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PO-CON1444E

Multi-residue analysis of pyrethroids in soil and sediment using QuEChERS by LC/MS/MS

ASMS 2014 TP 560

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Introduction

Pytrethroids are one of the most widely used commercial household insecticides in agricultural or non-agricultural application sites. Synthetic pyrethroids are poorly water-soluble, but are strongly adsorbed to soil, therefore these compounds are increasingly being found in soil or sediments. Recently, soil and sediment contamination by pyrethroids has been detected in both urban and agricultural area, and it's becoming a global concern due to the influence on the insects and aquatic invertebrates. Therefore, quick, high-sensitive and universal analysis methods are required. The analysis of pyrethroids is typically performed by GC or GC/MS because of their hydrophobicity. In this study, we report the development of a simultaneous analysis technique for trace amounts of pyrethroids by LC/MS/MS.

Materials and Methods

Materials

Sample	Sampling point
Soil	Residential garden (Kyoto, Japan)
Sediment	Lake Biwa (Shiga, Japan)

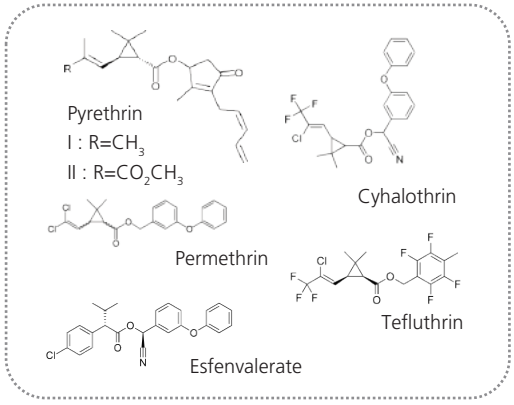

Figure 1 Chemical structure of pyrethroids

Sample preparation

Sample preparation was carried out by the use of the QuEChERS method. In case of the soil samples, hydration of sample with water before acetonitrile extraction is required to improve the recovery and operability. Result of several different extraction methods that changed the amount of the soil and water added, we finally adopted a combination of 5 g soil (or 10 g sediment) and 5 mL water, and the following procedures were based on the original QuEChERS method.

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Step 1 : Acetonitrile extraction

Weigh 5 g soil / 10 g sediment
(Add STDs solution)

↓

Add 5mL water

↓

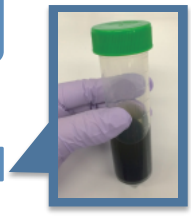
Add 10mL acetonitrile

↓

Add salt mixture*1
- 4g $MgSO_4$
- 1g NaCl
- 1g Trisodium citrate dehydrate
- 0.5g Disodium hydrogencitrate sesquihydrate

↓

Shake vigorously by hand 1min.



↓

Centrifuge for 10min. (Extract 1)

*1 : Q-sep QuEChERS Extraction Salts (RESTEK)

Step 2 : Clean-up

Transfer 6mL Extract 1 into dSPE tube*2
- 900 mg $MgSO_4$
- 150 mg PSA
- 45 mg GCB

↓

Shake vigorously by hand 1min.

↓

Centrifuge for 5min.

↓

Transfer the supernatant into a vial

↓

Filtration using disposable filter

↓

LC/MS/MS analysis

*2 : Q-sep QuEChERS dSPE Tubes (RESTEK)

LC/MS/MS analsis

HPLC conditions (Nexera UHPLC system, Shimadzu)

Column	: Phenomenex Kinetex 2.6 µm PFP 100Å (100 mm x 2.1 mm I.D.)
Mobile phase	: A 5mM ammonium acetate - water
	: B Methanol
Gradient program	: 40 % B (0 min.) → 100 % B (10 -12 min.) → 40 % B (12.01-15 min.)
Flow rate	: 0.2 mL / min.
Column temperature	: 40 °C
Injection volume	: 1 µL

MS conditions (LCMS-8050, Shimadzu)

Ionization	: ESI (positive / negative)
Interface temperature	: 100 °C
DL temperature	: 100 °C
Heat block temperature	: 400 °C
Nebulizing gas	: 3.0 L / min.
Drying gas	: 15.0 L / min.
Heating gas	: 3.0 L / min.

