Supplementary Information

Microcapsule oil dispersion for 1-methylcyclopropene's controlled release in open environments

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1. Preparation and characterization of 1-MCP microcapsule granules (1-MCP/MCG)

1.1. Materials.

Sodium amide ($NaNH_2$) at a purity of 98%, tetrahydrofuran (THF) at a purity of 99+%, were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd. (China). 3-Chloro-2-methylpropene (3-CMP) at a purity of 98%, alpha-Cyclodextrin (α-CD) at a purity of 98% were obtained from Sa'en Chemical Technology (Shanghai) Co., Ltd. (China). Deionized water was obtained from College of Science, China Agricultural University.

1.2. Preparation of 1-MCP microcapsule granules (1-MCP/MCG).

Farley Fisher et al. prepared 1-MCP by using $NaNH_2$ and 3-CMP to remove hydrogen chloride by gamma elimination. In this study, the method was improved (Fig. S1) and 1-MCP gas was obtained. At the same time, 1-MCP gas was introduced into a saturated aqueous solution of α-CD. It was reported to be effective gas carriers that α-CD are used as a gas container. After precipitation of white suspension, 1-MCP/MCG was obtained by filtration, drying and pulverizing.

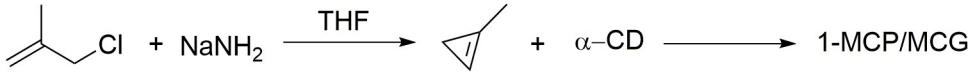

Fig. S1 The preparation of 1-MCP/MCG.

1.3. Characterization of 1-MCP/MCG

Qualitative and quantitative analysis. The qualitative analysis of 1-MCP was measured

on a GCMS-QP2010 SE gas chromatograph mass spectrometer (SHIMADZU) with a Rtx-5Sil MS column (30 m, 0.25 mm ID, 0.25 μm; Restek, USA). The injection pot and detector temperatures were set at 150 and 200 °C, respectively. The column temperature was 150 °C with a hold time of 3 min and the totally analysis time was 3 min. The quantitative analysis of 1-MCP was measured on a GC-2010 Plus gas chromatograph (SHIMADZU) with a Rtx-5 column (30 m, 0.25 mm ID, 0.25 μm; Restek, USA). The injection pot and detector temperatures were set at 150 and 200 °C, respectively. The column temperature was 150 °C with a hold time of 3 min and the totally analysis time was 3 min. Quantification of 1-MCP was accomplished using an external standard method. The isobutylene gas standard of 100 μL/L concentration was used. It was presumed that quantities of 1-MCP had a response factor similar to that of isobutylene.

Fourier transform infrared spectroscopy (FTIR). FTIR spectra were recorded from 4000 to 400 cm^{-1}, using a Fourier transform model Tracer-IR 1000 infrared spectrometer (SHIMADZU) on samples prepared as KBr disks.

^{1}H nuclear magnetic resonance analysis (^{1}H NMR). ^{1}H NMR spectra were obtained using a 300 MHz spectrometer (Bruker Avance DPX300 MHz). Dimethyl sulfoxide (DMSO-d_6) was adopted as the solvent to dissolve all the samples.

Thermal analysis. Thermogravimetric (TG) curves were recorded on a PerkinElmer

STA6000 (PerkinElmer) synchronous thermal analyzer. Samples of 8 mg were weighed into aluminum pans for analysis at a heating rate of 10 °C/min from 30 to 550 °C under a nitrogen flow at 20 mL min^{-1}.

2. Results and discussion

2.1. The results of qualitative and quantitative analysis.

The GCMS chromatogram and mass spectrogram of 1-MCP in 1-MCP/MCG are shown in Figs. S2 and S3, respectively. It was proved that 1-MCP was in 1-MCP/MCG. The content of 1-MCP in 1-MCP/MCG was 3.30% (w/w).

