Magnitude and decline of pesticide co-formulant residues in vegetables and fruits: results from field trials compared to estimated values

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Supporting information
## Supporting information 1: Details on field trials, test sites, and selected substances

Table SI 1.1: Layout of the test site for the residue trials in vegetables. Dates should be read as dd/mm/yy.

| Treatment | crop (variety) |
|-----------|---------------|
| **PPP** co-formulants *a.s.* | application rate (PPP) date |
| untreated control 3 | 3 x 40 plants planting: 03/06/19 15 plants planting: 02/07/19 3 x 18 plants planting: 25/06/19 3 x 18 plants planting: 09/07/19 4 x 18 plants planting: 23/07/19 4 x 18 plants planting: 23/07/19 |
| **Flint** DBNS trifl oxy-strobin | 0.4 kg/ha 16/08/19 3 x 40 plants planting: 03/06/19 15 plants planting: 02/07/19 BBCH at application: 47-48 3 x 18 plants planting: 25/06/19 BBCH at application: 47-48 3 x 18 plants planting: 09/07/19 BBCH at application: 47-48 4 x 18 plants planting: 23/07/19 BBCH at application: 46 4 x 18 plants planting: 23/07/19 |
| untreated control 2 | 3 x 40 plants planting: 03/06/19 15 plants planting: 02/07/19 3 x 18 plants planting: 25/06/19 3 x 18 plants planting: 09/07/19 4 x 18 plants planting: 23/07/19 4 x 18 plants planting: 23/07/19 |
| **Input** DMDA spiroxa-mine; prothio-conazole | 1.25 kg/ha 16/08/19 3 x 40 plants planting: 03/06/19 BBCH at application: 47-48 15 plants planting: 02/07/19 BBCH at application: 47-48 3 x 18 plants planting: 25/06/19 BBCH at application: 47-48 3 x 18 plants planting: 09/07/19 BBCH at application: 47-48 4 x 18 plants planting: 23/07/19 BBCH at application: 46 4 x 18 plants planting: 23/07/19 |
| untreated control 1 | 3 x 40 plants planting: 03/06/19 15 plants planting: 02/07/19 3 x 18 plants planting: 25/06/19 3 x 18 plants planting: 09/07/19 4 x 18 plants planting: 23/07/19 4 x 18 plants planting: 23/07/19 |
| **Armicarb** docusate, SDS potassium hydrogen carbonate (KHCO₃) | 3 kg/ha 16/08/19 3 x 40 plants planting: 03/06/19 BBCH at application: 47-48 15 plants planting: 02/07/19 BBCH at application: 47-48 3 x 18 plants planting: 25/06/19 BBCH at application: 47-48 3 x 18 plants planting: 09/07/19 BBCH at application: 47-48 4 x 18 plants planting: 23/07/19 BBCH at application: 46 4 x 18 plants planting: 23/07/19 |

Plot size: 1.5 m x 7 m. Seedlings were purchased from Jud Bio-Jungpflanzen AG, Tägerwilen. The application of all plant protection products (PPPs) was conducted with a self-constructed plot sprayer, equipped with IDK 120 04 nozzles (distance between nozzles 25 cm) at a velocity of 3.6 km/h and a pressure of 1.7 bar.
Table SI 1.2: Further information on vegetable test site

| Location | Wädenswil, Switzerland (47°22′18″N/8°67′68″E) altitude 485 m above sea level |
|----------|----------------------------------------------------------------------------------|
| Soil properties | loamy silt clay 21% (w/w) silt 51% sand 28% pH: 7.1 org. C: 4% |
| Recent field history (cropping) | before 2017 apple orchard 2017 pumpkin 2018 celery and leaf lettuce |
| Fertilisation | fertilisation was carried out as follows (dates as dd/mm/yy): |
| | 24/06/19 celery N: 150 kg/ha P: 40 kg/ha K: 150 kg/ha |
| | 09/07/19 parsley N: 100 kg/ha P: 40 kg/ha K: 150 kg/ha |
| | 22/07/19 head lettuce N: 150 kg/ha P: 40 kg/ha K: 150 kg/ha |
| | 22/07/19 leaf lettuce N: 150 kg/ha P: 40 kg/ha K: 150 kg/ha |
| Plant protection measures applied in test crops | Prior to treatment with the tested PPPs, products with the following a.s. were applied. These products did not contain any of the investigated co-formulants or a.s. |
| | 03/07/19 clethodim (herbicide) 120 g/ha leek, rondini, celery |
| | 30/07/19 azoxystrobin (fungicide) 250 g/ha leaf lettuce, head lettuce |
| | 08/08/19 pymethrozine (insecticide) 250 g/ha parsley, celery |
| | 09/08/19 mancozeb (fungicide) 1250 g/ha parsley, celery |
| |metalaxyl-M (fungicide) 77 g/ha parsley, celery |

Figure SI 1.1: Vegetable test site in Wädenswil, Switzerland at the day of application (August 16, 2019) with the six tested crops (from left: leek, rondini, celery, parsley, head lettuce and oak leaf lettuce).
Figure SI 1.2: Application of investigated PPPs at the vegetable test site (crop: rondini).

Figure SI 1.3: Layout of the test site for residue trials in apples. In mixture with Flint, an additional PPP containing captan was applied (2 kg/ha of a WG formulation type with 800 g a.s./kg).
Table SI 1.3a: Weather data for the duration of the vegetable field trial sampling period (data from the meteorological station adjacent to the vegetable test site in Wädenswil, Switzerland)

