Electronic Supplementary Material (ESI) for RSC Advances. This journal is © The Royal Society of Chemistry 2022

## **Supplementary information**

## Analysis Method Development and Health Risk Assessment of Pesticide and

## Heavy Metal Residues in Dendrobium Candidum

Zihan Zhang<sup>a,1</sup>, Jiajin Song<sup>a,1</sup>, Houpu Zhang<sup>a</sup>, Zhiruo Zheng<sup>a</sup>, Tongxin Li<sup>a</sup>, Shenggan Wu<sup>e</sup>, Bowei He<sup>d</sup>, Bizeng Mao\*,<sup>b,c</sup>, Yunlong Yu<sup>a,c</sup>, Hua Fang\*,<sup>a,c</sup>

<sup>a</sup> Institute of Pesticide and Environmental Toxicology, College of Agriculture & Biotechnology, Zhejiang University, Hangzhou 310058, China
 <sup>b</sup> Institute of Biotechnology, College of Agriculture & Biotechnology, Zhejiang University, Hangzhou 310058, China

° Key Laboratory of Molecular Biology of Crop Pathogens and Insects, Ministry of
Agriculture, Zhejiang Provincial Key Laboratory of Biology of Crop Pathogens and Insects,
Zhejiang University, Hangzhou 310058, China

<sup>d</sup> Agricultural Technology Extension Center of Zhejiang Province, Hangzhou, 310020, China

<sup>e</sup> Institute of Quality and Standard of Agro-Products, Zhejiang Academy of Agricultural
Sciences, Hangzhou 310021, China

\*For correspondence.

E-mail: agri@zju.edu.cn, maobz@zju.edu.cn

Tel/Fax: (+86-571-88982810)

<sup>1</sup> Equal contribution

## Table legends

 ${\bf Table~S1}~{\bf Collection~information~of}~{\it Dendrobium~candidum~samples}$ 

Table S2 The optimum instrumental operating conditions for ICP-MS

Table S3 Pesticide residues in Dendrobium candidum

 Table S1 Collection information of Dendrobium candidum samples

| Tag   | Sampling location  | Sampling time |
|-------|--------------------|---------------|
| YLB   | Xianju, Zhejiang   | 2019.01       |
| WC    | Linan, Zhejiang    | 2019.01       |
| HQ    | Tonglu, Zhejiang   | 2019.01       |
| LXX   | Jiande, Zhejiang   | 2019.01       |
| SY-1  | Wujiang, Jiangsu   | 2019.01       |
| WZTD  | Longquan, Zhejiang | 2019.01       |
| KEB   | Puer, Yunnan       | 2019.01       |
| SXG   | Wuyi, Zhejiang     | 2019.01       |
| TH    | Taizhou, Zhejiang  | 2019.01       |
| GXS   | Nanning, Guangxi   | 2019.01       |
| WZTY  | Longquan, Zhejiang | 2019.01       |
| GXL   | Nanning, Guangxi   | 2019.01       |
| HQYT  | Tonglu, Zhejiang   | 2019.01       |
| YLB-2 | Xianju, Zhejiang   | 2019.01       |
| WZTX  | Longquan, Zhejiang | 2019.01       |
| XRL   | Menghai, Yunnan    | 2019.01       |
| DP    | Hangzhou, Zhejiang | 2019.01       |
| SY-2  | Wujiang, Jiangsu   | 2019.01       |
| SY    | Wujiang, jiangsu   | 2019.01       |
| NB    | Ningbo, Zhejiang   | 2019.01       |
| GXD   | Nanjing, Guangxi   | 2019.01       |
| WJX-W | Wenzhou, Zhejiang  | 2019.01       |
| XRC   | Menghai, Yunnan    | 2019.01       |
| TFTS  | Wenzhou, Zhejiang  | 2019.01       |
| TFTH  | Wenzhou, Zhejiang  | 2019.01       |
| H1    | Wenzhou, Zhejiang  | 2019.01       |
| Н6    | Wenzhou, Zhejiang  | 2019.01       |