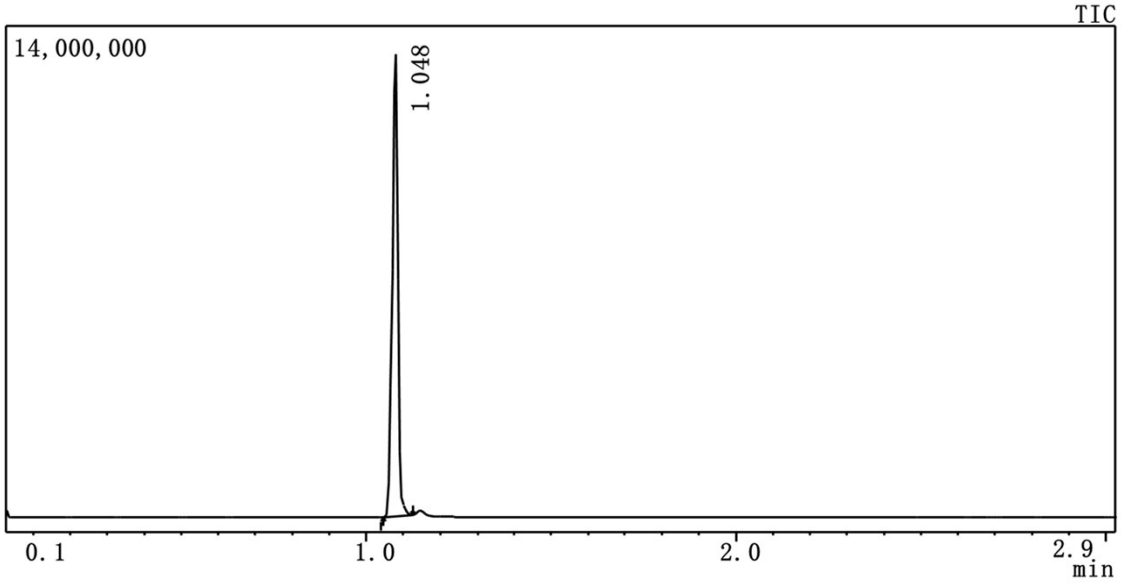

Fig. S2 The GCMS chromatogram of 1-MCP in 1-MCP/MCG.