| Date       | rainfall (mm) | rain intensity (mm/h) | max. temperature (°C) | min. temperature (°C) | mean temperature (°C) | sampling |
|------------|---------------|-----------------------|------------------------|------------------------|------------------------|----------|
|            |               |                       |                        |                        |                        |          |
| Vegetable field trial |               |                       |                        |                        |                        |          |
| 15.08.2019 | 1.8           | 6                     | 21.5                   | 11.8                   | 17                     | day -1 (control) |
| 16.08.2019 | 0             | 0                     | 24.2                   | 14                     | 18.8                   | day 0 (treatment) |
| 17.08.2019 | 0             | 0                     | 25.5                   | 13.8                   | 19.8                   | day 1     |
| 18.08.2019 | 27.8          | 40.8                  | 31.9                   | 15.8                   | 23.1                   | day 2 §   |
| 19.08.2019 | 11.3          | 15                    | 22.9                   | 16.6                   | 18.9                   | day 3 §   |
| 20.08.2019 | 28.9          | 15.6                  | 16.8                   | 12.7                   | 15.2                   |          |
| 21.08.2019 | 0             | 0                     | 20.7                   | 11.9                   | 16.2                   |          |
| 22.08.2019 | 0             | 0                     | 17.7                   | 12.6                   | 15.5                   |          |
| 23.08.2019 | 0             | 0                     | 20.6                   | 14.7                   | 17                     | day 7     |
| 24.08.2019 | 0             | 0                     | 25.6                   | 14.3                   | 18.6                   |          |
| 25.08.2019 | 0             | 0                     | 29.2                   | 13.8                   | 20.2                   |          |
| 26.08.2019 | 0             | 0                     | 29.7                   | 13.3                   | 20.5                   |          |
| 27.08.2019 | 0             | 0                     | 29.7                   | 14.3                   | 21.9                   |          |
| 28.08.2019 | 0             | 0                     | 29.2                   | 19.3                   | 23.2                   |          |
| 29.08.2019 | 12.7          | 25.8                  | 25.2                   | 16.3                   | 20                     |          |
| 30.08.2019 | 0             | 0                     | 28.3                   | 15                     | 21.1                   | day 14    |
| 31.08.2019 | 0             | 0                     | 27.8                   | 16.5                   | 21.1                   |          |
| 01.09.2019 | 30            | 35.4                  | 24.1                   | 15.4                   | 18.8                   |          |
| 02.09.2019 | 9.1           | 5.4                   | 15.9                   | 11.8                   | 14.6                   |          |
| 03.09.2019 | 0             | 0                     | 22.4                   | 10.4                   | 15.7                   |          |
| 04.09.2019 | 0             | 0                     | 25.2                   | 11.2                   | 17.6                   |          |
| 05.09.2019 | 5.4           | 6                     | 17.8                   | 11.2                   | 13.9                   |          |
| 06.09.2019 | 6.7           | 2.4                   | 14.2                   | 10.3                   | 12.2                   | day 21    |

§ rainfall on day 2 and day 3 was a single rain event. The entire rainfall (a total of 39 mm) occurred between sampling on day 2 and sampling on day 3.
Table SI 1.3b: Weather data for the duration of the apple field trial sampling period (data from the meteorological station adjacent to the vegetable test site in Wädenswil, Switzerland)

| Date (dd.mm.yyyy) | rainfall (mm) | rain intensity (mm/h) | max. temperature (°C) | min. temperature (°C) | mean temperature (°C) | sampling |
|-------------------|---------------|-----------------------|-----------------------|-----------------------|-----------------------|----------|
| 24.09.2019        | 5.5           | 7.2                   | 15.3                  | 8.6                   | 12.6                  | day -0 (control) |
| 25.09.2019        | 6.6           | 14.4                  | 18.8                  | 12.8                  | 14.6                  | day 1     |
| 26.09.2019        | 4             | 2.4                   | 17.1                  | 12.4                  | 14.5                  | day 2     |
| 27.09.2019        | 2.6           | 14.4                  | 23.8                  | 13.2                  | 17.1                  | day 3     |
| 28.09.2019        | 8.9           | 10.2                  | 19.9                  | 11.4                  | 15.4                  |          |
| 29.09.2019        | 0             | 0                     | 22.3                  | 9.4                   | 15.9                  |          |
| 30.09.2019        | 0             | 0                     | 20.6                  | 10.4                  | 15.9                  |          |
| 01.10.2019        | 9.7           | 16.8                  | 21.9                  | 9.8                   | 15.3                  |          |
| 02.10.2019        | 15.7          | 22.2                  | 16.1                  | 5.9                   | 12.5                  | day 8     |
| 03.10.2019        | 0             | 0                     | 14.3                  | 5.4                   | 9.1                   |          |
| 04.10.2019        | 7.6           | 3                     | 12.9                  | 6.2                   | 10                    |          |
| 05.10.2019        | 10.9          | 3                     | 14.7                  | 10.1                  | 12.1                  |          |
| 06.10.2019        | 17.6          | 10.8                  | 15.1                  | 10                    | 11.9                  |          |
| 07.10.2019        | 0             | 0                     | 15.7                  | 7.5                   | 11.1                  |          |
| 08.10.2019        | 0.1           | 0.6                   | 16.6                  | 7.2                   | 11.8                  | day 14    |
| 09.10.2019        | 56.5          | 14.4                  | 14.9                  | 8.4                   | 11.5                  |          |
| 10.10.2019        | 0.2           | 0.6                   | 16.1                  | 6.7                   | 11.7                  |          |
| 11.10.2019        | 0             | 0                     | 17.9                  | 6                     | 10.6                  |          |
| 12.10.2019        | 0             | 0                     | 20.2                  | 6.8                   | 13.3                  |          |
| 13.10.2019        | 0             | 0                     | 23.5                  | 9.5                   | 14.6                  |          |
| 14.10.2019        | 0             | 0                     | 22.1                  | 9.3                   | 14.5                  |          |
| 15.10.2019        | 21.9          | 10.8                  | 16                    | 8.8                   | 11.9                  | day 21    |
Table SI 1.4: Selected properties of the investigated co-formulants and active substances

| substance properties | co-formulant | active substance |
|----------------------|--------------|------------------|
| molecular mass [g/mol] | octanol/water partitioning coefficient log Pow [-] | water solubility at 20°C [mg/L] | vapour pressure at 25°C [Pa] |
| DMDA | 199.3<sup>a</sup> | 3.4<sup>a</sup> | 340<sup>a</sup> | 0.11<sup>a</sup> |
| docusate | 444.6<sup>a</sup> | 3.6<sup>b</sup> | 8.2 x 10<sup>3</sup> | (very low)<sup>c</sup> |
| SDS | 288.4<sup>a</sup> | ≥ 1.3 x 10<sup>2</sup>/1 x 10<sup>3</sup> | (very low)<sup>e</sup> |
| DBNS | 342.4<sup>a</sup> | (high)<sup>e</sup> | (very low)<sup>e</sup> |
| spiroxamine<sup>f</sup> | 297.5 | pH 5: 1.28 / 1.41 | pH 9: 4.88 / 5.08 | 4.0 x 10<sup>-3</sup> / 5.0 x 10<sup>-3</sup> (at 20°C) |
| trifloxystrobin<sup>f</sup> | 408.4 | 4.5 | 0.61 | 3.4 x 10<sup>-6</sup> |

Notes to table:
Despite the broad use of many PPP co-formulants in everyday products information on physico-chemical properties is hardly available and/or subject to uncertainties, as e.g. the case for surfactants. In the table we summarize the available information and/or give a qualitative estimate. In contrast, for active substances (a.s.) such information in general is publicly available.

