	195%*	95%	14%
31	Oryzalin	65%	39%*	117%	22%
32	Cyzaofamid	57%	28%	84%	18%
33	Diuron	100%	12%	99%	52%*
34	Penthiopyrad	58%	43%*	71%	20%
35	Tolfenpyrad	28%*	8%	67%	43%*
7	Imidacloprid-d_6 (RS)	57%	18%	77%	11%
17	Atrazine-$^{13}C_3$ (RS)	70%	12%	115%	3%

Table 6A. Recoveries of analytes on Chemcatcher passive sampler (47 mm diameter Hydrophilic-Lipophilic Balance HLB disk) laboratory control samples (LCSs), arranged by analyte number (Table 1) with Recovery Standards (RS) at the end of the Table. Performance data from Laboratory A, with high and low spiking levels of 100 ng/disk and 20 ng/disk, respectively. Mean and Relative Standard Deviation (RSD) values outside of Quality Assurance/Quality Control (QA/QC) requirements (Mean>150% or <50%, RSD>50%) are highlighted in red and an asterisk.

#	Analyte	High1	High2	High3	High Mean	High RSD	Low1	Low2	Low3	Low4	Low5	Low6	Low Mean	Low RSD
1	Flonicamid	95%	35%	26%	52%	-	-	-	-	-	-	-	-	-
2	Dinotefuron	37%	32%	18%	29%*	34%	2%	2%	1%	3%	2%	2%	2%*	32%
3	Thiabendazole	29%	15%	28%	24%*	-	2%	3%	2%	3%	2%	3%	3%*	22%
4	Thiamethoxam	224%	23%	66%	104%	-	281%	133%	145%	213%	150%	230%	192%*	31%
5	Sulfoxaflor	22%	76%	56%	51%	53%*	67%	68%	57%	57%	48%	61%	60%	12%
6	Clothianidin	93%	108%	78%	93%	16%	98%	64%	83%	90%	71%	92%	83%	16%
8	Imidacloprid	57%	87%	65%	70%	22%	116%	93%	83%	101%	52%	90%	89%	24%
9	Acetamiprid	48%	84%	65%	66%	27%	119%	93%	75%	94%	88%	81%	92%	17%
10	Tricyclazole	39%	82%	61%	61%	35%	111%	87%	61%	85%	83%	61%	81%	23%
12	Thiacloprid	76%	96%	76%	83%	14%	113%	89%	74%	92%	92%	76%	89%	16%
13	DCPMU	53%	92%	70%	72%	27%	121%	95%	75%	101%	91%	77%	93%	18%
14	Cymoxanil	41%	79%	55%	58%	33%	99%	85%	64%	86%	90%	67%	82%	17%
15	Ethaboxam	120%	77%	73%	90%	29%	85%	69%	59%	69%	78%	55%	69%	16%
16	Imidacloprid Urea	41%	88%	63%	64%	37%	77%	61%	48%	69%	75%	46%	63%	21%
18	Carboxin	99%	77%	72%	83%	17%	57%	54%	49%	52%	70%	53%	56%	13%
19	Cyantraniliprole	147%	86%	89%	107%	32%	98%	82%	79%	80%	89%	70%	83%	12%
20	DCPU	42%	86%	68%	65%	34%	110%	89%	77%	94%	90%	79%	90%	13%
21	Penoxsulam	154%	87%	89%	110%	35%	102%	80%	83%	83%	85%	84%	86%	9%
22	Chlorantraniliprole	127%	83%	86%	99%	25%	90%	67%	64%	71%	84%	64%	73%	15%
23	Fluridone	118%	86%	88%	97%	18%	87%	69%	53%	67%	80%	54%	68%	20%
24	Desthio-Prothioconazole	128%	85%	87%	100%	24%	81%	73%	62%	73%	85%	67%	74%	12%
26	Mandipropamide	147%	87%	90%	108%	31%	104%	81%	69%	80%	90%	68%	82%	17%
27	Ibuprofen-d_5	135%	85%	89%	103%	27%	81%	71%	48%	80%	92%	64%	73%	21%
28	Methoxyfenozide	123%	75%	84%	94%	27%	90%	67%	46%	64%	67%	50%	64%	24%
29	Oxathiapiprolin	116%	88%	99%	101%	14%	142%	154%	123%	158%	119%	129%	138%	12%
30	Tebufenozide	102%	101%	98%	100%	2%	106%	96%	100%	40%	94%	67%	84%	30%
31	Oryzalin	89%	96%	105%	97%	8%	84%	72%	134%	0%	69%	51%	68%	64%*
32	Cyzaofamid	105%	87%	84%	92%	12%	121%	121%	91%	131%	116%	103%	114%	13%
33	Diuron	95%	104%	99%	99%	5%	92%	110%	132%	131%	229%	185%	147%	35%
34	Penthiopyrad	104%	86%	90%	93%	10%	139%	149%	124%	150%	127%	137%	138%	8%
35	Tolfenpyrad	-	-	-	-	-	-	-	-	-	-	-	-	-
7	Imidacloprid-d_6 (RS)	58%	85%	66%	70%	20%	125%	72%	87%	105%	49%	92%	88%	30%
17	Atrazine-$^{13}C_3$ (RS)	38%	87%	60%	62%	40%	75%	50%	53%	63%	64%	48%	59%	18%

Table 6B. Recoveries of analytes on Chemcatcher passive sampler (47 mm diameter Hydrophilic-Lipophilic Balance HLB disk) laboratory control samples (LCSs), arranged by analyte number (Table 1). Performance data from Laboratory B, with high spiking levels of 50 ng/disk. Mean and Relative Standard Deviation (RSD) values outside of Quality Assurance/Quality Control (QA/QC) requirements (Mean>150% or <50%, RSD>50%) are highlighted in red and an asterisk.

