

Contract 18-C0159 Final Method Report

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Extraction of Pyrethroid Pesticides from Municipal Sewage Sludge

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Sample Preparation

Samples were freeze dried and homogenized to a fine powder. Approximately 0.5 g of dried sample was spiked with 25 ng 4,4'-DDE $^{13}\text{C}_2$ as an analytical surrogate. Sample preparation was based on the USGS TM5-C3 methods for the determination of pesticides in sediment using gas chromatography/mass spectrometry (Hladik and McWayne 2012). Briefly, anhydrous sodium sulfate was added to samples and loaded into Accelerated Solvent Extraction (ASE) cells with a prebaked GF/F filter. Ottawa sand was added to fill any remaining dead space in the cell and were loaded into the ASE sample tray. Samples were extracted using dichloromethane (DCM) under the following conditions: pressure 1,500 psi, temperature 100 °C and heat for 5 minutes, and purge at 60 percent of the volume for three cycles. Approximately 40 mL of DCM-extract was ultimately collected for each sample and evaporated to 1 mL. The sample vial was rinsed with two 3 mL fractions of hexane:acetone (3:1 v/v%) and added to the extract and evaporated to 3 mL. A 0.45 μm PTFE syringe filter was preconditioned with 2 fractions of 3 mL DCM and used to filter the extract, followed by 1 mL DCM and 1 mL 3:1 hexane:acetone, and evaporated to 1 mL and transferred to an autosampler vial. The previous vial was rinsed with 2 fractions of 0.5 mL DCM, added to the extract and evaporated to 0.5 mL. Twenty microliters of the extract were used to make a ten-fold dilution of the sample and was fortified with 20 ng dibromooctafluorobiphenyl (DBFOB).

Data Acquisition

Analysis was carried out on an Agilent 6890 Gas Chromatograph to an Agilent 5973N Mass Spectrometer. Separation was achieved on an Agilent HP-5MS column (30 m x 0.25 mm, 0.25 μm) and the mass spectrometer was run in negative chemical ionization (NCI) mode with selected ion monitoring (SIM) used to maximize sensitivity. A 35-minute run time was used with a stepwise temperature gradient. Oven temperature was held at 200 °C for the initial 15 min, followed by an increase to 290 °C over 3.8 min, and ending with a 10 min ramp to 300 °C. Details of the analytical settings are found in Appendix 1.

Target Quantification

Agilent MassHunter Quantitative Analysis was used to perform target concentration. A 13-point internal standard calibration curve was used using concentrations from 0.1-500 ppb and fit with a second order polynomial fit with $R^2 > 0.999$ for all compounds. Limits of detection and quantification were determined by a signal-to-noise ratio greater than 3 and 10, respectively. A

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linear limit of quantification was observed to further validate reliable quantification limits and was determined by the lowest calibration point where an accurate (70-130%) concentration was able to be calculated.