<sup>a</sup> Substance properties according to the respective registration dossier of the European Chemicals Agency (ECHA), available under https://echa.europa.eu/information-on-chemicals accessed: 20/07/2020

<sup>b</sup> No reliable log Pow-values are available for surfactants. For docusate ECHA reports a log Pow of 2.0, that was estimated on basis of the water solubility and on the saturation of n-octanol. For SDS a value of ≤ -2.03 is reported by ECHA (see a), estimated in the same way. In contrast, a log Pow for SDS of 1.6 is reported in NLM (reference see d), illustrating the uncertainties coming along with these values.

<sup>c</sup> Values for vapour pressure were not available for all surfactants. However, based on their chemical structure it can be concluded that docusate, SDS, and DBNS are not volatile (very low vapour pressure). An estimated vapour pressure of 1.6 x 10<sup>-12</sup> Pa for docusate and a vapour pressure of <1.8 Pa for SDS, respectively is reported by ECHA (reference see a).

<sup>d</sup> Substance properties according to the data base of the US national library of medicine (NLM), available under https://pubchem.ncbi.nlm.nih.gov/ accessed: 20/07/2020.

<sup>e</sup> No value for water solubility for DBNS is available. Based on the chemical structure and in comparison with the other surfactants docusate and SDS, a high water solubility can be assumed (grams per litre).

<sup>f</sup> Substance properties for a.s. are reported according to EFSA’s conclusion on spiroxamine<sup>1</sup> and on trifloxystrobin<sup>2</sup>, respectively. Separate values are reported for the two diastereomers (cis / trans) of spiroxamine.

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<sup>1</sup> European Food Safety Authority; Conclusion on the peer review of the pesticide risk assessment of the active substance spiroxamine. EFSA Journal 2010;8(10)1719. [102 pp.]. doi:10.2903/j.efsa.2010 1719. Available online: www.efsa.europa.eu

<sup>2</sup> EFSA (European Food Safety Authority), 2017. Conclusion on the peer review of the pesticide risk assessment of the active substance trifloxystrobin. EFSA Journal 2017;15(10):4989, 29 pp. https://doi.org/10.2903/j.efsa.2017.4989
Supporting Information 2: Further information on development and performance of the analytical method

Table SI 2.1: Ion transitions and collision energies used for quantification and confirmation of target compounds by LC-MS/MS

|                  | primary ion transition (m/z) | collision energy (eV) | secondary ion transition (m/z) | collision energy (eV) | retention time (min) |
|------------------|------------------------------|-----------------------|-------------------------------|-----------------------|----------------------|
| **positive mode** |                              |                       |                               |                       |                      |
| DMDA             | 200.2→102.2                  | 30                    | 200.2→116.1                   | 28                    | 5.5                  |
| spiroxamine      | 298.3→100.1                  | 42                    | 298.3→144.1                   | 27                    | 6.4                  |
| trifloxystrobin  | 409.2→186.0                  | 15                    | 409.2→206.1                   | 10                    | 5.5                  |
| **negative mode**|                              |                       |                               |                       |                      |
| docusate         | 421.2→81.2                   | -50                   | 421.2→227.1                   | -30                   | 5.4                  |
| SDS              | 265.1→96.9                   | -34                   | 265.1→80.0                    | -90                   | 4.6                  |
| DBNS             | 319.1→289.1                  | -46                   | 319.1→259.1                   | -68                   | 3.9                  |

Figure SI 2.1: LC-MS/MS (MRM) chromatograms of extracts of celery (day 3) treated with DBNS and trifloxystrobin (left), DMDA and spiroxamine (middle), or SDS and docusate (right), respectively. The broad peak for DBNS likely is due to the presence of several, partially separated isomers. Likewise, spiroxamine consists of two diastereomers which are only partially resolved under the chosen chromatographic conditions. The small peak at 6.2 min. in the mass trace for trifloxystrobin is a matrix component which did not interfere with our measurements. Note: positive and negative ion transitions were acquired in separate chromatographic runs.
Table SI 2.2: Reference materials used for quantification of analytes

| substance | purity | source |
|-----------|--------|--------|
| DMDA      | 99.1%  | Alfa Caesar, Haverhill MA |
| docusate  | 99.6%  | ACROS Organics, NJ |
| SDS       | 97.2%  | Pan Reac Applichem, Barcelona, Spain |
| DBNS\(^a\) | \(\approx 10\)% | TFL Ledertechnik GmbH, Weil am Rhein, Germany |
| spiroxamine | 98.3% | Bayer, Leverkusen, Germany |
| trifloxystrobin | 99.4% | Sigma-Aldrich, St. Louis, MO |

\(^a\) Technical product Dispergator B Gran, which consists \(\approx 40\text{-}50\)% of a mixture of various (butyl) naphthalene sulfonates (the reaction product of naphthalene and butanol, sulfonated and neutralised). The content of dibutyl naphthalene sulfonate in the dispersing agent was estimated from HPLC-UV analysis assuming identical response of all individual components. Dispergator B Gran was kindly provided by Syngenta.