#	Analyte	High1	High2	High3	High4	High Mean	High RSD
1	Flonicamid	5%	5%	5%	5%	5%*	0%
2	Dinotefuron	69%	67%	70%	68%	69%	2%
3	Thiabendazole	99%	99%	98%	98%	99%	1%
4	Thiamethoxam	13%	12%	14%	12%	13%*	8%
5	Sulfoxaflor	98%	90%	87%	94%	92%	5%
6	Clothianidin	110%	103%	108%	104%	106%	3%
8	Imidacloprid	85%	91%	87%	81%	86%	5%
9	Acetamiprid	82%	83%	83%	86%	84%	2%
10	Tricyclazole	124%	123%	121%	121%	122%	1%
12	Thiacloprid	98%	99%	98%	93%	97%	3%
13	DCPMU	139%	131%	136%	134%	135%	2%
14	Cymoxanil	24%	24%	25%	25%	25%*	2%
15	Ethaboxam	82%	81%	77%	75%	79%	4%
16	Imidacloprid Urea	22%	23%	20%	20%	21%*	7%
18	Carboxin	119%	128%	122%	120%	122%	3%
19	Cyantraniliprole	27%	27%	26%	28%	27%*	3%
20	DCPU	83%	83%	83%	82%	83%	1%
21	Penoxsulam	36%	37%	36%	35%	36%*	2%
22	Chlorantraniliprole	34%	35%	33%	35%	34%*	3%
23	Fluridone	55%	58%	57%	55%	56%	3%
24	Desthio-Prothioconazole	52%	50%	51%	50%	51%	2%
26	Mandipropamide	30%	31%	32%	30%	31%*	3%
27	Ibuprofen-d_5	-	-	-	-	-	-
28	Methoxyfenozide	28%	30%	23%	29%	28%*	11%
29	Oxathiapiprolin	45%	43%	47%	46%	45%*	4%
30	Tebufenozide	0%	0%	0%	0%	0%*	-
31	Oryzalin	7%	5%	7%	8%	7%*	19%
32	Cyzaofamid	65%	60%	66%	61%	63%	5%
33	Diuron	105%	107%	106%	106%	106%	1%
34	Penthiopyrad	40%	40%	37%	39%	39%*	4%
35	Tolfenpyrad	51%	54%	53%	47%	51%	6%

Table 6C. Recoveries of analytes on Chemcatcher passive sampler (47 mm diameter Hydrophilic-Lipophilic Balance HLB disk) laboratory control samples (LCSs), arranged by analyte number (Table 1). Performance data from Laboratory C, with low spiking levels of 5 ng/disk. Mean and Relative Standard Deviation (RSD) values outside of Quality Assurance/Quality Control (QA/QC) requirements (Mean>150% or <50%, RSD>50%) are highlighted in red and an asterisk.

#	Analyte	Low1	Low2	Low3	Low4	Low5	Low6	Low7	Low Mean	Low RSD
1	Flonicamid	74%	75%	79%	96%	98%	81%	112%	88%	16%
2	Dinotefuron	80%	72%	79%	90%	79%	107%	72%	83%	15%
3	Thiabendazole	36%	45%	36%	37%	36%	72%	43%	44%*	30%
4	Thiamethoxam	77%	78%	81%	102%	85%	109%	81%	88%	14%
5	Sulfoxaflor	80%	70%	78%	96%	80%	96%	56%	79%	18%
6	Clothianidin	75%	74%	86%	103%	98%	93%	62%	84%	17%
8	Imidacloprid	64%	73%	69%	94%	70%	91%	71%	76%	15%
9	Acetamiprid	86%	80%	78%	92%	65%	97%	83%	83%	12%
10	Tricyclazole	81%	78%	65%	93%	70%	91%	69%	78%	14%
12	Thiacloprid	58%	67%	66%	91%	69%	72%	61%	69%	16%
13	DCPMU	63%	62%	74%	77%	74%	59%	52%	66%	14%
14	Cymoxanil	75%	52%	45%	43%	58%	80%	71%	61%	25%
15	Ethaboxam	109%	109%	239%	215%	204%	367%	345%	227%*	45%
16	Imidacloprid Urea	63%	51%	60%	57%	61%	121%	86%	71%	34%
18	Carboxin	54%	45%	87%	78%	106%	35%	35%	63%	44%
19	Cyantraniliprole	81%	80%	23%	36%	39%	69%	68%	57%	41%
20	DCPU	85%	63%	83%	64%	66%	59%	56%	68%	17%
21	Penoxsulam	71%	67%	82%	81%	95%	79%	74%	78%	12%
22	Chlorantraniliprole	72%	73%	96%	100%	121%	80%	75%	88%	21%
23	Fluridone	89%	70%	83%	66%	70%	70%	64%	73%	13%
24	Desthio-Prothioconazole	64%	52%	37%	46%	57%	59%	50%	52%	17%
26	Mandipropamide	94%	77%	81%	75%	73%	67%	70%	77%	12%
27	Ibuprofen-d_5	-	-	-	-	-	-	-	-	-
28	Methoxyfenozide	79%	76%	74%	68%	76%	88%	63%	75%	11%
29	Oxathiapiprolin	86%	95%	67%	85%	80%	115%	92%	89%	17%
30	Tebufenozide	73%	73%	97%	96%	104%	71%	63%	82%	19%
31	Oryzalin	92%	92%	107%	153%	178%	155%	109%	127%	27%
32	Cyzaofamid	59%	59%	83%	88%	73%	76%	67%	72%	16%
33	Diuron	81%	75%	88%	80%	72%	79%	59%	76%	12%
34	Penthiopyrad	66%	66%	61%	70%	52%	60%	53%	61%	11%
35	Tolfenpyrad	21%	21%	32%	71%	28%	48%	46%	38%*	47%

Table 6X. Recoveries of analytes on Chemcatcher passive sampler (47 mm diameter Hydrophilic-Lipophilic Balance HLB disk) laboratory control samples (LCSs), arranged by analyte number (Table 1) with Recovery Standards (RS) at the end of the Table. Summary of performance data from all laboratories, with high and low spiking levels of 50-100 ng/disk and 5-20 ng/disk, respectively. Mean and Relative Standard Deviation (RSD) values outside of Quality Assurance/Quality Control (QA/QC) requirements (Mean>150% or <50%, RSD>50%) are highlighted in red and an asterisk.