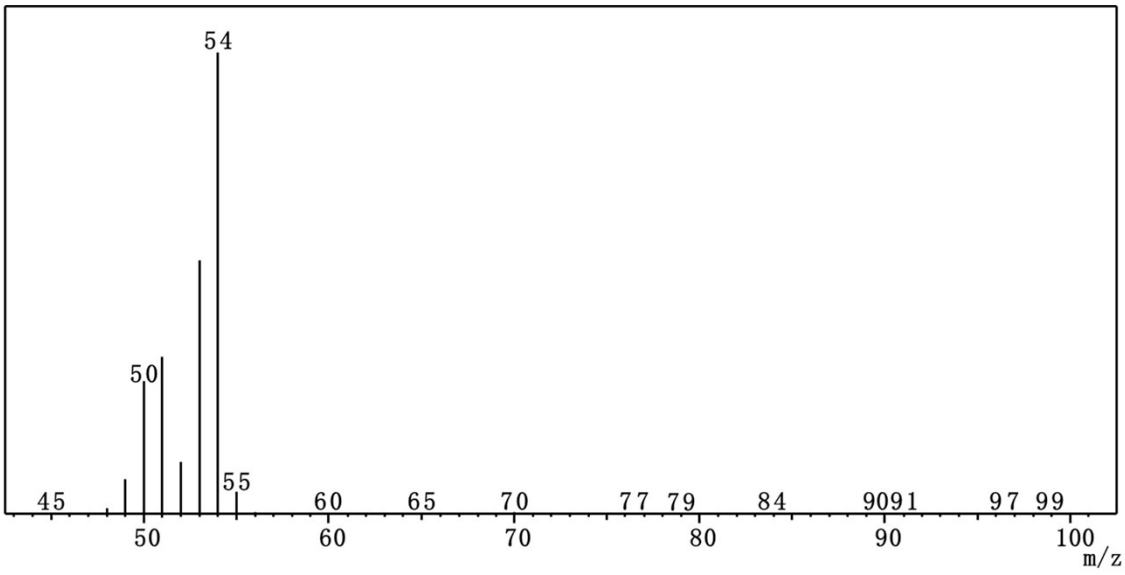

Fig. S3 The GCMS mass spectrogram of 1-MCP in 1-MCP/MCG.

2.2. The Results of FTIR, ^{1}H NMR and TG.

FTIR, ^{1}H NMR and TG were used to characterize the products of 1-MCP/MCG. The results are shown in Fig. S4.