Table SI 2.3: Calibration range and concentration levels of reference standards used for quantification of co-formulants and active substances

| co-formulant or a.s. | calibration range (mg/kg) | standard series (mg/kg) | correlation coefficient \(r^2\) | linear | LOQ (mg/kg) |
|----------------------|---------------------------|-------------------------|-------------------------------|--------|-------------|
| docusate             | 0.001 - 1.0               | 0.001, 0.005, 0.01, 0.05, 0.1, 0.5, 1.0 | \(\geq 0.99\)               | yes    | 0.001       |
| SDS                  | 0.01 - 1.0                | 0.01, 0.05, 0.1, 0.5, 1.0 | \(\geq 0.98\)               | yes    | 0.01        |
| DBNS                 | 0.001 - 1.0               | 0.001, 0.005, 0.01, 0.05, 0.1, 0.5, 1.0 | \(\geq 0.99\)               | yes    | 0.001       |
| DMDA                 | 0.001 - 0.50              | 0.001, 0.005, 0.01, 0.05, 0.1, 0.5 | \(\geq 0.98\)               | yes    | 0.001       |
| spiroxamine          | 0.001 - 0.10              | 0.001, 0.005, 0.01, 0.05, 0.1 | \(\geq 0.99\)               | yes    | 0.001       |
| trifloxystrobin      | 0.001 - 0.10              | 0.001, 0.005, 0.01, 0.05, 0.1 | \(\geq 0.99\)               | yes    | 0.001       |

Reference standards were prepared in acetonitrile using the reference substances as given in Table SI 2.2. Standard concentrations were corrected for the purity of the reference substances, except for DNBS, where the quantification refers to the technical product Dispergator B Gran.
Table SI 2.4: Storage stability of co-formulants and a.s., determined by comparison of residues measured in freshly prepared extracts with extracts from the homogenate of the same sample after storage at -20°C during 60-120 days.

| matrix      | docusate stability (%) | SDS stability (%) | DBNS stability (%) | DMDA stability (%) | spiroxamine stability (%) | trifl oxy-strobin stability (%) |
|-------------|------------------------|-------------------|--------------------|--------------------|--------------------------|-------------------------------|
| leaf lettuce| 102 #                  | 116 #             | 109 ##             | 121 #              | 124 #                    | 76 ##                         |
| head lettuce| 100                    | 115               | 94                 | 126                | 75                       | 105                          |
| celery      | 89                     | 104               | 102                | 120                | 95                       | 122                          |
| parsley     | 119                    | 130               | 125                | 108 ##             | 105 ##                   | 127 #                        |
| rondini     | 86 ##                  | n.a.              | 98                 | 120                | 99                       | 97 #                         |
| leek        | 82                     | 76                | 96                 | 77                 | 72                       | 66 #                         |
| apple       | 96                     | 106               | 121 n.a.           | n.a.               | n.a.                     | 94                           |
| mean        | 94                     | 108               | 106               | 112                | 95                       | 98                           |

The stability was determined by re-analysis of the samples from day 0, with the exception of some values that were determined from day 1 (#) or day 2 (##) samples. The indicated storage stability values represent the mean as calculated from two separately processed subsamples (value in stored sample expressed in % of the value before storage).

*n.a.*: not applicable, as residues were below or close to limit of quantification (SDS in rondini) or stability experiments were not conducted (DMDA and spiroxamine in apple).
|                | docusate | SDS    | DBNS     | DMDA     | spiroxamine | trifloxystrobin |
|----------------|----------|--------|----------|----------|-------------|-----------------|
| **leaf lettuce** |          |        |          |          |             |                 |
| spike levels (mg/kg) | 0.01; 0.02; 0.1; 0.5 | 0.05 | 0.01; 0.05 | 0.01; 0.02; 0.1; 0.5 | 0.02; 0.1; 0.5 | -               |
| n               | 5        | 2      | 3        | 5        | 3           |                 |
| recovery (%): mean (range) | 105 (93-136) | 57 (52-61) | 95 (93-101) | 97 (87-111) | 101 (88-114) | -               |
| **head lettuce** |          |        |          |          |             |                 |
| spike levels (mg/kg) | 0.01; 0.02; 0.1; 0.5 | 0.05 | 0.01; 0.05 | 0.01; 0.02; 0.1; 0.5 | 0.02; 0.1; 0.5 | -               |
| n               | 5        | 2      | 3        | 5        | 3           |                 |
| recovery (%): mean (range) | 95 (90-98) | 58 (57-60) | 95 (94-96) | 98 (91-106) | 96 (90-102) | -               |
| **celery**      |          |        |          |          |             |                 |
| spike levels (mg/kg) | 0.01; 0.02; 0.1; 0.5 | 0.05 | 0.01; 0.05 | 0.01; 0.02; 0.1; 0.5 | 0.02; 0.1; 0.5 | -               |
| n               | 5        | 2      | 3        | 5        | 3           |                 |
| recovery (%): mean (range) | 95 (88-102) | 58 (57-59) | 98 (94-100) | 96 (84-106) | 101 (87-112) | -               |
| **parsley**     |          |        |          |          |             |                 |
| spike levels (mg/kg) | 0.01; 0.02; 0.1; 0.5 | 0.05 | 0.01; 0.05 | 0.01; 0.02; 0.1; 0.5 | 0.02; 0.1; 0.5 | -               |
| n               | 5        | 2      | 3        | 5        | 3           |                 |
| recovery (%): mean (range) | 92 (79-109) | 68 (67-69) | 118 (112-122) | 82 (70-89) | 82 (74-89) | -               |
| **rondini**     |          |        |          |          |             |                 |
| spike levels (mg/kg) | 0.01; 0.05; 0.1 | 0.05; 0.1 | 0.01; 0.05; 0.1 | 0.01; 0.05; 0.1 | 0.01; 0.05; 0.1 | 0.005; 0.025; 0.5; 0.1 |
| n               | 6        | 4      | 3        | 6        | 6           | 6               |
| recovery (%): mean (range) | 98 (87-121) | 90 (82-87) | 81 (78-83) | 113 (101-129) | 110 (89-126) | 97 (91-110)     |
| **leek**        |          |        |          |          |             |                 |
| spike levels (mg/kg) | 0.01; 0.02; 0.1; 0.5 | 0.05 | 0.01; 0.05 | 0.01; 0.02; 0.1; 0.5 | 0.02; 0.1; 0.5 | -               |
| n               | 5        | 2      | 3        | 5        | 3           |                 |
| recovery (%): mean (range) | 90 (81-102) | 67 (62-72) | 110 (103-116) | 88 (77-95) | 88 (78-94) | -               |
| **apple**       |          |        |          |          |             |                 |
| spike levels (mg/kg) | 0.02; 0.05; 0.1; 0.5 | 0.02; 0.05; 0.1; 0.5 | 0.02; 0.05; 0.1; 0.5 | -    | -           | 0.01; 0.05; 0.1 |
| n               | 6        | 10     | 10       | -        | -           | 6               |
| recovery (%): mean (range) | 94 (74-106) | 76 (59-92) | 89 (86-110) | -    | -           | 100 (97-104)    |
| overall mean recovery (%) | 96 | 68 | 98 | 96 | 96 | 99           |
Supporting Information 3: Further information on results and discussion