#	Analyte	Total High Mean	Total High RSD	Total Low Mean	Total Low RSD
1	Flonicamid	25%*	132%*	47%*	99%*
2	Dinotefuron	52%	42%	45%*	94%*
3	Thiabendazole	67%	60%*	25%*	94%*
4	Thiamethoxam	52%	151%*	136%	49%
5	Sulfoxaflor	75%	36%	70%	21%
6	Clothianidin	101%	11%	84%	16%
8	Imidacloprid	79%	16%	82%	21%
9	Acetamiprid	76%	19%	87%	15%
10	Tricyclazole	96%	37%	80%	18%
12	Thiacloprid	91%	11%	78%	20%
13	DCPMU	108%	33%	79%	24%
14	Cymoxanil	39%*	54%*	70%	25%
15	Ethaboxam	84%	20%	154%*	71%*
16	Imidacloprid Urea	40%*	67%*	67%	30%
18	Carboxin	105%	22%	60%	34%
19	Cyantraniliprole	61%	77%*	69%	33%
20	DCPU	75%	21%	78%	20%
21	Penoxsulam	68%	67%*	82%	11%
22	Chlorantraniliprole	62%	60%*	81%	20%
23	Fluridone	74%	33%	71%	16%
24	Desthio-Prothioconazole	72%	42%	62%	22%
26	Mandipropamide	64%	72%*	79%	14%
27	Ibuprofen-d_5	103%	27%	73%	21%
28	Methoxyfenozide	56%	69%*	70%	18%
29	Oxathiapiprolin	69%	45%	111%	26%
30	Tebufenozide	43%*	125%*	83%	24%
31	Oryzalin	45%*	107%*	100%	48%
32	Cyzaofamid	75%	22%	91%	27%
33	Diuron	103%	4%	109%	46%
34	Penthiopyrad	62%	47%	96%	42%
35	Tolfenpyrad	29%*	94%*	21%*	115%*
7	Imidacloprid-d_6 (RS)	70%	20%	88%	30%
17	Atrazine-$^{13}C_3$ (RS)	62%	40%	59%	18%

Table 7. Summary of Method Detection Limits (MDLs, ng/L) of analytes in aqueous matrices, arranged by analyte number (Table 1) with Recovery Standards (RS) at the end of the Table, following Solid Phase Extraction (SPE) with Hydrophilic-Lipophilic Balance (HLB) cartridge (6cc, 500 mg sorbent). A spiking level of 20 ng/L, 50 ng/L, and 5 ng/L was used to determine the MDLs for Laboratory A, Laboratory B, and Laboratory C, respectively.

#	Analyte	Lab A	Lab B	Lab C	MIN	MAX
1	Flonicamid	406.4	3.46	4.4	3.5	406.4
2	Dinotefuron	43.5	3.2	1	1.0	43.5
3	Thiabendazole	3.74	1.03	1	1.0	3.7
4	Thiamethoxam	34.36	15.8	0.9	0.9	34.4
5	Sulfoxaflor	26.62	2.26	1.1	1.1	26.6
6	Clothianidin	13.42	1.12	1.3	1.1	13.4
8	Imidacloprid	13.21	2.46	1.1	1.1	13.2
9	Acetamiprid	4.71	3.1	1.6	1.6	4.7
10	Tricyclazole	11.17	3.29	0.8	0.8	11.2
12	Thiacloprid	6.73	3.18	1.1	1.1	6.7
13	DCPMU	5.57	4.45	0.7	0.7	5.6
14	Cymoxanil	10.17	3.24	2.3	2.3	10.2
15	Ethaboxam	9.75	19.1	20.4	9.8	20.4
16	Imidacloprid Urea	7.59	1.91	3.1	1.9	7.6
18	Carboxin	3.09	3.34	3.3	3.1	3.3
19	Cyantraniliprole	3.85	0.92	2.9	0.9	3.9
20	DCPU	5.18	4.87	1.3	1.3	5.2
21	Penoxsulam	5.93	2	1.1	1.1	5.9
22	Chlorantraniliprole	6.41	1.01	2.4	1.0	6.4
23	Fluridone	6.43	1.41	1.5	1.4	6.4
24	Desthio-Prothioconazole	9.17	2	1.3	1.3	9.2
26	Mandipropamide	8.36	1.55	2.1	1.6	8.4
27	Ibuprofen-d_5	21.97	-	-	0.0	0.0
28	Methoxyfenozide	22.89	1.7	1.8	1.7	22.9
29	Oxathiapiprolin	468.07	1.56	3.4	1.6	468.1
30	Tebufenozide	341.68	20	1.6	1.6	341.7
31	Oryzalin	308.34	3.85	4.6	3.9	308.3
32	Cyzaofamid	631.25	3.27	1.8	1.8	631.3
33	Diuron	451.25	3.58	1.3	1.3	451.3
34	Penthiopyrad	480.26	1.59	1.3	1.3	480.3
35	Tolfenpyrad	1.36	2.38	1	1.0	2.4
7	Imidacloprid-d_6 (RS)	14.55	-	-	14.6	14.6
17	Atrazine-$^{13}C_3$ (RS)	3.64	-	-	3.6	3.6

Table 8. Summary of Method Detection Limits (MDLs, ng/disk) of analytes on Chemcatcher passive samplers on Hydrophilic-Lipophilic Balance (HLB) disk (47 mm diameter) used as sorbent media, arranged by analyte number (Table 1) with Recovery Standards (RS) at the end of the Table. A spiking level of 20 ng/disk, 50 ng/disk, 5 ng/disk was used to determine the MDLs for Laboratory A, Laboratory B, and Laboratory C, respectively.