Table S2 The optimum instrumental operating conditions for ICP-MS

| Conditions                          | Values                         |  |  |  |  |  |  |
|-------------------------------------|--------------------------------|--|--|--|--|--|--|
| RF power                            | 1200W                          |  |  |  |  |  |  |
| Plasma gas                          | 13 L/min Ar                    |  |  |  |  |  |  |
| Auxiliary gas                       | 0.70 L/min Ar                  |  |  |  |  |  |  |
| Nebulizer pressure                  | 0.9 bar                        |  |  |  |  |  |  |
| Number of scans                     | 60                             |  |  |  |  |  |  |
| Nebulizer                           | Concentric nebulizer           |  |  |  |  |  |  |
| Sampler cone                        | Nickel 1.0 mm orifice diameter |  |  |  |  |  |  |
| Skimmer cone                        | Nickel 0.7 mm orifice diameter |  |  |  |  |  |  |
| Detection method                    | Pulse and analog counting      |  |  |  |  |  |  |
| Scanning method                     | Peak jump                      |  |  |  |  |  |  |
| Peristaltic pump speed              | 30 rpm                         |  |  |  |  |  |  |
| Number of detection points per peak | 3                              |  |  |  |  |  |  |
| Repeat times                        | 3                              |  |  |  |  |  |  |

 Table S3-1Pesticide residues in Dendrobium candidum

| Pesticide           | YI   | YLB  |       | WC    |        | HQ    |       | LXX   |      | SY-1 |        | TD    | MRL                               |
|---------------------|------|------|-------|-------|--------|-------|-------|-------|------|------|--------|-------|-----------------------------------|
| Pesticide           | Mean | RSD  | Mean  | RSD   | Mean   | RSD   | Mean  | RSD   | Mean | RSD  | Mean   | RSD   | μg/kg                             |
| Dichlorvos          | ND   | ND   | ND    | ND    | ND     | ND    | ND    | ND    | ND   | ND   | ND     | ND    | 200(Refer to root vegetables)     |
| α-BHC               | ND   | ND   | ND    | ND    | ND     | ND    | ND    | ND    | ND   | ND   | ND     | ND    |                                   |
| β-ВНС               | ND   | ND   | ND    | ND    | ND     | ND    | ND    | ND    | ND   | ND   | ND     | ND    | 200(Traditional Chinese medicine) |
| ү-ВНС               | ND   | ND   | ND    | ND    | ND     | ND    | ND    | ND    | ND   | ND   | ND     | ND    | 200(Traditional Chinese medicine) |
| δ-ВНС               | ND   | ND   | ND    | ND    | ND     | ND    | ND    | ND    | ND   | ND   | ND     | ND    |                                   |
| Chlorothalonil      | 0.18 | 1.65 | ND    | ND    | ND     | ND    | ND    | ND    | ND   | ND   | ND     | ND    | 10000(Refer to tea)               |