Table SI 3.1: Measured concentrations of co-formulants and active substances in vegetables and apples sampled from field trials

| Sampling (day) | Replicate | Mean | deviation from mean [%] | Replicate | Mean | deviation from mean [%] |
|---------------|-----------|------|-------------------------|-----------|------|-------------------------|
|               | A [mg/kg] | B [mg/kg] | | A [mg/kg] | B [mg/kg] | | |
| DMDA          | leek      | apple | | | | |
| QC [%]        | (spike level) | 90 (0.013) | 88 (0.013) | 89 | - | - | - | - | - | - | - |
| -1            | <0.001 | <0.001 | - | - | - | - | - | - | - |
| 0             | 0.24 | 0.28 | 0.26 | 7.0 | - | - | - | - | - | - | - |
| 1             | 0.023 | 0.026 | 0.024 | 7.2 | - | - | - | - | - | - | - |
| 2             | 0.008 | 0.006 | 0.007 | 15 | - | - | - | - | - | - | - |
| 3             | 0.002 | 0.002 | 0.002 | 5.4 | - | - | - | - | - | - | - |
| 7             | 0.001 | 0.001 | 0.001 | 4.0 | - | - | - | - | - | - | - |
| 14            | 0.002 | 0.003 | 0.002 | 17 | - | - | - | - | - | - | - |
| 21            | <0.001 | <0.001 | <0.001 | - | - | - | - | - | - | - | - |
| leaf lettuce  | rondini | | | | | |
| QC [%]        | (spike level) | 95 (0.23) | 91 (0.18) | 93 | 85 (0.061) | 78 (0.51) | 81 | 96 (0.23) | 91 (0.18) | 93 | 85 (0.061) | 78 (0.51) | 81 |
| -1            | <0.001 | <0.001 | <0.001 | <0.001 | - | - | - | - | - | - | - |
| 0             | 3.5 | 3.0 | 3.2 | 7.2 | <0.001 | <0.001 | - | - | - | - | - |
| 1             | 0.13 | 0.11 | 0.12 | 8.7 | <0.001 | <0.001 | - | - | - | - | - |
| 2             | 0.028 | 0.034 | 0.031 | 9.2 | <0.001 | <0.001 | - | - | - | - | - |
| 3             | 0.007 | 0.007 | 0.007 | 0.94 | <0.001 | <0.001 | - | - | - | - | - |
| 7             | 0.001 | 0.001 | 0.001 | 2.7 | <0.001 | <0.001 | - | - | - | - | - |
| 14            | <0.001 | <0.001 | <0.001 | - | - | - | - | - | - | - | - |
| head lettuce  | celery | | | | | |
| QC [%]        | (spike level) | 116 (0.050) | 106 (0.051) | 111 | 93 (0.13) | 84 (0.14) | 88 | 69 (0.23) | 71 (0.23) | 70 | | |
| -1            | <0.001 | <0.001 | <0.001 | <0.001 | - | - | - | - | - | - | - |
| 0             | 5.7 | 5.0 | 5.4 | 6.4 | 8.8 | 8.5 | 8.6 | 1.3 | - | - | - |
| 1             | 0.18 | 0.07 | 0.12 | 42 | 11.9 | 10.1 | 11.0 | 8.1 | - | - | - |
| 2             | 0.023 | 0.016 | 0.020 | 17 | 9.8 | 9.7 | 9.7 | 8.7 | 0.49 | - | - |
| 3             | 0.002 | 0.002 | 0.002 | 15 | 4.9 | 5.8 | 5.3 | 8.7 | - | - | - |
| 7             | <0.001 | <0.001 | - | - | 6.4 | 7.0 | 6.7 | 4.6 | - | - | - |
| 14            | <0.001 | <0.001 | - | - | 1.6 | 1.5 | 1.6 | 0.45 | - | - | - |
| parsley       | | | | | | |
| QC [%]        | (spike level) | 69 (0.23) | 71 (0.23) | 70 | | | | | | | | |
| -1            | <0.001 | <0.001 | | | | | | | | | | | |
| 0             | 9.1 | 8.8 | 9.0 | 1.7 | | | | | | | | | |
| 1             | 8.6 | 8.0 | 8.3 | 3.5 | | | | | | | | | |
| 2             | 7.3 | 7.8 | 7.5 | 3.0 | | | | | | | | | |
| 3             | 4.8 | 4.7 | 4.8 | 0.25 | | | | | | | | | |
| 7             | 4.7 | 4.8 | 4.7 | 0.70 | | | | | | | | | |
| 14            | 2.0 | 1.9 | 1.9 | 1.5 | | | | | | | | | |
Table SI 3.1: continued