#	Analyte	Lab A	Lab B	Lab C	MIN	MAX
1	Flonicamid	134.3	3.0	2.3	2.3	134.3
2	Dinotefuron	4422.6	1.0	1.9	1.0	4422.6
3	Thiabendazole	6.74	0.57	2.0	0.6	6.7
4	Thiamethoxam	14.51	20	2.0	2.0	20.0
5	Sulfoxaflor	17.45	2.67	2.2	2.2	17.5
6	Clothianidin	14.98	2.2	2.3	2.2	15.0
8	Imidacloprid	6.37	5.38	1.9	1.9	6.4
9	Acetamiprid	2.84	4.29	1.7	1.7	4.3
10	Tricyclazole	5	2.43	1.7	1.7	5.0
12	Thiacloprid	5.75	2.04	1.7	1.7	5.8
13	DCPMU	3.12	1.89	1.5	1.5	3.1
14	Cymoxanil	2.29	1.71	2.3	1.7	2.3
15	Ethaboxam	2.2	1.19	16.0	1.2	16.0
16	Imidacloprid Urea	4.82	0.74	3.9	0.7	4.8
18	Carboxin	2.07	7.5	4.4	2.1	7.5
19	Cyantraniliprole	2.19	0.59	3.7	0.6	3.7
20	DCPU	1.28	3.16	1.8	1.3	3.2
21	Penoxsulam	4.11	0.86	1.4	0.9	4.1
22	Chlorantraniliprole	1.6	0.64	2.9	0.6	2.9
23	Fluridone	2.92	1.44	1.4	1.4	2.9
24	Desthio-Prothioconazole	3.29	0.72	1.4	0.7	3.3
26	Mandipropamide	3.35	0.53	1.4	0.5	3.4
27	Ibuprofen-d_5	4834.91	-	-	-	-
28	Methoxyfenozide	11.29	1.54	1.3	1.3	11.3
29	Oxathiapiprolin	93.51	0.9	2.3	0.9	93.5
30	Tebufenozide	210.16	20	2.5	2.5	210.2
31	Oryzalin	149.27	9.57	5.5	5.5	149.3
32	Cyzaofamid	205.27	1.23	1.7	1.2	205.3
33	Diuron	712.48	1.52	1.4	1.4	712.5
34	Penthiopyrad	98.13	1.25	1.0	1.0	98.1
35	Tolfenpyrad	26.04	2.46	2.8	2.5	26.0
7	Imidacloprid-d_6 (RS)	5.18	-	-	5.2	5.2
17	Atrazine-$^{13}C_3$ (RS)	2.07	-	-	2.1	2.1

Table 9A. Recoveries of analyte Matrix Spikes (MSs) in 1 L river water, arranged by analyte number (Table 1) with Recovery Standards (RS) at the end of the Table, following Solid Phase Extraction (SPE) with Hydrophilic-Lipophilic Balance (HLB) cartridge (6cc, 500 mg sorbent). Performance data from Laboratory A, with a spiking level of 20 ng/L. Mean and Relative Standard Deviation (RSD) values outside of Quality Assurance/Quality Control (QA/QC) requirements (Mean>150% or <50%, RSD>30%) are highlighted in red or in asterisk.

	Analyte	MS1	MS2	MS3	MS4	Mean	RSD
1	Flonicamid	0%	0%	0%	0%	0%*	-
2	Dinotefuron	-	-	-	-	-	-
3	Thiabendazole	1%	1%	2%	1%	1%*	40%*
4	Thiamethoxam	-	-	-	-	-	-
5	Sulfoxaflor	-	-	-	-	-	-
6	Clothianidin	103%	111%	100%	130%	111%	12%
8	Imidacloprid	120%	194%	107%	195%	154%*	31%*
9	Acetamiprid	88%	103%	95%	102%	97%	7%
10	Tricyclazole	103%	111%	102%	109%	106%	4%
12	Thiacloprid	16%	24%	26%	25%	23%*	20%
13	DCPMU	30%	36%	39%	40%	36%*	12%
14	Cymoxanil	54%	60%	63%	62%	60%	7%
15	Ethaboxam	53%	61%	64%	63%	60%	8%
16	Imidacloprid Urea	368%	490%	497%	527%	471%*	15%
18	Carboxin	27%	28%	32%	30%	29%*	8%
19	Cyantraniliprole	46%	52%	57%	57%	53%	10%
20	DCPU	43%	49%	51%	49%	48%*	7%
21	Penoxsulam	75%	90%	98%	94%	89%	11%
22	Chlorantraniliprole	70%	79%	88%	86%	81%	10%
23	Fluridone	55%	67%	75%	72%	67%	13%
24	Desthio-Prothioconazole	58%	65%	72%	71%	67%	10%
26	Mandipropamide	68%	82%	88%	87%	81%	11%
27	Ibuprofen-d_5	-	-	-	-	-	-
28	Methoxyfenozide	50%	68%	75%	74%	67%	17%
29	Oxathiapiprolin	76%	89%	96%	91%	88%	10%
30	Tebufenozide	0%	0%	0%	14%	4%*	200%*
31	Oryzalin	82%	0%	92%	72%	62%	68%*
32	Cyzaofamid	59%	70%	76%	72%	69%	11%
33	Diuron	-	-	-	-	-	-
34	Penthiopyrad	59%	70%	75%	72%	69%	10%
35	Tolfenpyrad	63%	84%	91%	83%	80%	15%
7	Imidacloprid-d_6 (RS)	174%	162%	231%	242%	202%*	20%
17	Atrazine-$^{13}C_3$ (RS)	32%	35%	50%	37%	39%*	21%

Table 9B. Recoveries of analyte Matrix Spikes (MSs) in 1 L river water, arranged by analyte number (Table 1), following Solid Phase Extraction (SPE) with Hydrophilic-Lipophilic Balance (HLB) cartridge (6cc, 500 mg sorbent). Performance data from Laboratory B, with a spiking level of 50 ng/L. Mean and Relative Standard Deviation (RSD) values outside of Quality Assurance/Quality Control (QA/QC) requirements (Mean>150% or <50%, RSD>30%) are highlighted in red and an asterisk.