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Table 1 MRM transitions of pyrethroids

Compounds	Polarity	Quantitative ion (*m/z*)	Confirmation ion (*m/z*)
pyrethrin-I	+	329.20>161.20	329.20>105.20
pyrethrin-II	+	373.20>161.20	373.20>105.20
fenpropathrin	+	367.20>125.20	367.20>181.20
cycloprothrin	+	498.90>181.10	498.90>229.20
deltamethrin	+	522.80>280.90	522.80>181.10
esfenvalrate	+	437.10>167.30	437.10>125.30
cypermethrin	+	433.10>191.10	433.10>181.20
cyfluthrin	+	450.90>191.00	450.90>206.10
ethofenprox	+	394.20>177.30	394.20>107.20
permethrin	+	408.10>183.30	408.10>355.20
cyhalothrin	+	467.10>225.10	467.10>141.10
bifenthrin	+	440.00>181.20	440.00>166.10
acrinathrin	+	559.00>208.20	559.00>181.10
acrinathrin	-	540.10>372.20	540.10>345.30
silafluofen	+	426.20>287.10	426.20>168.20

High Speed Mass Spectrometer

Ultra Fast Scanning
- 30,000 u / sec.

Ultra Fast Polarity Switching
- 5 msec.

Ultra Fast MRM
- Max. 555 transitions / sec

Figure 2 LCMS-8050 triple quadrupole mass spectrometer

Result

MRM of pyrethroid standards

In this study, we selected and evaluated 15 pyrethroids (pyrethrin, fenpropathrin, cycloprothrin, deltamethrin, esfenvarelate, cypermethrin, cyfluthrin, ethofenprox, permethrin, cyhalothrin, bifenthrin, acrinathrin, tefluthrin, silafruofen) which are the most widely used for household or agrocultural insecticides worldwide.
Except for tefluthrin, which was not ionized by LC/MS under conditions tested, all other 14 compounds were successfully detected in ESI positive mode or in both positive and negative mode.

Multi-residue analysis of pyrethroids in soil and sediment using QuEChERS by LC/MS/MS