| Sampling (day) | Replicate | Mean [mg/kg] | deviation from mean [%] | Replicate | Mean [mg/kg] | deviation from mean [%] |
|---------------|-----------|--------------|--------------------------|-----------|--------------|--------------------------|
|               | A         | B            |                          |           |              |                          |
|               | A         | B            |                          |           |              |                          |
|               | A         | B            |                          |           |              |                          |
|               | A         | B            |                          |           |              |                          |
|               | A         | B            |                          |           |              |                          |
|               | A         | B            |                          |           |              |                          |
| docusate      |           |              |                          |           |              |                          |
| QC [%] (spike level) | 77 (0.026) | 101 (0.026) | 89 (1.1) | 92 (0.12) | 91 | 91 |
| leek          |           |              |                          |           |              |                          |
| -1            | 0.001     | 0.003        |                          | 0.001     | <0.001       |                          |
| 0             | 1.3       | 1.6          | 1.5                      | 7.9       | 0.40         | 0.40                     |
| 1             | 0.79      | 1.34         | 1.07                     | 26        | 0.084        | 0.10                     |
| 2             | 0.59      | 0.72         | 0.65                     | 9.9       | 0.045        | 0.040                    |
| 3             | 0.12      | 0.17         | 0.14                     | 16        | 0.072        | 0.060                    |
| 7             | 0.11      | 0.14         | 0.13                     | 15        | 0.038        | 0.037                    |
| 14            | 0.032     | 0.043        | 0.038                    | 14        | 0.035        | 0.030                    |
| 21            | 0.011     | 0.018        | 0.014                    | 24        | 0.022        | 0.025                    |
| apple         |           |              |                          |           |              |                          |
| -1            | <0.001    | <0.001       |                          | <0.001    | <0.001       |                          |
| 0             | 6.3       | 5.6          | 6.0                      | 5.4       | 0.007        | 0.008                    |
| 1             | 3.2       | 2.9          | 3.1                      | 4.8       | 0.013        | 0.013                    |
| 2             | 3.0       | 2.8          | 2.9                      | 3.3       | 0.019        | 0.020                    |
| 3             | 0.17      | 0.16         | 0.16                     | 3.1       | 0.003        | 0.004                    |
| 7             | 0.025     | 0.024        | 0.025                    | 3.7       | 0.003        | 0.003                    |
| 14            | <0.001    | <0.001       |                          | <0.001    | <0.001       |                          |
| leaf lettuce  |           |              |                          |           |              |                          |
| -1            | <0.001    | <0.001       |                          | <0.001    | <0.001       |                          |
| 0             | 7.6       | 7.3          | 7.4                      | 2.5       | 7.0          | 7.6                      |
| 1             | 3.6       | 4.0          | 3.8                      | 5.6       | 5.1          | 6.8                      |
| 2             | 2.3       | 2.3          | 2.3                      | 0.47      | 4.9          | 5.2                      |
| 3             | 0.097     | 0.108        | 0.10                     | 5.7       | 0.82         | 0.91                     |
| 7             | 0.018     | 0.020        | 0.019                    | 5.3       | 0.40         | 0.46                     |
| 14            | 0.002     | 0.001        | 0.002                    | 14        | 0.13         | 0.16                     |
| rondini       |           |              |                          |           |              |                          |
| -1            | <0.001    | <0.001       |                          | <0.001    | <0.001       |                          |
| 0             | 7.6       | 7.3          | 7.4                      | 2.5       | 7.0          | 7.6                      |
| 1             | 3.6       | 4.0          | 3.8                      | 5.6       | 5.1          | 6.8                      |
| 2             | 2.3       | 2.3          | 2.3                      | 0.47      | 4.9          | 5.2                      |
| 3             | 0.097     | 0.108        | 0.10                     | 5.7       | 0.82         | 0.91                     |
| 7             | 0.018     | 0.020        | 0.019                    | 5.3       | 0.40         | 0.46                     |
| 14            | 0.002     | 0.001        | 0.002                    | 14        | 0.13         | 0.16                     |
| head lettuce  |           |              |                          |           |              |                          |
| -1            | <0.001    | <0.001       |                          | <0.001    | <0.001       |                          |
| 0             | 7.6       | 7.3          | 7.4                      | 2.5       | 7.0          | 7.6                      |
| 1             | 3.6       | 4.0          | 3.8                      | 5.6       | 5.1          | 6.8                      |
| 2             | 2.3       | 2.3          | 2.3                      | 0.47      | 4.9          | 5.2                      |
| 3             | 0.097     | 0.108        | 0.10                     | 5.7       | 0.82         | 0.91                     |
| 7             | 0.018     | 0.020        | 0.019                    | 5.3       | 0.40         | 0.46                     |
| 14            | 0.002     | 0.001        | 0.002                    | 14        | 0.13         | 0.16                     |
| celery        |           |              |                          |           |              |                          |
| -1            | <0.001    | <0.001       |                          | <0.001    | <0.001       |                          |
| 0             | 7.6       | 7.3          | 7.4                      | 2.5       | 7.0          | 7.6                      |
| 1             | 3.6       | 4.0          | 3.8                      | 5.6       | 5.1          | 6.8                      |
| 2             | 2.3       | 2.3          | 2.3                      | 0.47      | 4.9          | 5.2                      |
| 3             | 0.097     | 0.108        | 0.10                     | 5.7       | 0.82         | 0.91                     |
| 7             | 0.018     | 0.020        | 0.019                    | 5.3       | 0.40         | 0.46                     |
| 14            | 0.002     | 0.001        | 0.002                    | 14        | 0.13         | 0.16                     |
| parsley       |           |              |                          |           |              |                          |
| -1            | <0.001    | <0.001       |                          | <0.001    | <0.001       |                          |
| 0             | 10.0      | 10.5         | 10.3                     | 2.1       | 7.0          | 7.6                      |
| 1             | 8.6       | 8.4          | 8.5                      | 1.3       | 7.0          | 7.6                      |
| 2             | 6.2       | 6.1          | 6.1                      | 0.95      | 4.9          | 5.2                      |
| 3             | 0.15      | 0.16         | 0.16                     | 2.8       | 0.82         | 0.91                     |
| 7             | 0.054     | 0.056        | 0.055                    | 2.2       | 0.40         | 0.46                     |
| 14            | <0.001    | <0.001       |                          | <0.001    | <0.001       |                          |
| Sampling (day) | Replicate Mean | deviation from mean [%] | Replicate Mean | deviation from mean [%] |
|---------------|----------------|-------------------------|----------------|-------------------------|
|               | A [mg/kg] | B [mg/kg] |               | A [mg/kg] | B [mg/kg] |
| QC [%] (spike level) | leek | apple | SDS | leaf lettuce | rondini | celery | parsley |
| -1 | n.a. | n.a. | - | n.a. | n.a. | - | - | - |
| 0 | 0.53 | 0.75 | 0.64 | 17 | 0.20 | 0.20 | 0.20 | 0.21 |
| 1 | 0.30 | 0.58 | 0.44 | 32 | 0.047 | 0.056 | 0.051 | 8.4 |
| 2 | 0.21 | 0.27 | 0.24 | 12 | 0.022 | 0.020 | 0.021 | 5.0 |
| 3 | 0.026 | 0.050 | 0.038 | 31 | 0.028 | 0.026 | 0.027 | 4.8 |
| 7 | 0.022 | 0.038 | 0.030 | 26 | 0.021 | 0.018 | 0.020 | 5.4 |
| 14 | <0.01 | 0.016 | - | - | 0.017 | 0.013 | 0.015 | 13 |
| 21 | 0.010 | 0.021 | 0.016 | 33 | <0.01 | 0.010 | - | - |
| QC [%] (spike level) | 86 (0.15) | 75 (0.14) | 81 | n.a. | n.a. | - | - | - |
| -1 | <0.01 | <0.01 | - | <0.01 | <0.01 | - | - | - |
| 0 | 2.3 | 2.2 | 2.2 | 1.9 | <0.01 | <0.01 | - | - |
| 1 | 0.85 | 0.79 | 0.82 | 3.5 | 0.012 | 0.011 | 0.012 | 3.1 |
| 2 | 0.81 | 0.78 | 0.80 | 2.3 | 0.013 | 0.014 | 0.013 | 2.9 |
| 3 | 0.015 | <0.01 | - | - | <0.01 | <0.01 | - | - |
| 7 | <0.01 | <0.01 | - | - | <0.01 | <0.01 | - | - |
| 14 | <0.01 | <0.01 | - | - | <0.01 | <0.01 | - | - |
| QC [%] (spike level) | 65 (0.10) | 58 (0.10) | 61 | 102 (0.13) | 103 (0.13) | 102 | - | - |
| -1 | <0.01 | <0.01 | - | <0.01 | <0.01 | - | - | - |
| 0 | 3.6 | 3.5 | 3.5 | 0.4 | 3.7 | 3.6 | 3.7 | 1.0 |
| 1 | 1.2 | 1.4 | 1.3 | 6.0 | 2.4 | 2.9 | 2.6 | 11 |
| 2 | 0.84 | 0.85 | 0.85 | 0.22 | 2.3 | 2.3 | 2.3 | 0.78 |
| 3 | <0.01 | <0.01 | - | - | 0.050 | 0.053 | 0.052 | 2.9 |
| 7 | 0.011 | <0.01 | - | - | 0.017 | 0.014 | 0.015 | 7.2 |
| 14 | <0.01 | <0.01 | - | - | <0.01 | <0.01 | - | - |
| QC [%] (spike level) | 113 (0.13) | 104 (0.13) | 109 | - | - | - | - | - |
| -1 | <0.01 | <0.01 | - | - | - | - | - | - |
| 0 | 6.2 | 6.4 | 6.3 | 1.8 | - | - | - | - |
| 1 | 4.7 | 4.3 | 4.5 | 3.6 | - | - | - | - |
| 2 | 3.2 | 3.3 | 3.3 | 1.8 | - | - | - | - |
| 3 | 0.019 | 0.020 | 0.020 | 2.6 | - | - | - | - |
| 7 | 0.011 | 0.014 | 0.013 | 11 | - | - | - | - |
| 14 | <0.01 | <0.01 | - | - | - | - | - | - |
Table SI 3.1: continued