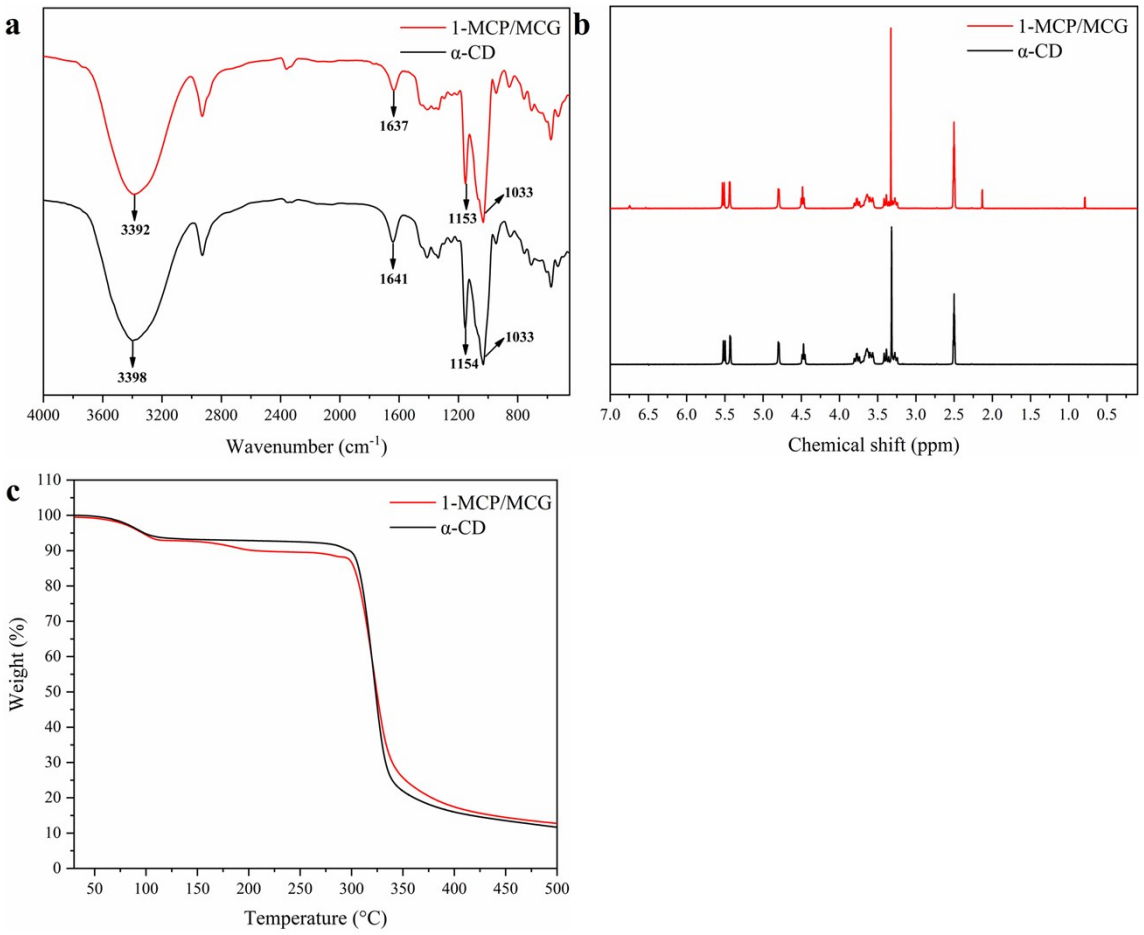

Fig. S4 Characterization results of 1-MCP/MCG, a. FTIR, b. ^{1}H NMR, c. TG.

The FTIR spectrum (Fig. S4a) showed that the infrared spectra of α-CD and 1-MCP/MCG were very similar, because for small molecules such as 1-MCP, the content of 1-MCP in 1-MCP/MCG was very low by 3.30% (w/w). The characteristic peaks of 1-MCP were easily masked by the absorption peaks of α-CD. Compared with α-CD and 1-MCP/MCG, they exhibited strong-OH characteristic absorption near 3440 cm^{-1} (ν (O-H)). Absorption peak of in-plane bending vibration was near 1640 cm^{-1} (δ (O-H)). Asymmetric vibration of C-O-C bond and stretching vibration of C-C/C-O bond attributed to α-CD

occurred around 1028~1160 cm^{-1} (ν (C-O)). This indicated that 1-MCP has been completely encapsulated by α-CD.

The ^{1}H NMR spectra of 1-MCP/MCG and α-CD are shown in Fig. S4b, and their characteristic displacements were shown in Table S1. The results showed that 1-MCP/MCG contained the host α-CD and the guest 1-MCP.

Table S1 ^{1}H NMR characteristic shift (δ) data of α-CD and 1-MCP/MCG.

Sample	H-1	H-2	H-3	H-4	H-5	H-6	CH	CH2	CH3
α-CD	4.796	3.385	3.774	3.269	3.585	3.654			
1-MCP/MCG	4.796	3.386	3.773	3.274	3.584	3.654	6.746	0.790	2.132

The TG diagrams of 1-MCP/MCG and α-CD are shown in Fig. S4c. For α-CD, weightlessness mainly occurred in two stages. The first weightlessness stage occurred at 50~100 °C, because the product loosed moisture. The second weightlessness stage occurred at 300~400 °C, because the product carbonized and decomposed. For 1-MCP/MCG, weightlessness mainly occurred in three stages. The first and third weightlessness stages were the same as the first and second weightlessness stages of α-CD. Compared with α-CD, the second weightlessness stage of 1-MCP/MCG occurred at 150~200 °C, because 1-MCP got away from 1-MCP/MCG. This proved that 1-MCP existed in 1-MCP/MCG.

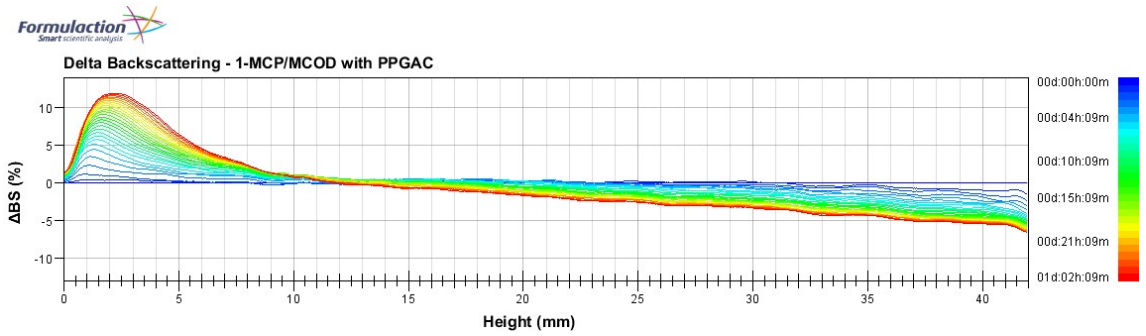

Fig. S5 Changes in backscattering (delta backscattering) as a function of sample height (0 to 42 mm) and time (from 0:00 to 26:00 h) of 1-MCP/MCOD prepared using PPGAC.