	Analyte	MS1	MS2	MS3	MS4	Mean	RSD
1	Flonicamid	48%	50%	47%	63%	52%	14%
2	Dinotefuron	45%	49%	50%	56%	50%	9%
3	Thiabendazole	46%	41%	45%	55%	47%*	13%
4	Thiamethoxam	22%	20%	31%	24%	24%*	20%
5	Sulfoxaflor	35%	29%	36%	37%	34%*	10%
6	Clothianidin	42%	40%	43%	42%	42%*	3%
8	Imidacloprid	41%	40%	43%	38%	41%*	5%
9	Acetamiprid	60%	62%	57%	64%	61%	5%
10	Tricyclazole	57%	49%	50%	57%	53%	8%
12	Thiacloprid	32%	30%	31%	28%	30%*	6%
13	DCPMU	33%	43%	39%	51%	42%*	18%
14	Cymoxanil	70%	81%	74%	83%	77%	8%
15	Ethaboxam	7%	7%	8%	8%	8%*	8%
16	Imidacloprid Urea	29%	22%	22%	20%	23%*	17%
18	Carboxin	39%	35%	46%	42%	41%*	11%
19	Cyantraniliprole	40%	45%	53%	62%	50%	19%
20	DCPU	33%	43%	39%	51%	42%*	18%
21	Penoxsulam	17%	18%	21%	25%	20%*	18%
22	Chlorantraniliprole	39%	44%	43%	53%	45%*	13%
23	Fluridone	74%	61%	60%	63%	65%	10%
24	Desthio-Prothioconazole	46%	40%	33%	51%	43%*	18%
26	Mandipropamide	61%	58%	50%	66%	59%	11%
27	Ibuprofen-d_5	-	-	-	-	-	-
28	Methoxyfenozide	45%	42%	51%	61%	50%*	17%
29	Oxathiapiprolin	47%	57%	64%	62%	58%	13%
30	Tebufenozide	-	-	-	-	-	-
31	Oryzalin	26%	22%	14%	17%	20%*	27%
32	Cyzaofamid	134%	103%	94%	112%	111%	15%
33	Diuron	64%	78%	68%	80%	73%	11%
34	Penthiopyrad	66%	60%	48%	75%	62%	18%
35	Tolfenpyrad	83%	92%	105%	97%	94%	10%

Table 9C. Recoveries of analyte Matrix Spikes (MSs) in 1 L river water, arranged by analyte number (Table 1) with Recovery Standards (RS) at the end of the Table, following Solid Phase Extraction (SPE) with Hydrophilic-Lipophilic Balance (HLB) cartridge (6cc, 500 mg sorbent). Performance data from Laboratory C, with a spiking level of 20 ng/L. Mean and Relative Standard Deviation (RSD) values outside of Quality Assurance/Quality Control (QA/QC) requirements (Mean>150% or <50%, RSD>30%) are highlighted in red or in asterisk.

	Analyte	MS1	MS2	MS3	Mean	RSD
1	Flonicamid	104%	93%	109%	102%	8%
2	Dinotefuron	135%	126%	128%	130%	4%
3	Thiabendazole	96%	68%	101%	88%	20%
4	Thiamethoxam	144%	157%	133%	145%	8%
5	Sulfoxaflor	126%	126%	122%	125%	2%
6	Clothianidin	119%	148%	121%	129%	13%
8	Imidacloprid	139%	170%	146%	152%*	11%
9	Acetamiprid	154%	186%	153%	164%*	11%
10	Tricyclazole	132%	172%	124%	143%	18%
12	Thiacloprid	97%	132%	95%	108%	19%
13	DCPMU	273%	267%	297%	279%*	6%
14	Cymoxanil	83%	92%	92%	89%	6%
15	Ethaboxam	155%	161%	175%	164%*	6%
16	Imidacloprid Urea	161%	187%	153%	167%*	11%
18	Carboxin	27%	27%	30%	28%*	6%
19	Cyantraniliprole	102%	111%	100%	104%	6%
20	DCPU	64%	76%	92%	77%	18%
21	Penoxsulam	18%	14%	13%	15%*	18%
22	Chlorantraniliprole	117%	122%	120%	120%	2%
23	Fluridone	76%	76%	85%	79%	7%
24	Desthio-Prothioconazole	73%	75%	71%	73%	3%
26	Mandipropamide	109%	111%	109%	110%	1%
27	Ibuprofen-d_5	-	-	-	-	-
28	Methoxyfenozide	95%	68%	84%	82%	16%
29	Oxathiapiprolin	223%	228%	251%	234%*	6%
30	Tebufenozide	85%	100%	104%	96%	10%
31	Oryzalin	137%	145%	112%	131%	13%
32	Cyzaofamid	70%	80%	82%	77%	8%
33	Diuron	70%	74%	66%	70%	6%
34	Penthiopyrad	75%	72%	70%	72%	3%
35	Tolfenpyrad	69%	60%	80%	70%	14%
7	Imidacloprid-d_6 (RS)	151%	143%	147%	147%	3%

Table 9X. Summary of performance data from all laboratories. Recoveries of analyte Matrix Spikes (MSs) in 1 L river water, arranged by analyte number (Table 1) with Recovery Standards (RS) at the end of the Table, following Solid Phase Extraction (SPE) with Hydrophilic-Lipophilic Balance (HLB) cartridge (6cc, 500 mg sorbent). The spiking amount in 1 L river water was 20 ng for Laboratory A and C, and 50 ng for Laboratory B. Mean and Relative Standard Deviation (RSD) values outside of Quality Assurance/Quality Control (QA/QC) requirements (Mean>150% or <50%, RSD>30%) are highlighted in red and an asterisk.