| sampling (day) | replicate | mean | deviation from mean [%] | replicate | mean | deviation from mean [%] |
|----------------|-----------|------|-------------------------|-----------|------|-------------------------|
|                | A [mg/kg] | B [mg/kg] | [mg/kg] | A [mg/kg] | B [mg/kg] | [mg/kg] |
| QC [%] (spike level) |           |       |                        |           |       |                        |
| leek            | 89 (0.0093) | 94 (0.013) | 92 | 74 (1.2) | 74 (1.2) | 74 |
| -1              | <0.001    | <0.001 | <0.001                  | <0.001    | <0.001 | <0.001                  |
| 0               | 0.065     | 0.085 | 0.075 13 | 0.012 | 0.013 | 0.012 6.6 |
| 1               | 0.067     | 0.093 | 0.080 17 | 0.003 | 0.002 | 0.003 14 |
| 2               | 0.045     | 0.049 | 0.047 3.4 | <0.001 | 0.0021 | - |
| 3               | 0.011     | 0.012 | 0.011 5.4 | 0.001 | 0.001 | 0.001 4.9 |
| 7               | 0.005     | 0.006 | 0.005 11 | <0.001 | <0.001 | - |
| 14              | 0.001     | 0.002 | 0.002 4.5 | <0.001 | <0.001 | - |
| 21              | 0.002     | <0.001 | - | <0.001 | <0.001 | - |
| leaf lettuce    | 66 (0.11) | 71 (0.11) | 69 | 106 (1.1) | 95 (0.12) | 100 |
| -1              | 0.014     | 0.013 | <0.001 | <0.001 | <0.001 | <0.001 |
| 0               | 0.41      | 0.40 | 0.40 0.70 | 0.002 | 0.002 | 0.002 12 |
| 1               | 0.22      | 0.24 | 0.23 2.5 | 0.001 | 0.001 | 0.001 1.0 |
| 2               | 0.21      | 0.20 | 0.21 0.57 | 0.001 | 0.001 | 0.001 7.4 |
| 3               | 0.039     | 0.039 | 0.039 0.69 | <0.001 | <0.001 | - |
| 7               | 0.011     | 0.012 | 0.011 2.1 | <0.001 | <0.001 | - |
| 14              | 0.002     | 0.002 | 0.002 20 | <0.001 | <0.001 | - |
| head lettuce    | 104 (0.10) | 98 (0.017) | 101 | 110 (0.12) | 110 0.11 | 110 |
| -1              | 0.008     | 0.007 | 0.007 | 0.006 | 0.49 2.8 |
| 0               | 0.66      | 0.64 | 0.65 1.5 | 0.50 | 0.48 | 0.49 2.8 |
| 1               | 0.41      | 0.33 | 0.37 11 | 0.72 | 0.55 | 0.63 13 |
| 2               | 0.27      | 0.27 | 0.27 0.26 | 0.48 | 0.41 | 0.44 7.1 |
| 3               | 0.018     | 0.016 | 0.017 7.5 | 0.024 | 0.023 | 0.023 3.5 |
| 7               | 0.003     | 0.003 | 0.003 6.0 | 0.009 | 0.011 | 0.010 13 |
| 14              | <0.001    | <0.001 | - | 0.002 | 0.002 | 0.002 8.4 |
| parsley         | 146 (0.12) | 149 (0.12) | 148 | - | - | - |
| -1              | <0.001    | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| 0               | 0.81      | 0.75 | 0.78 3.6 | - | - | - |
| 1               | 0.53      | 0.54 | 0.53 0.68 | - | - | - |
| 2               | 0.46      | 0.50 | 0.48 3.8 | - | - | - |
| 3               | 0.017     | 0.020 | 0.019 7.8 | - | - | - |
| 7               | 0.005     | 0.004 | 0.004 9.7 | - | - | - |
| 14              | <0.001    | 0.002 | - | - | - | - |
Table SI 3.1: continued