| Chlorpyrifos        | ND   | ND   | 0.10  | 1.96  | ND     | ND    | ND    | ND    | ND   | ND   | ND     | ND    | 2000(Refer to tea)                |
| Isocarbophos        | ND   | ND   | ND    | ND    | ND     | ND    | ND    | ND    | ND   | ND   | ND     | ND    | 50(Refer to tea)                  |
| p,p'-DDE            | ND   | ND   | ND    | ND    | ND     | ND    | ND    | ND    | ND   | ND   | ND     | ND    |                                   |
| o,p'-DDT            | ND   | ND   | ND    | ND    | ND     | ND    | ND    | ND    | ND   | ND   | ND     | ND    | 200/E 1:: 1 CI: 1:: )             |
| p,p'-DDD            | ND   | ND   | ND    | ND    | ND     | ND    | ND    | ND    | ND   | ND   | ND     | ND    | 200(Traditional Chinese medicine) |
| p,p'-DDT            | ND   | ND   | ND    | ND    | ND     | ND    | ND    | ND    | ND   | ND   | ND     | ND    |                                   |
| Fenpropathrin       | ND   | ND   | ND    | ND    | ND     | ND    | ND    | ND    | ND   | ND   | 0.06   | 1.69  | 50000Refer to tea)                |
| λ-cyhalothrin       | ND   | ND   | ND    | ND    | ND     | ND    | ND    | ND    | ND   | ND   | ND     | ND    | 15000(Refer to tea)               |
| Cypermethrin        | ND   | ND   | ND    | ND    | ND     | ND    | ND    | ND    | ND   | ND   | ND     | ND    | 20000(Refer to tea)               |
| Difenoconazole      | ND   | ND   | ND    | ND    | 0.11   | 3.51  | ND    | ND    | ND   | ND   | ND     | ND    | 500(Refer to ginseng)             |
| Azoxystrobin        | ND   | ND   | ND    | ND    | ND     | ND    | 0.23  | 17.70 | ND   | ND   | 0.39   | 14.13 | 1000(Refer to ginseng)            |
| Carbendazim         | ND   | ND   | ND    | ND    | ND     | ND    | ND    | ND    | ND   | ND   | ND     | ND    | 1000(Refer to Panax notoginseng)  |
| Thiophanate-methyl  | ND   | ND   | ND    | ND    | ND     | ND    | ND    | ND    | ND   | ND   | ND     | ND    | 5000(Refer to tea)                |
| Chlorantraniliprole | ND   | ND   | ND    | ND    | ND     | ND    | ND    | ND    | ND   | ND   | 233.33 | 4.68  | 500(Refer to radish)              |
| Tebuconazole        | ND   | ND   | ND    | ND    | ND     | ND    | ND    | ND    | ND   | ND   | ND     | ND    | 3000(Refer to Panax notoginseng)  |
| Procymidone         | ND   | ND   | ND    | ND    | ND     | ND    | ND    | ND    | ND   | ND   | ND     | ND    | 5000(Refer to edible fungi)       |
| Prochloraz          | ND   | ND   | 76.24 | 13.39 | 103.27 | 8.37  | 30.76 | 4.12  | ND   | ND   | ND     | ND    | 15000(Refer to Dendrobium)        |
| Pyraclostrobin      | ND   | ND   | ND    | ND    | 67.92  | 11.09 | ND    | ND    | ND   | ND   | ND     | ND    | 10000(Refer to tea)               |