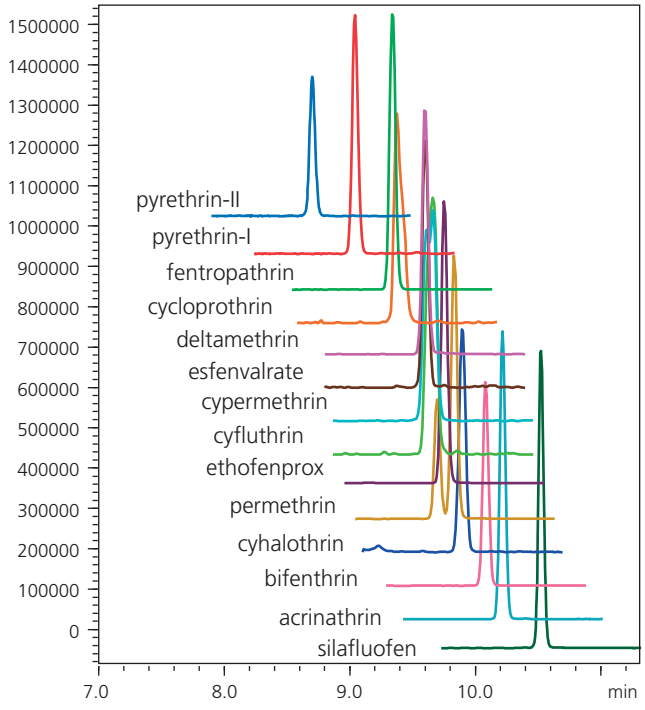

Figure 3 MRM chromatograms

Table 2 Calibration curves

compounds	min. conc.	max. conc.	r^2
pyrethrin I	0.5	500	0.9996
pyrethrin II	0.5	500	0.9997
fenpropathrin	0.02	100	0.9993
cycloprothrin	0.5	100	0.9991
deltamethrin	0.05	100	0.9992
esfenvalerate	0.5	100	0.9990
cypermethrin	0.05	100	0.9986
cyfluthrin	0.5	100	0.9976
ethofenprox	0.01	100	0.9993
trans-permethrin	0.02	100	0.9996
cis-permethrin	0.02	100	0.9994
cyhalothrin	0.1	100	0.9993
bifenthrin	0.02	100	0.9995
acrinathrin (+)	0.1	100	0.9987
acrinathrin (-)	0.5	500	0.9993
silafluofen	0.01	100	0.9999

(ppb)

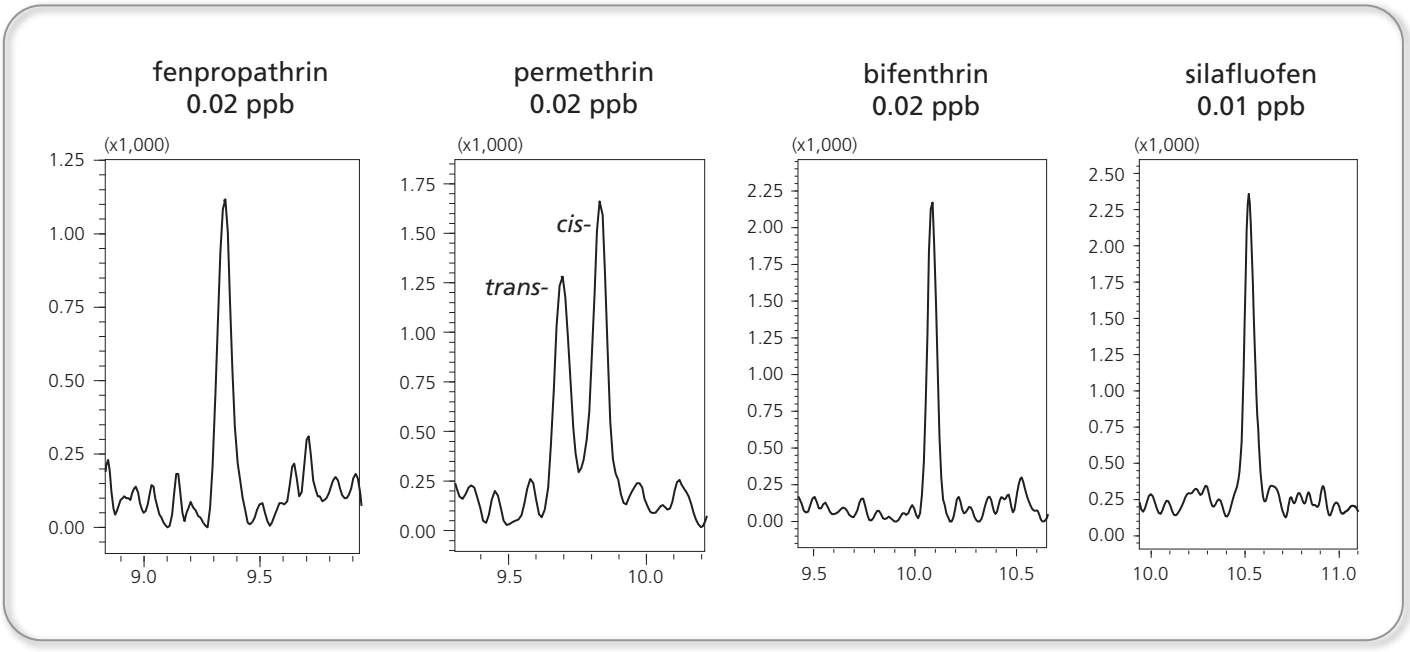

Figure 4 MRM chromatograms of the LOQs of typical pyrethroids

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Recovery from soil and sediment matrices

All target compounds showed good recoveries from soil and sediment matrices in the range 70-120% by the QuEChERS method. Neither matrix effect (Ion suppression or enhancement) nor sample preparation losses were observed.