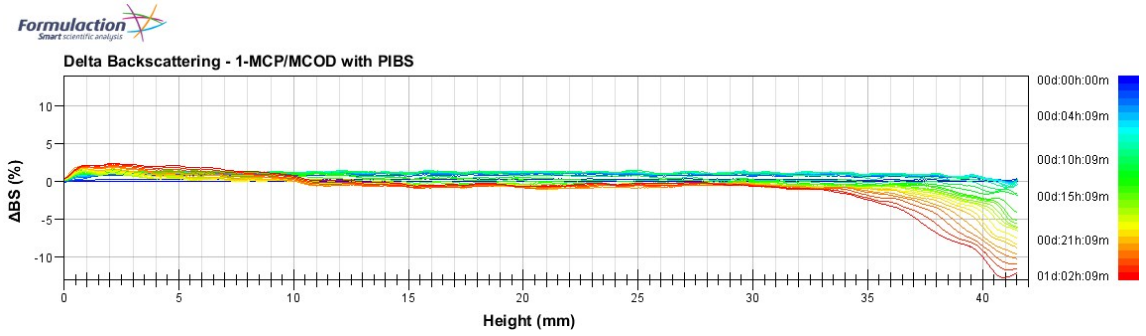

Fig. S6 Changes in backscattering (delta backscattering) as a function of sample height (0 to 42 mm) and time (from 0:00 to 26:00 h) of 1-MCP/MCOD prepared using PIBS.

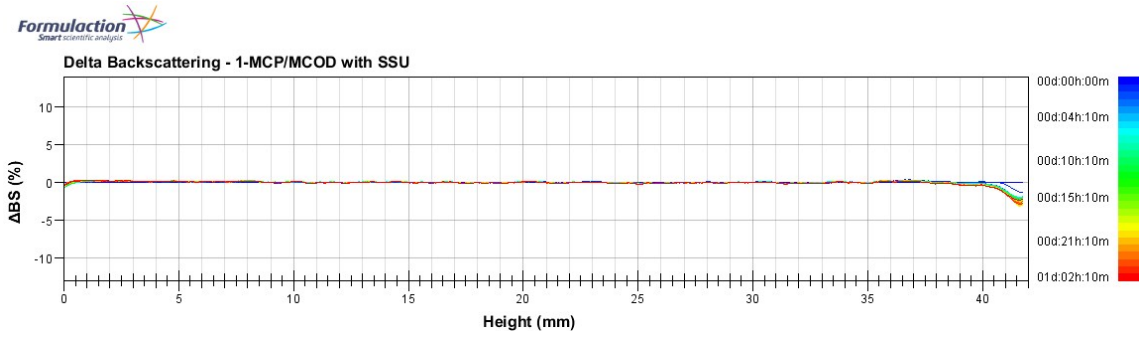

Fig. S7 Changes in backscattering (delta backscattering) as a function of sample height (0 to 42 mm) and time (from 0:00 to 26:00 h) of 1-MCP/MCOD prepared using SSU.

Table S2 Physical and chemical properties of 1-MCP/MCOD formulation after and before storage stability test.

Time	Fresh formulation	After 7 days	After 14 days
Temperature	Room temperature	0 °C	54 °C
Appearance	White solid-liquid suspension	White solid-liquid suspension	White solid-liquid suspension
Content of 1-MCP	0.80%	0.80%	0.79%
Particle size (D_{50})	3.28 μm	3.35 μm	3.54 μm
Particle size (Span)	1.984	1.841	1.452
Density	0.9743 g/mL	0.9751 g/mL	0.9790 g/mL
Viscosity	320 mPa·s	320 mPa·s	325 mPa·s
pH (1%)	7.08	7.10	7.15
Moisture	2.25%	2.24%	2.21%
Emulsion stability	Qualified	Qualified	Qualified

Table S3 Relationship between 1-MCP measured concentrations / relative concentration in the airtight box at different dilution factors.

