Supporting Information

Translocation, distribution and degradation of prochloraz-loaded mesoporous silica nanoparticles in cucumber plant

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Preparation of suspension concentrates

In order to compare the distribution and degradation of p-MSNs and prochloraz, conventional prochloraz SC and p-MSNs SC were prepared by bead milling process, respectively. In the proposed SC, Morwet D425 was used as dispersant. As the active ingredient, prochloraz accounted for 20 % in both p-MSNs and conventional SC. The particle size and distribution of conventional SC were carried out by BT-9300ST laser particle size distribution analyzer (Bettersize Instruments Ltd., Liaoning, China). The D_{50} and D_{90} of the particle size was 1.397 and 3.771 μm for conventional SC, respectively.

Sample preparation and analytical method

A modified QuEChERS method was carried out to measure the concentration levels of prochloraz and its metabolite 2,4,6-TCP in cucumber plants. The procedure involved miniaturized extraction of 2.0 g homogenized sample with acetonitrile, followed by liquid–liquid partition by adding 3.0 g of sodium chloride. After that, the processes of cleanup and residual water removal were carried out by mixing 1 mL of acetonitrile extract with some loose sorbents. For prochloraz analysis, 150 mg of anhydrous magnesium sulfate and 25 mg of PSA were used as the sorbent; for 2,4,6-TCP analysis, 150 mg of anhydrous magnesium sulfate and 5 mg of MWCNTs were used. The samples of treated leaves were diluted 20-fold before injection. HPLC-MS/MS was then operated for confirmatory and quantitative analysis of prochloraz and 2,4,6-TCP.

Prochloraz and 2,4,6-TCP determinations were performed on an Agilent 1200 HPLC equipped with a reversed-phase column (ZORBAX SB-C18, 3.5 μm, 2.1 mm ×50 mm, Agilent, USA) at 30 ºC. The mobile phase was acetonitrile/water (80/20, v/v) with a flow rate of 0.3 mL/min. The injection volume was 5 μL. An Agilent 6410 Triple Quad LC/MS system with ESI source was conducted for the mass spectrometric analysis. Nitrogen was introduced as the nebulizer and collision gas. The parameters of operation were as followed: gas temperature, 350 ºC; gas flow, 8 L/min; nebulizer gas, 35 psi; capillary voltage, 4,000 V. The multiple reaction monitoring mode was used to monitor the precursor-product ion transitions. Agilent Mass Hunter Data Acquisition and Qualitative Analysis and Quantitative Analysis software was employed for method development and data acquisition. Table S1 showed the multiple reaction monitoring transitions and other HPLC−MS/MS parameters for prochloraz and 2,4,6-TCP analysis.

Analytical method validation

The matrix-matched calibration solutions were obtained from calibration solutions in extracts of blank samples at five different concentrations for prochloraz and 2,4,6-TCP in the range of 0.005 ~ 1 mg/L. To evaluate the precision and accuracy of the sample preparation method, prochloraz and 2,4,6-TCP were spiked at four fortified levels of 0.005, 0.01, 0.1 and 1 mg/kg in blank leaf, root and cucumber samples, respectively. Each spiked level test was repeated five times to verify the repeatability of the proposed method. Recovery rate was the amount determined as a

64 percentage of the amount of prochloraz or 2,4,6-TCP originally spiked into the blank
65 samples. The repeatability of the proposed method was shown as a relative standard
66 deviation (RSD, %, n=5). Limits of quantification (LOQs) were determined as the
67 concentration of the compound giving a signal to noise ratio (S/N) of 10 for the target
68 ion, which was calculated by Agilent Mass Hunter Qualitative Analysis software.

Table S1. MRM transitions and other HPLC−MS/MS parameters for prochloraz and 2,4,6-TCP analysis

Compound	Retention time (min)	Fragmentor (V)	Quantifying ions	Qualifying ions	Collision energy (V)	Ionization mode
prochloraz	1.28	80	376.2/308.2	376.2/266.2	10;10	positive
2,4,6-TCP	1.38	80	195.0/158.8	195.0/93.2	40;10	negative

Table S2. Average recoveries at fortified levels of 0.005, 0.01, 0.1 and 1 mg/kg, RSDs (n=5), LOQs, linear equation, determination coefficients (R^2) of prochloraz and its metabolite 2,4,6-TCP in leaf, root and cucumber.

Compound	Sample	Linear equation	R^2	LOQ (mg/kg)	Average recovery % (RSD %)			
					0.005 mg/kg	0.01 mg/kg	0.1 mg/kg	1 mg/kg
prochloraz	Leaf	y = 2907302 x - 8257	0.9997	0.002	71 (6)	80 (5)	91 (4)	92 (6)
	Root	y = 1966195 x - 1473	0.9999	0.001	78 (9)	89 (4)	87 (3)	81 (5)
	Cucumber	y = 2051555 x - 83	0.9991	0.001	77 (10)	92 (6)	78 (7)	82 (7)
2,4,6-TCP	Leaf	y = 31071x + 97	0.9998	0.005	81 (8)	90 (6)	74 (8)	73 (6)
	Root	y = 43113x - 199	0.9981	0.002	79 (7)	83 (7)	77 (10)	82 (5)
	Cucumber	y = 26186 x + 718	0.9997	0.002	73 (9)	81 (9)	83 (6)	89 (4)