#	Analyte	Lab A Mean	Lab A RSD	Lab B Mean	Lab B RSD	Lab C Mean	Lab C RSD	Total Mean	Total RSD
1	Flonicamid	0%*	-	52%	14%	102%	8%	47%*	92%*
2	Dinotefuron	-	-	50%	9%	130%	4%	84%	51%*
3	Thiabendazole	1%*	40%*	47%*	13%	88%	20%	42%*	90%*
4	Thiamethoxam	-	-	24%*	20%	145%	8%	76%	85%*
5	Sulfoxaflor	-	-	34%*	10%	125%	2%	73%	66%*
6	Clothianidin	111%	12%	42%*	3%	129%	13%	91%	45%*
8	Imidacloprid	154%*	31%*	41%*	5%	152%*	11%	112%	56%*
9	Acetamiprid	97%	7%	61%	5%	164%*	11%	102%	43%*
10	Tricyclazole	106%	4%	53%	8%	143%	18%	97%	41%*
12	Thiacloprid	23%*	20%	30%*	6%	108%	19%	49%*	81%*
13	DCPMU	36%*	12%	42%*	18%	279%*	6%	104%	108%*
14	Cymoxanil	60%	7%	77%	8%	89%	6%	74%	18%
15	Ethaboxam	60%	8%	8%*	8%	164%*	6%	69%	94%*
16	Imidacloprid Urea	471%*	15%	23%*	17%	167%*	11%	225%*	92%*
18	Carboxin	29%*	8%	41%*	11%	28%*	6%	33%*	20%
19	Cyantraniliprole	53%	10%	50%	19%	104%	6%	66%	39%*
20	DCPU	48%*	7%	42%*	18%	77%	18%	54%	32%*
21	Penoxsulam	89%	11%	20%*	18%	15%*	18%	44%*	83%*
22	Chlorantraniliprole	81%	10%	45%*	13%	120%	2%	78%	40%*
23	Fluridone	67%	13%	65%	10%	79%	7%	69%	13%
24	Desthio-Prothioconazole	67%	10%	43%*	18%	73%	3%	60%	25%
26	Mandipropamide	81%	11%	59%	11%	110%	1%	81%	27%
27	Ibuprofen-d_5	-	-	-	-	-	-	-	-
28	Methoxyfenozide	67%	17%	50%*	17%	82%	16%	65%	26%
29	Oxathiapiprolin	88%	10%	58%	13%	234%*	6%	117%	66%*
30	Tebufenozide	4%*	200%*	-	-	96%	10%	43%*	116%*
31	Oryzalin	62%	68%*	20%*	27%	131%	13%	65%	80%*
32	Cyzaofamid	69%	11%	111%	15%	77%	8%	87%	26%
33	Diuron	-	-	73%	11%	70%	6%	71%	9%
34	Penthiopyrad	69%	10%	62%	18%	72%	3%	67%	13%
35	Tolfenpyrad	80%	15%	94%	10%	70%	14%	82%	17%
7	Imidacloprid-d_6 (RS)	202%*	20%	-	-	147%	3%	179%*	23%
17	Atrazine-$^{13}C_3$ (RS)	39%*	21%	-	-	-	-	39%*	21%

Table 10A. Recoveries of analyte Matrix Spikes (MSs) on river-water exposed Chemcatcher passive sampler on Hydrophilic-Lipophilic Balance (HLB) disk (47 mm diameter) used as sorbent media, arranged by analyte number (Table 1) with Recovery Standards (RS) at the end of the Table. Performance data from Laboratory A, with a spiking level of 20 ng/disk. Mean and Relative Standard Deviation (RSD) values outside of Quality Assurance/Quality Control (QA/QC) requirements (Mean>150% or <50%, RSD>50%) are highlighted in red and an asterisk.

	Analyte	MS1	MS2	MS3	Mean	RSD
1	Flonicamid	648%	287%	806%	580%*	46%
2	Dinotefuron	-	-	-	-	-
3	Thiabendazole	73%	119%	88%	93%	25%
4	Thiamethoxam	-	-	-	-	-
5	Sulfoxaflor	-	-	-	-	-
6	Clothianidin	64%	59%	64%	62%	5%
8	Imidacloprid	88%	65%	79%	77%	15%
9	Acetamiprid	25%	12%	18%	18%*	35%
10	Tricyclazole	80%	72%	86%	79%	9%
12	Thiacloprid	23%	18%	0%	14%*	89%*
13	DCPMU	42%	39%	18%	33%*	40%
14	Cymoxanil	79%	78%	48%	68%	26%
15	Ethaboxam	78%	73%	42%	64%	30%
16	Imidacloprid Urea	62%	56%	32%	50%	32%
18	Carboxin	43%	41%	21%	35%*	35%
19	Cyantraniliprole	66%	64%	31%	54%	37%
20	DCPU	59%	57%	42%	53%	18%
21	Penoxsulam	108%	107%	73%	96%	21%
22	Chlorantraniliprole	106%	99%	55%	87%	32%
23	Fluridone	97%	89%	34%	73%	47%
24	Desthio-Prothioconazole	89%	82%	51%	74%	27%
26	Mandipropamide	89%	90%	59%	79%	22%
27	Ibuprofen-d_5	-	-	-	-	-
28	Methoxyfenozide	75%	58%	28%	54%	44%
29	Oxathiapiprolin	123%	111%	79%	104%	22%
30	Tebufenozide	-	-	-	-	-
31	Oryzalin	108%	66%	27%	67%	60%*
32	Cyzaofamid	87%	73%	33%	64%	44%
33	Diuron	-	-	-	-	-
34	Penthiopyrad	81%	69%	43%	64%	30%
35	Tolfenpyrad	-	-	-	-	-
7	Imidacloprid-d_6 (RS)	52%	71%	128%	84%	47%
17	Atrazine-$^{13}C_3$ (RS)	43%	46%	3%	31%*	78%*

Table 10B. Recoveries of analyte Matrix Spikes (MSs) on river-water exposed Chemcatcher passive sampler on Hydrophilic-Lipophilic Balance (HLB) disk (47 mm diameter) used as sorbent media, arranged by analyte number (Table 1). Performance data from Laboratory B, with a spiking level of 50 ng/disk. Mean and Relative Standard Deviation (RSD) values outside of Quality Assurance/Quality Control (QA/QC) requirements (Mean>150% or <50%, RSD>50%) are highlighted in red and an asterisk.