Time (h)	Measured concentration (μL L^{-1})			Relative concentration		
	Dilution factor 30	Dilution factor 20	Dilution factor 10	Dilution factor 30	Dilution factor 20	Dilution factor 10
1	28.71	42.37	119.96	1.00	1.00	1.00
2	25.69	39.90	129.21	0.89	0.94	1.08
3	24.88	34.25	140.49	0.87	0.81	1.17
4	24.09	32.77	148.69	0.84	0.77	1.24
5	23.12	30.78	157.80	0.81	0.73	1.32
6	22.31	28.34	163.42	0.78	0.67	1.36
7	21.50	26.67	163.90	0.75	0.63	1.37
8	20.74	25.94	163.31	0.72	0.61	1.36
9	20.00	25.09	165.55	0.70	0.59	1.38
10	19.51	23.75	163.22	0.68	0.56	1.36
11	18.32	23.95	167.48	0.64	0.57	1.40
12	18.98	22.35	168.44	0.66	0.53	1.40
13	17.90	21.12	162.94	0.62	0.50	1.36
14	16.90	20.55	162.72	0.59	0.49	1.36
20	14.33	16.74	179.32	0.50	0.40	1.49
21	14.00	16.03	175.49	0.49	0.38	1.46
22	13.68	15.75	169.22	0.48	0.37	1.41
23	13.44	15.43	171.54	0.47	0.36	1.43
24	12.55	15.11	169.25	0.44	0.36	1.41
25	12.13	14.76	167.70	0.42	0.35	1.40

26	11.98	14.12	170.71	0.42	0.33	1.42
28	11.95	13.59	169.60	0.42	0.32	1.41
31	11.91	12.96	168.43	0.41	0.31	1.40
36	10.5	11.89	167.92	0.37	0.28	1.40

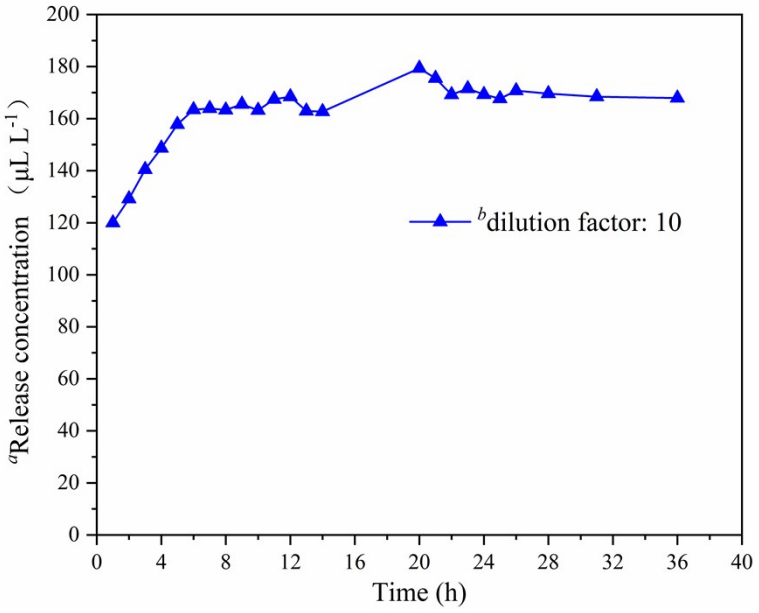

Fig. S8 The relationship between the release concentrations of 1-MCP at dilution factor 10 and the release time in the airtight box.