ND means not detected

Table S3-2 Pesticide residues in Dendrobium candidum

| Pesticide           | KI    | KEB   |       | SXG  |      | TH   |        | GXS   |       | WZTY  |       | XL    | MRL                               |
|---------------------|-------|-------|-------|------|------|------|--------|-------|-------|-------|-------|-------|-----------------------------------|
|                     | Mean  | RSD   | Mean  | RSD  | Mean | RSD  | mg/kg  | RSD   | Mean  | RSD   | Mean  | RSD   | μg/kg                             |
| Dichlorvos          | ND    | ND    | ND    | ND   | ND   | ND   | ND     | ND    | ND    | ND    | ND    | ND    | 200(Refer to root vegetables)     |
| α-BHC               | ND    | ND    | ND    | ND   | ND   | ND   | ND     | ND    | ND    | ND    | ND    | ND    |                                   |
| β-ВНС               | ND    | ND    | 0.11  | 3.33 | ND   | ND   | ND     | ND    | ND    | ND    | ND    | ND    | 200/T 1'.' 1 Cl ' 1'.' )          |
| ү-ВНС               | ND    | ND    | ND    | ND   | ND   | ND   | ND     | ND    | ND    | ND    | ND    | ND    | 200(Traditional Chinese medicine) |
| δ-ВНС               | ND    | ND    | ND    | ND   | ND   | ND   | ND     | ND    | ND    | ND    | ND    | ND    |                                   |
| Chlorothalonil      | ND    | ND    | 0.26  | 2.31 | ND   | ND   | ND     | ND    | ND    | ND    | ND    | ND    | 10000(Refer to tea)               |
| Chlorpyrifos        | ND    | ND    | ND    | ND   | ND   | ND   | ND     | ND    | ND    | ND    | ND    | ND    | 2000(Refer to tea)                |
| Isocarbophos        | ND    | ND    | ND    | ND   | ND   | ND   | ND     | ND    | ND    | ND    | ND    | ND    | 50(Refer to tea)                  |
| p,p'-DDE            | ND    | ND    | ND    | ND   | ND   | ND   | ND     | ND    | ND    | ND    | ND    | ND    |                                   |
| o,p'-DDT            | ND    | ND    | ND    | ND   | ND   | ND   | ND     | ND    | ND    | ND    | ND    | ND    | 200/T 1'.' 1 Cl.' 1'.')           |
| p,p'-DDD            | ND    | ND    | ND    | ND   | ND   | ND   | ND     | ND    | ND    | ND    | ND    | ND    | 200(Traditional Chinese medicine) |
| p,p'-DDT            | ND    | ND    | ND    | ND   | ND   | ND   | ND     | ND    | ND    | ND    | ND    | ND    |                                   |
| Fenpropathrin       | ND    | ND    | ND    | ND   | ND   | ND   | ND     | ND    | ND    | ND    | ND    | ND    | 5000(Refer to tea)                |
| λ-cyhalothrin       | ND    | ND    | ND    | ND   | ND   | ND   | ND     | ND    | 0.23  | 1.21  | ND    | ND    | 15000(Refer to tea)               |
| Cypermethrin        | ND    | ND    | ND    | ND   | ND   | ND   | ND     | ND    | ND    | ND    | ND    | ND    | 20000(Refer to tea)               |
| Difenoconazole      | ND    | ND    | ND    | ND   | ND   | ND   | 0.36   | 8.21  | ND    | ND    | 0.34  | 14.83 | 500(Refer to ginseng)             |
| Azoxystrobin        | 0.20  | 11.50 | ND    | ND   | ND   | ND   | ND     | ND    | 0.74  | 4.63  | ND    | ND    | 1000(Refer to ginseng)            |
| Carbendazim         | ND    | ND    | ND    | ND   | ND   | ND   | ND     | ND    | 3.16  | 10.76 | 2.92  | 7.44  | 1000(Refer to Panax notoginseng)  |
| Thiophanate-methyl  | ND    | ND    | ND    | ND   | ND   | ND   | ND     | ND    | ND    | ND    | ND    | ND    | 5000(Refer to tea)                |
| Chlorantraniliprole | ND    | ND    | ND    | ND   | ND   | ND   | ND     | ND    | ND    | ND    | ND    | ND    | 500(Refer to radish)              |
| Tebuconazole        | ND    | ND    | ND    | ND   | ND   | ND   | ND     | ND    | ND    | ND    | ND    | ND    | 3000(Refer to Panax notoginseng)  |
| Procymidone         | ND    | ND    | ND    | ND   | ND   | ND   | 312.83 | 6.36  | ND    | ND    | 20.06 | 8.59  | 5000(Refer to edible fungi)       |
| Prochloraz          | 27.69 | 0.87  | ND    | ND   | ND   | ND   | 128.40 | 12.98 | 84.28 | 5.28  | ND    | ND    | 15000(Refer to Dendrobium)        |
| Pyraclostrobin      | 3.42  | 9.12  | 77.38 | 7.23 | 3.78 | 5.22 | 27.68  | 2.25  | 16.83 | 5.57  | 12.98 | 3.87  | 10000(Refer to tea)               |