	Analyte	MS1	MS2	MS3	MS4	Mean	RSD
1	Flonicamid	31%	50%	47%	48%	44%*	20%
2	Dinotefuron	18%	11%	13%	21%	16%*	29%
3	Thiabendazole	15%	11%	13%	22%	15%*	31%
4	Thiamethoxam	17%	15%	16%	11%	15%*	18%
5	Sulfoxaflor	36%	40%	33%	35%	36%*	8%
6	Clothianidin	21%	19%	19%	17%	19%*	9%
8	Imidacloprid	21%	25%	22%	20%	22%*	10%
9	Acetamiprid	29%	36%	33%	36%	34%*	10%
10	Tricyclazole	30%	38%	29%	34%	33%*	13%
12	Thiacloprid	28%	32%	28%	30%	30%*	6%
13	DCPMU	35%	36%	39%	34%	36%*	6%
14	Cymoxanil	23%	40%	22%	50%	34%*	40%
15	Ethaboxam	7%	11%	9%	8%	9%*	20%
16	Imidacloprid Urea	19%	16%	13%	12%	15%*	21%
18	Carboxin	22%	27%	25%	34%	27%*	19%
19	Cyantraniliprole	31%	45%	33%	38%	37%*	17%
20	DCPU	38%	47%	40%	35%	40%*	13%
21	Penoxsulam	61%	44%	33%	40%	45%*	27%
22	Chlorantraniliprole	35%	44%	44%	35%	40%*	13%
23	Fluridone	36%	67%	72%	47%	56%	30%
24	Desthio-Prothioconazole	24%	29%	36%	27%	29%*	18%
26	Mandipropamide	49%	43%	61%	46%	50%*	16%
27	Ibuprofen-d_5	-	-	-	-	-	-
28	Methoxyfenozide	44%	42%	66%	34%	47%*	29%
29	Oxathiapiprolin	50%	57%	68%	49%	56%	16%
30	Tebufenozide	-	-	-	-	-	-
31	Oryzalin	23%	29%	29%	22%	26%*	15%
32	Cyzaofamid	97%	110%	106%	86%	100%	11%
33	Diuron	38%	46%	40%	46%	43%*	10%
34	Penthiopyrad	52%	58%	60%	48%	55%	10%
35	Tolfenpyrad	47%	43%	47%	48%	46%*	5%

Table 10C. Recoveries of analyte Matrix Spikes (MSs) on river-water exposed Chemcatcher passive sampler on Hydrophilic-Lipophilic Balance (HLB) disk (47 mm diameter) used as sorbent media, arranged by analyte number (Table 1) with Recovery Standards (RS) at the end of the Table. Performance data from Laboratory C, with a spiking level of 20 ng/disk. Mean and Relative Standard Deviation (RSD) values outside of Quality Assurance/Quality Control (QA/QC) requirements (Mean>150% or <50%, RSD>50%) are highlighted in red and an asterisk.

	Analyte	MS1	MS2	MS3	Mean	RSD
1	Flonicamid	83%	67%	64%	71%	14%
2	Dinotefuron	70%	61%	48%	60%	19%
3	Thiabendazole	49%	66%	45%	53%	21%
4	Thiamethoxam	95%	120%	100%	105%	13%
5	Sulfoxaflor	80%	90%	79%	83%	7%
6	Clothianidin	101%	118%	97%	105%	11%
8	Imidacloprid	112%	116%	89%	106%	14%
9	Acetamiprid	107%	141%	98%	115%	20%
10	Tricyclazole	77%	108%	84%	90%	18%
12	Thiacloprid	69%	79%	57%	68%	16%
13	DCPMU	213%	230%	238%	227%*	6%
14	Cymoxanil	51%	47%	42%	47%*	10%
15	Ethaboxam	127%	158%	130%	138%	12%
16	Imidacloprid Urea	111%	127%	107%	115%	9%
18	Carboxin	23%	28%	27%	26%*	10%
19	Cyantraniliprole	66%	75%	75%	72%	7%
20	DCPU	48%	66%	54%	56%	16%
21	Penoxsulam	75%	81%	80%	79%	4%
22	Chlorantraniliprole	106%	91%	116%	104%	12%
23	Fluridone	45%	51%	47%	48%*	6%
24	Desthio-Prothioconazole	47%	62%	52%	54%	14%
26	Mandipropamide	74%	86%	68%	76%	12%
27	Ibuprofen-d_5	-	-	-	-	-
28	Methoxyfenozide	53%	74%	56%	61%	19%
29	Oxathiapiprolin	195%	201%	194%	197%*	2%
30	Tebufenozide	61%	74%	66%	67%	10%
31	Oryzalin	63%	109%	90%	87%	26%
32	Cyzaofamid	46%	56%	53%	52%	10%
33	Diuron	53%	57%	55%	55%	4%
34	Penthiopyrad	43%	42%	48%	44%*	7%
35	Tolfenpyrad	8%	9%	8%	8%*	7%
7	Imidacloprid-d_6 (RS)	116%	126%	102%	115%	11%

Table 10X. Summary of performance data from all laboratories. Recoveries of analyte Matrix Spikes (MSs) on river-water exposed Chemcatcher passive sampler on Hydrophilic-Lipophilic Balance (HLB) disk (47 mm diameter) used as sorbent media, arranged by analyte number (Table 1) with Recovery Standards (RS) at the end of the Table. The spiking amount per exposed Chemcatcher water was 20 ng for Laboratory A and Laboratory C, and 50 ng for Laboratory B. Mean and Relative Standard Deviation (RSD) values outside of Quality Assurance/Quality Control (QA/QC) requirements (Mean>150% or <50%, RSD>50%) are highlighted in red and an asterisk.