[a] Release concentrations of 1-MCP which have been obtained from GC method. [b] (1-MCP/MCOD + water) / (1-MCP/MCOD) (weight) = 10.

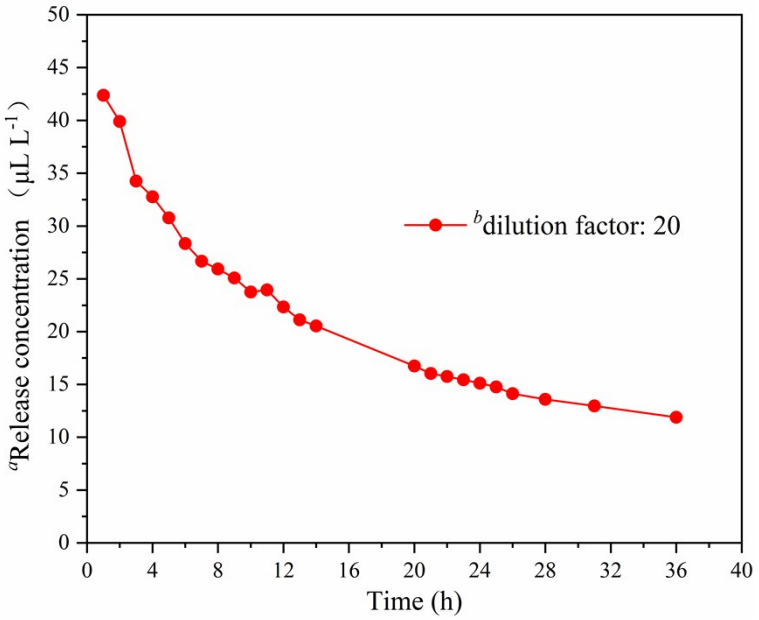

Fig. S9 The relationship between the release concentrations of 1-MCP at dilution factor 20 and the release time in the airtight box.

[a] Release concentrations of 1-MCP which have been obtained from GC method. [b] (1-MCP/MCOD + water) / (1-MCP/MCOD) (weight) = 20.

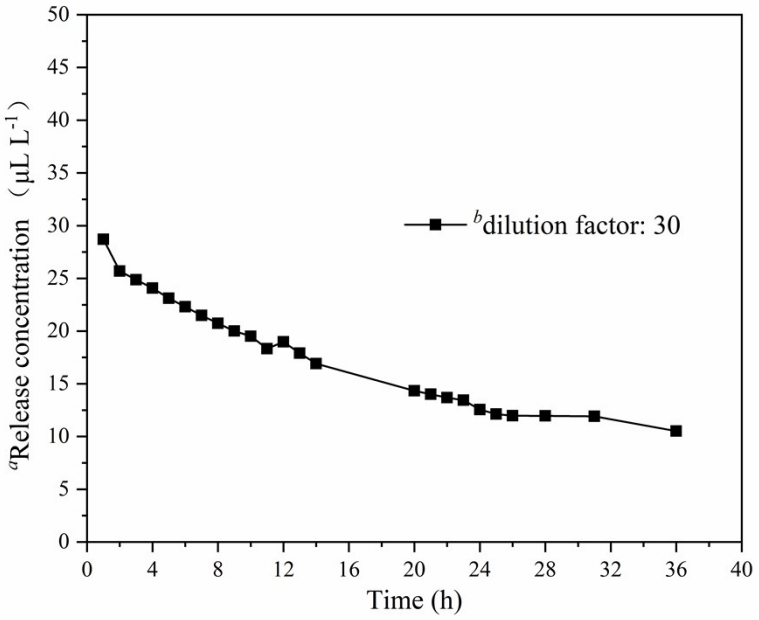

Fig. S10 The relationship between the release concentrations of 1-MCP at dilution factor

30 and the release time in the airtight box.

[a] Release concentrations of 1-MCP which have been obtained from GC method. [b] (1-MCP/MCOD + water) / (1-MCP/MCOD) (weight) = 30.