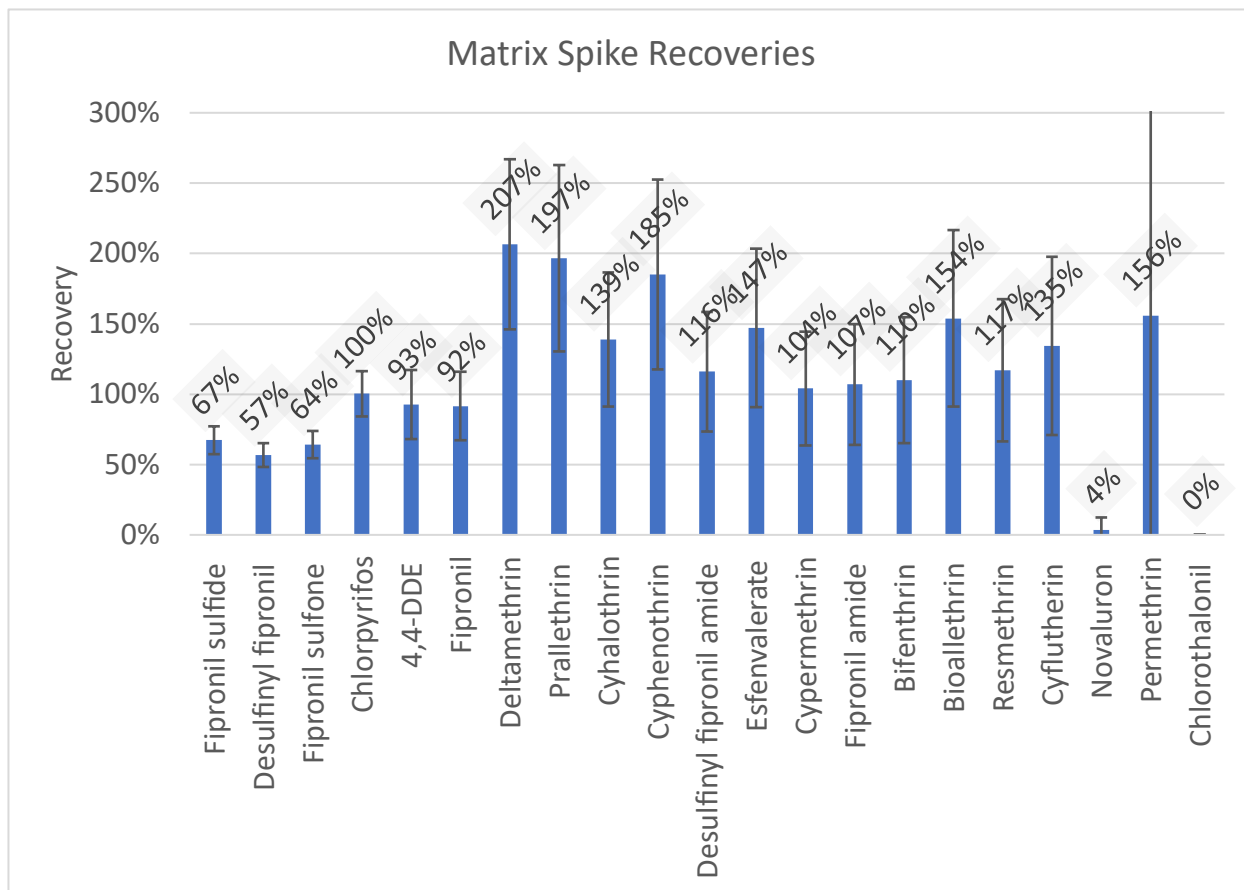
Method Validation

Twenty-one target compounds were spiked into four matrix spike samples (3220257, 3220251, 3220248, and 3220242), and two matrix spike duplicates (3220251 and 3220248). Recoveries averaged between 57-140% for most compounds, with the exception of chlorothanolil and novaluron which were not sufficiently recovered, and are therefore not included in this technique. Deltamethrin, prallethrin, cyphenothrin, esfenvalerate and bioallethrin were recovered at greater than 150%. Permethrin was poorly recovered in most samples and had a coefficient of variation >300% and was therefore not included in this study. Higher than standard variation was observed across samples; this is believed to have been related to the diverse physical composition of these samples, particularly their diverse organic carbon profiles. Dissolved Organic Carbon (DOC) in aqueous samples has been shown to inhibit recovery of hydrophobic compounds from surface waters (Hladik et al, 2004) and from runoff and stream water (Liu et al 2004). Freeze drying of samples was added to reduce some compositional variation (e.g., moisture content), however organic content, particle size, and other physical characteristics remain diverse, and because of this we believe a range of extractability of pyrethroids was observed. Further analysis would be required to confirm this hypothesis.

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References

Hladik, Michelle & McWayne, M.M.. (2012). Methods of analysis - determination of pesticides in sediment using gas chromatography/mass spectrometry. USGS Techniques and Methods Report 5-C3.

Hladik M, Orlando J, Kuivila K. Collection of Pyrethroids in Water and Sediment Matrices: Development and Validation of a Standard Operating Procedure. Scientific Investigations Report 2009-5012. (2009).

Liu W, Gan JJ, Lee S, Kabashima JN. Phase distribution of synthetic pyrethroids in runoff and stream water. Environ Toxicol Chem. 2004 Jan;23(1):7-11. doi: 10.1897/03-183. PMID: 14768860.

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Appendix I

INSTRUMENT CONTROL PARAMETERS: 5973N MSD

C:\MSDCHEM\1\METHODS\220223_NCI_PESTICIDES_SIM.M
Fri Mar 04 18:10:55 2022

Control Information

Sample Inlet : GC
Injection Source : GC ALS
Mass Spectrometer : Enabled

No Sample Prep method has been assigned to this method.

=====
6890 GC METHOD
=====

OVEN

Equilibration time: 3.00 min
Maximum temp: 325 C
Initial temp: 100 C (On)
Initial time: 1.00 min
Ramps:
Rate Final temp Final time
1 15.00 200 0.00
2 3.80 290 0.00
3 10.00 300 4.00
4 0 (Off)
Post temp: 50 C
Post time: 0.00 min
Run time: 36.35 min

FRONT INLET (SPLIT/SPLITLESS)

Mode: Pulsed Splitless
Initial temp: 280 C (On)
Pressure: 10.5 psi (On)
Pulse pressure: 20.0 psi
Pulse time: 0.50 min

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Purge flow: 40.0 mL/min
Purge time: 0.75 min
Total flow: 43.7 mL/min
Gas saver: On
Saver flow: 20.0 mL/min
Saver time: 2.00 min
Gas type: Helium

BACK INLET (SPLIT/SPLITLESS)

Mode: Split
Initial temp: 50 C (Off)
Pressure: 0.0 psi (Off)
Total flow: 45.0 mL/min
Gas saver: Off
Gas type: Helium

COLUMN 1

Capillary Column
Model Number: 1909S-433UI
Description: DB-5ms
Max temperature: 350 C
Nominal length: 30.0 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Mode: constant flow
Initial flow: 1.0 mL/min
Nominal init pressure: 10.5 psi
Average velocity: 37 cm/sec
Inlet: Front Inlet
Outlet: MSD
Outlet pressure: vacuum