#	Analyte	Lab A Mean	Lab A RSD	Lab B Mean	Lab B RSD	Lab C Mean	Lab C RSD	Total Mean	Total RSD
1	Flonicamid	580%*	46%	44%*	20%	71%	14%	213%*	133%*
2	Dinotefuron	-	-	16%*	29%	60%	19%	35%*	71%*
3	Thiabendazole	93%	25%	15%*	31%	53%	21%	50%	73%*
4	Thiamethoxam	-	-	15%*	18%	105%	13%	53%	91%*
5	Sulfoxaflor	-	-	36%*	8%	83%	7%	56%	45%
6	Clothianidin	62%	5%	19%*	9%	105%	11%	58%	66%*
8	Imidacloprid	77%	15%	22%*	10%	106%	14%	64%	61%*
9	Acetamiprid	18%*	35%	34%*	10%	115%	20%	54%	83%*
10	Tricyclazole	79%	9%	33%*	13%	90%	18%	64%	45%
12	Thiacloprid	14%*	89%*	30%*	6%	68%	16%	36%*	67%*
13	DCPMU	33%*	40%	36%*	6%	227%*	6%	92%	101%*
14	Cymoxanil	68%	26%	34%*	40%	47%*	10%	48%*	40%
15	Ethaboxam	64%	30%	9%*	20%	138%	12%	64%	90%*
16	Imidacloprid Urea	50%	32%	15%*	21%	115%	9%	56%	81%*
18	Carboxin	35%*	35%	27%*	19%	26%*	10%	29%*	27%
19	Cyantraniliprole	54%	37%	37%*	17%	72%	7%	52%	35%
20	DCPU	53%	18%	40%*	13%	56%	16%	49%*	21%
21	Penoxsulam	96%	21%	45%*	27%	79%	4%	70%	37%
22	Chlorantraniliprole	87%	32%	40%*	13%	104%	12%	73%	45%
23	Fluridone	73%	47%	56%	30%	48%*	6%	59%	37%
24	Desthio-Prothioconazole	74%	27%	29%*	18%	54%	14%	50%*	45%
26	Mandipropamide	79%	22%	50%*	16%	76%	12%	67%	27%
27	Ibuprofen-d_5	-	-	-	-	-	-	-	-
28	Methoxyfenozide	54%	44%	47%*	29%	61%	19%	53%	30%
29	Oxathiapiprolin	104%	22%	56%	16%	197%*	2%	113%	56%*
30	Tebufenozide	-	-	-	-	67%	10%	67%	10%
31	Oryzalin	67%	60%*	26%*	15%	87%	26%	57%	63%*
32	Cyzaofamid	64%	44%	100%	11%	52%	10%	75%	36%
33	Diuron	-	-	43%*	10%	55%	4%	48%*	15%
34	Penthiopyrad	64%	30%	55%	10%	44%*	7%	54%	23%
35	Tolfenpyrad	-	-	46%*	5%	8%*	7%	30%*	68%*
7	Imidacloprid-d_6 (RS)	84%	47%	-	-	115%	11%	99%	31%
17	Atrazine-$^{13}C_3$ (RS)	31%*	78%*	-	-			31%*	78%*

Table 11. Initial Demonstration of Capability (IDC) quality control requirements. Please see the relevant references in the Method for full details.

Method reference	Requirement	Specification	Acceptance Criteria
Section 8.2	Establish stable RTs	Inject a midpoint calibration standard (e.g., 50 ng/mL) under optimized LC/MS/MS to establish stable RTs.	RT of each analyte is within ± 0.2 min of target RT in the midpoint calibration standard.
Section 8.3	Initial calibration	Calibration curves with at least five calibration standards with the lowest standard at or below LOQ.	R^2 of the linear calibration curve must be ≥0.99, with the lowest calibration point at or below LOQ.
Section 7.2.1	Demonstration of low system background	Analyze a method blank after the highest standard in the calibration range.	All the method analytes are less than the MDL.
Section 7.2.2	IPR	Extract and analyze at least 3 replicate LCSs spiked with an appropriate concentration of analytes.	Mean R% must be within a range of 50-150 for both matrices. RSD must be within 30% for aqueous matrices and 50% for Chemcatcher. Only analytes that meet these criteria shall be included in the laboratory report.
Section 7.2.3	MDL determination	Determine MDL using at least 7 MS and 7 method blank samples according to the procedure at 40 CFR 136, appendix B.	Record MDL values for use for ODC. (These acceptance criteria may be updated based on results from the multi-laboratory evaluation.)
Section 7.2.4	LOQ	LOQ is established by each laboratory.	LOQ must be equal to or greater than the MDL and within the calibration range.

Table 12. Ongoing Quality Control (QC) requirements. Please see the relevant references in the Method for full details.

Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Section 7.3.1	Method blank	Include one method blank per sample batch.	All method analytes are below MDL.
Section 7.3.2	CCV	At the beginning of each analysis batch. Subsequent CCVs (e.g., a midpoint calibration standard) are required every 24 h during the same analysis period.	All CCVs must be within 70–130% of the expected concentration, and each analyte's RT must be within ±0.2 min of the target RT.
Section 7.3.3	Solvent blank	Inject a solvent blank after injecting the calibration standards and the CCV solution. Subsequent solvent blanks are injected every 7 samples or after every suspect dirty sample.	No analytes are detected in the solvent blank.
Section 7.3.4	LCS	Include one LCS per sample batch.	The R% must be within 50–150% of the expected value.
Section 7.3.5	Instrument sensitivity	Inject a midpoint calibration standard to check instrument sensitivity every 24 h before the analysis of any standards and samples.	Instrument sensitivity must be ≥50 of the initial calibration level
Section 7.3.6	Recovery of recovery standards	Spike all samples with labeled recovery standards compounds.	The R% must be within 50–150%
Section 7.3.7	MS	Include one MS per sample batch.	The R% must be within 50–150%. If the R% of MS falls outside but the R% of LCS still meets the criteria, document MS failure, and flag the associated sample to indicate potential matrix interference.
Section 7.3.8	MSD or laboratory replicate	Include one MSD or a laboratory replicate sample per sample batch.	The RSD between the replicate samples must be within ±30% for aqueous matrices and ±50% for Chemcatcher.
Section 7.3.9	Verification of MDL	At least once every thirteen months, and if the method is modified in a way that could affect sensitivity or if a sustained decline in performance is observed.	If the verified MDL is within 0.5 to 2.0 times the existing MDL, and fewer than 3% of the method blank results (for the individual analyte) have numerical results above the existing MDL, then the existing MDL may optionally be left unchanged. Otherwise, adjust the MDL to the new verification MDL.
Section 7.3.10	OPR	At least 3 OPR (replicate LCSs spiked with an appropriate concentration of analytes) at least every thirteen months.	If the verified precision and recovery are within the range of 50-150% of the existing results, the existing procedure may optionally be left unchanged. Otherwise, analysis of samples must be halted until the precision and recovery are resumed.