Table S4 Days after application and cumulative fruit drop (No. apples per tree) of "Jinhong".

Treatment	Cumulative fruit drop (No. apples per tree)					Total number of apples
	Aug. 11	Aug. 14	Aug. 15	Aug. 16	Aug. 23	
1-MCP/MCOD, airtight tent, 3 μL L^{-1}	0	0	0	0	5	302
1-MCP/MCOD, airtight tent, 30 μL L^{-1}	0	9	11	12	27	315
1-MCP/MCOD, open 3 μL L^{-1}	0	4	9	9	14	437
1-MCP/MCOD, open 30 μL L^{-1}	8	8	8	8	18	291
CK-1	0	17	21	28	94	384
CK-2	0	16	24	32	112	326

Table S5 Days after application and cumulative fruit drop (%) of "Jinhong".

Treatment	Cumulative fruit drop (%)				
	Aug. 11	Aug. 14	Aug. 15	Aug. 16	Aug. 23
1-MCP/MCOD, airtight tent, 3 μL L^{-1}	0	0	0	0	1.7
1-MCP/MCOD, airtight tent, 30 μL L^{-1}	0	2.9	3.5	3.8	8.6
1-MCP/MCOD, open 3 μL L^{-1}	0	0.9	2.1	2.1	3.2
1-MCP/MCOD, open 30 μL L^{-1}	0	2.7	2.7	2.7	6.2
CK-1	0	4.4	5.5	7.3	24.5
CK-2	0	4.9	7.4	9.8	34.4

Table S6 Days after application and cumulative fruit drop (No. apples per tree) of "Longfeng".

Treatment	Cumulative fruit drop (No. apples per tree)					Total number of apples
	Sept. 3	Sept. 9	Sept. 14	Sept. 16	Sept. 21	
1-MCP/MCOD, airtight tent, 0.3 μL L^{-1}	0	23	50	73	135	887
1-MCP/MCOD, airtight tent, 1 μL L^{-1}	0	11	18	21	25	501
1-MCP/MCOD, airtight tent, 3 μL L^{-1}	0	5	8	8	21	475
1-MCP/MCOD, open 0.3 μL L^{-1}	0	8	18	24	71	197
1-MCP/MCOD, open 1 μL L^{-1}	0	5	15	16	38	289
1-MCP/MCOD, open 3 μL L^{-1}	0	9	13	13	15	249
1-MCP/MCG fumigated 1 μL L^{-1}	0	13	26	27	33	635
CK-1	0	11	48	64	153	582
CK-2	0	23	45	83	248	584

Table S7 Days after application and cumulative fruit drop (%) of "Longfeng".

Treatment	Cumulative fruit drop (%)				
	Sept. 3	Sept. 9	Sept. 14	Sept. 16	Sept. 21
1-MCP/MCOD, airtight tent, 0.3 μL L^{-1}	0	2.6	5.6	8.2	15.2
1-MCP/MCOD, airtight tent, 1 μL L^{-1}	0	2.2	3.6	4.2	5.0
1-MCP/MCOD, airtight tent, 3 μL L^{-1}	0	1.1	1.7	1.7	4.4
1-MCP/MCOD, open 0.3 μL L^{-1}	0	4.1	9.1	12.2	36.0
1-MCP/MCOD, open 1 μL L^{-1}	0	1.7	5.2	5.5	13.1
1-MCP/MCOD, open 3 μL L^{-1}	0	3.6	5.2	5.2	6.0
1-MCP/MCG, fumigated 1 μL L^{-1}	0	2.0	4.1	4.3	5.2
CK-1	0	1.9	8.2	11.0	26.3
CK-2	0	3.9	7.7	14.2	42.5

The two apple cultivars at different harvest time and different 1-MCP concentrations, which showed the efficacy of the 1-MCP/MCOD formulation, could be compared with each other.