COLUMN 2

(not installed)

FRONT DETECTOR (NO DET)

BACK DETECTOR (NO DET)

SIGNAL 1

Save Data: Off

SIGNAL 2

Save Data: Off

THERMAL AUX 2

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Use: MSD Transfer Line Heater
Initial temp: 280 C (On)

POST RUN

Post Time: 0.00 min

INJECTOR 1

Solvent Wash Mode: A, B
Waste Bottle Use: A Only
Sample Volume (uL): 1.500
Syringe size (uL): 5.0
Pre washes from bottle A: 2
Pre washes from bottle B: 2
Post washes from bottle A: 2
Post washes from bottle B: 2
Viscosity delay (seconds): 0
Pre injection dwell (min): 0.00
Post injection dwell (min): 0.00
Sample skim depth (mm): 0.0 (Off)
Plunger Speed: Fast
Solvent saver: Off

ALS ERRORS:

On missing vial: pause

TIME TABLE

Time(min) Parameter & Setpoint

Column 1 Inventory Number :

Column 2 Inventory Number :

MS ACQUISITION PARAMETERS

General Information

Tune File : ncich4.u

Acquisition Mode : SIM

MS Information

Solvent Delay : 3.00 min

EMV Mode : Relative

Relative Voltage : 0

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Resulting EM Voltage : 2035

[Sim Parameters]

GROUP 1

Group ID : 1

Resolution : Low

Plot 1 Ion : 85.00

Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(85.00, 100) (163.00, 100) (182.00, 100)

GROUP 2

Group ID : 2

Resolution : Low

Group Start Time : 7.60

Plot 1 Ion : 208.10

Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(208.10, 100) (263.90, 100) (265.90, 100)
(316.00, 100) (352.00, 100) (354.00, 100)
(453.85, 100) (455.80, 100) (457.80, 100)

GROUP 3

Group ID : 3

Resolution : Low

Group Start Time : 10.50

Plot 1 Ion : 169.00

Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(169.00, 100) (179.05, 100) (211.90, 100)
(312.95, 100) (322.00, 100) (324.00, 100)

GROUP 4

Group ID : 4

Resolution : Low

Group Start Time : 11.30

Plot 1 Ion : 330.95

Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(132.05, 100) (134.05, 100) (167.10, 100)
(168.10, 100) (284.00, 100) (287.20, 100)
(288.00, 100) (330.95, 100) (350.95, 100)
(365.95, 100) (383.95, 100) (385.95, 100)

GROUP 5

Group ID : 6

Resolution : Low

Group Start Time : 13.10

Plot 1 Ion : 346.95

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Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(346.95, 100) (370.00, 100) (372.00, 100)
(382.95, 100) (406.00, 100) (415.95, 100)

GROUP 6

Group ID : 7
Resolution : Low
Group Start Time : 16.30
Plot 1 Ion : 402.00
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(402.00, 100) (409.95, 100) (411.95, 100)

GROUP 7

Group ID : 8
Resolution : Low
Group Start Time : 17.40
Plot 1 Ion : 167.10
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(167.00, 100) (167.10, 100) (205.05, 100)
(241.00, 100) (331.20, 100) (332.20, 100)
(349.20, 100) (386.15, 100)

GROUP 8

Group ID : 9
Resolution : Low
Group Start Time : 19.60
Plot 1 Ion : 241.00
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(167.10, 100) (168.00, 100) (205.00, 100)
(241.00, 100) (243.00, 100)

GROUP 9

Group ID : 10
Resolution : Low
Group Start Time : 21.10
Plot 1 Ion : 207.00
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(171.00, 100) (207.00, 100) (208.00, 100)

GROUP 10

Group ID : 11
Resolution : Low
Group Start Time : 22.50
Plot 1 Ion : 171.00
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(171.00, 100) (207.00, 100) (208.00, 100)

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GROUP 11

Group ID : 12
Resolution : Low
Group Start Time : 25.50
Plot 1 Ion : 79.00
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(79.00, 100) (80.90, 100) (167.00, 100)
(211.05, 100) (213.00, 100)

[MSZones]

MS Source : 150 C maximum 300 C
MS Quad : 150 C maximum 200 C

END OF MS ACQUISITION PARAMETERS

TUNE PARAMETERS for SN: US02080150

Trace Ion Detection is OFF.

EMISSION : 60.568
ENERGY : 235.008
REPELLER : 3.821
IONFOCUS : 101.545
ENTRANCE_LE : 47.000
EMVOLTS : 2035.294
Actual EMV : 2035.29
GAIN FACTOR : <Unable to calculate gain factor.>
AMUGAIN : 2251.000
AMUOFFSET : 136.000
FILAMENT : 1.000
DCPOLARITY : 0.000
ENTLENSOFFS : 5.522
MASSGAIN : 241.000
MASSOFFSET : -8.000
CI Flow Rate: 40
CI A/B Gas : 1

END OF TUNE PARAMETERS

END OF INSTRUMENT CONTROL PARAMETERS