ND means no detected

Table S3-3 Pesticide residues in Dendrobium candidum

| Pesticide           | HQ   | HQYT |      | YLB-2 |        | WZTX  |      | XRL   |        | DP   |       | -2   | MRL                               |
|---------------------|------|------|------|-------|--------|-------|------|-------|--------|------|-------|------|-----------------------------------|
|                     | Mean | RSD  | Mean | RSD   | Mean   | RSD   | Mean | RSD   | Mean   | RSD  | Mean  | RSD  | μg/kg                             |
| Dichlorvos          | ND   | ND   | ND   | ND    | ND     | ND    | ND   | ND    | ND     | ND   | ND    | ND   | 200(Refer to root vegetables)     |
| α-BHC               | ND   | ND   | ND   | ND    | ND     | ND    | ND   | ND    | ND     | ND   | ND    | ND   |                                   |
| β-ВНС               | ND   | ND   | ND   | ND    | ND     | ND    | ND   | ND    | ND     | ND   | ND    | ND   | 200/T1'ti1 Chi1')                 |
| ү-ВНС               | ND   | ND   | ND   | ND    | ND     | ND    | ND   | ND    | ND     | ND   | ND    | ND   | 200(Traditional Chinese medicine) |
| δ-ВНС               | ND   | ND   | ND   | ND    | ND     | ND    | ND   | ND    | ND     | ND   | ND    | ND   |                                   |
| Chlorothalonil      | ND   | ND   | ND   | ND    | ND     | ND    | ND   | ND    | ND     | ND   | ND    | ND   | 10000(Refer to tea)               |
| Chlorpyrifos        | ND   | ND   | ND   | ND    | ND     | ND    | 0.07 | 2.15  | ND     | ND   | ND    | ND   | 2000(Refer to tea)                |
| Isocarbophos        | ND   | ND   | ND   | ND    | ND     | ND    | ND   | ND    | ND     | ND   | ND    | ND   | 50(Refer to tea)                  |
| p,p'-DDE            | ND   | ND   | ND   | ND    | ND     | ND    | ND   | ND    | ND     | ND   | ND    | ND   |                                   |
| o,p'-DDT            | ND   | ND   | ND   | ND    | ND     | ND    | ND   | ND    | ND     | ND   | ND    | ND   | 200/T 1'' 1 CI ' 1''              |
| p,p'-DDD            | ND   | ND   | ND   | ND    | ND     | ND    | ND   | ND    | ND     | ND   | ND    | ND   | 200(Traditional Chinese medicine) |
| p,p'-DDT            | ND   | ND   | ND   | ND    | ND     | ND    | ND   | ND    | ND     | ND   | ND    | ND   |                                   |
| Fenpropathrin       | ND   | ND   | ND   | ND    | ND     | ND    | ND   | ND    | ND     | ND   | ND    | ND   | 5000(Refer to tea)                |
| λ-cyhalothrin       | ND   | ND   | ND   | ND    | ND     | ND    | ND   | ND    | ND     | ND   | ND    | ND   | 15000(Refer to tea)               |
| Cypermethrin        | ND   | ND   | ND   | ND    | ND     | ND    | ND   | ND    | ND     | ND   | ND    | ND   | 20000(Refer to tea)               |
| Difenoconazole      | ND   | ND   | ND   | ND    | ND     | ND    | ND   | ND    | ND     | ND   | ND    | ND   | 500(Refer to ginseng)             |
| Azoxystrobin        | ND   | ND   | ND   | ND    | 0.40   | 4.12  | 0.46 | 15.94 | ND     | ND   | ND    | ND   | 1000(Refer to ginseng)            |
| Carbendazim         | ND   | ND   | ND   | ND    | ND     | ND    | ND   | ND    | ND     | ND   | ND    | ND   | 1000(Refer to Panax notoginseng)  |
| Thiophanate-methyl  | ND   | ND   | ND   | ND    | ND     | ND    | ND   | ND    | ND     | ND   | ND    | ND   | 5000(Refer to tea)                |
| Chlorantraniliprole | ND   | ND   | ND   | ND    | ND     | ND    | ND   | ND    | ND     | ND   | 48.29 | 7.36 | 500(Refer to radish)              |
| Tebuconazole        | ND   | ND   | ND   | ND    | ND     | ND    | ND   | ND    | ND     | ND   | ND    | ND   | 3000(Refer to Panax notoginseng)  |
| Procymidone         | ND   | ND   | ND   | ND    | ND     | ND    | ND   | ND    | ND     | ND   | ND    | ND   | 5000(Refer to edible fungi)       |
| Prochloraz          | ND   | ND   | ND   | ND    | 47.65  | 12.11 | ND   | ND    | 145.29 | 4.29 | 10.28 | 0.82 | 15000(Refer to Dendrobium)        |
| Pyraclostrobin      | ND   | ND   | ND   | ND    | 211.84 | 3.67  | ND   | ND    | ND     | ND   | ND    | ND   | 10000(Refer to tea)               |

ND means not detected