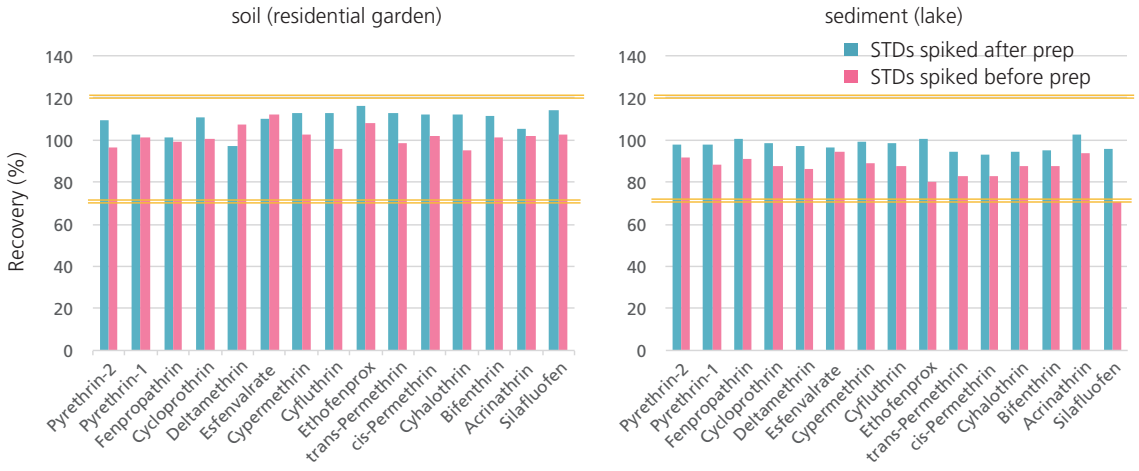

Figure 5 Recovery of 14 pyrethroids from soil and sediment matrices (10 ppb spiked)

Quantitative analysis of soil and sediment

The quantitative analysis of the soil and sediment sample was performed. Ethofenprox and permethrin was detected from the soil sample at approximately 0.02 and 0.06 µg / kg, respectively.

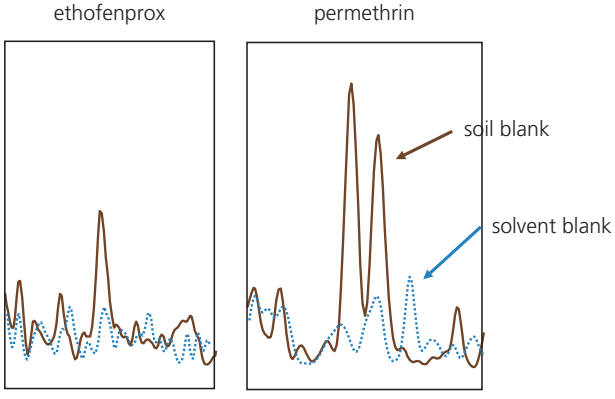

Figure 6 Chromatograms of prethroids in the soil

Table 3 Result of quantitative analysis in the soil and sediment

	soil	sediment
pyrethrin-I	n.d.	n.d.
pyrethrin-II	n.d.	n.d.
fenpropathrin	n.d.	n.d.
cycloprothrin	n.d.	n.d.
deltamethrin	n.d.	n.d.
esfenvalrate	n.d.	n.d.
cypermethrin	n.d.	n.d.
cyfluthrin	n.d.	n.d.
ethofenprox	0.01 ppb*	n.d.
permethrin	0.03 ppb	n.d.
cyhalothrin	n.d.	n.d.
bifenthrin	n.d.	n.d.
acrinathrin	n.d.	n.d.
silafluofen	n.d.	n.d.

n.d. : not detected
* : <LOQ

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Conclusions

- A method for quantification of 14 pyrethroids in soil and sediment at ppt-level concentrations was developed by LC/MS/MS.
- In this study, neither matrix effect nor sample preparation losses were observed in the recovery test, demonstrating the applicability of QuEChERS method to sample preparation of soil and sediment.

First Edition: June, 2014

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