| sampling (day) | replicate | mean | deviation from mean [mg/kg] | deviation from mean [mg/kg] |
|---------------|-----------|------|----------------------------|----------------------------|
| QC [%] (spike level) | A [mg/kg] | B [mg/kg] | A [mg/kg] | B [mg/kg] |
| -1 | <0.001 | <0.001 | - | - | - | - | - | - |
| 0 | 0.79 | 0.95 | 0.87 | 9.3 | - | - | - | - |
| 1 | 0.53 | 0.61 | 0.57 | 7.1 | - | - | - | - |
| 2 | 0.48 | 0.41 | 0.44 | 7.8 | - | - | - | - |
| 3 | 0.26 | 0.27 | 0.26 | 1.2 | - | - | - | - |
| 7 | 0.11 | 0.099 | 0.10 | 4.7 | - | - | - | - |
| 14 | 0.057 | 0.048 | 0.053 | 9.3 | - | - | - | - |
| 21 | 0.014 | 0.013 | 0.014 | 0.50 | - | - | - | - |
| QC [%] (spike level) | A [mg/kg] | B [mg/kg] | A [mg/kg] | B [mg/kg] |
| -1 | <0.001 | <0.001 | 0.004 | 0.001 |
| 0 | 6.3 | 5.9 | 6.1 | 3.5 | 0.005 | 0.004 | 0.004 | 3.8 |
| 1 | 4.3 | 4.3 | 4.3 | 0.08 | 0.008 | 0.008 | 0.008 | 5.5 |
| 2 | 2.8 | 3.0 | 2.9 | 2.3 | 0.007 | 0.008 | 0.007 | 5.8 |
| 3 | 0.88 | 0.81 | 0.85 | 4.0 | 0.008 | 0.009 | 0.008 | 8.5 |
| 7 | 0.35 | 0.34 | 0.34 | 2.3 | 0.017 | 0.017 | 0.017 | 2.0 |
| 14 | 0.026 | 0.029 | 0.027 | 4.7 | 0.008 | 0.008 | 0.008 | 4.6 |
| QC [%] (spike level) | A [mg/kg] | B [mg/kg] | A [mg/kg] | B [mg/kg] |
| -1 | <0.001 | <0.001 | <0.001 | 0.001 |
| 0 | 11 | 10 | 11 | 3.3 | 4.9 | 4.8 | 4.8 | 1.3 |
| 1 | 5.1 | 4.2 | 4.6 | 9.6 | 4.6 | 3.9 | 4.2 | 8.7 |
| 2 | 3.4 | 3.0 | 3.2 | 5.2 | 3.0 | 3.1 | 3.1 | 2.5 |
| 3 | 1.3 | 0.63 | 0.99 | 36 | 1.4 | 1.7 | 1.6 | 9.0 |
| 7 | 0.50 | 0.31 | 0.41 | 23 | 1.2 | 1.3 | 1.2 | 3.4 |
| 14 | 0.037 | 0.033 | 0.035 | 7.0 | 0.20 | 0.18 | 0.19 | 3.3 |
| QC [%] (spike level) | A [mg/kg] | B [mg/kg] | A [mg/kg] | B [mg/kg] |
| -1 | <0.001 | 0.001 | 0.001 | 0.001 |
| 0 | 5.4 | 5.3 | 5.3 | 1.3 |
| 1 | 3.9 | 3.7 | 3.8 | 2.0 |
| 2 | 2.9 | 3.1 | 3.0 | 3.2 |
| 3 | 1.5 | 1.4 | 1.5 | 1.1 |
| 7 | 0.81 | 0.84 | 0.83 | 2.0 |
| 14 | 0.20 | 0.17 | 0.18 | 7.3 |
| sampling (day) | replicate | mean | deviation from mean [%] | replicate | mean | deviation from mean [%] |
|---------------|-----------|------|-------------------------|-----------|------|-------------------------|
|               | A [mg/kg] | B [mg/kg] |                         | A [mg/kg] | B [mg/kg] |                         |
| trifloxystrobin |           |       |                          |           |       |                          |
| leek          |           |       |                          |           |       |                          |
| QC [%] (spike level) | 118 (0.0072) | 91 (0.015) | 105 | 74 (0.70) | 79 (0.70) | 76 |
| -1           | <0.001    | <0.001 | <0.001                  | <0.001    | <0.001 | <0.001                  |
| 0            | 0.77      | 0.84  | 0.80 4.4 | 0.13      | 0.15  | 0.14 6.9 |
| 1            | 0.88      | 1.10  | 0.99 11 | 0.12      | 0.10  | 0.11 6.8 |
| 2            | 0.55      | 0.55  | 0.55 0.02 | 0.093     | 0.094 | 0.094 0.20 |
| 3            | 0.38      | 0.39  | 0.39 1.4 | 0.072     | 0.070 | 0.071 1.5 |
| 7            | 0.059     | 0.090 | 0.075 21 | 0.066     | 0.066 | 0.066 0.25 |
| 14           | 0.023     | 0.032 | 0.027 17 | 0.064     | 0.064 | 0.064 0.43 |
| 21           | 0.009     | 0.014 | 0.011 21 | 0.035     | 0.050 | 0.042 17 |
| apple        |           |       |                          |           |       |                          |
| QC [%] (spike level) | 96 (0.10) | 96 (0.10) | 96 | 96 (0.66) | 102 (0.11) | 99 |
| -1           | <0.001    | <0.001 | <0.001                  | <0.001    | <0.001 | <0.001                  |
| 0            | 5.9       | 6.0   | 6.0 0.42 | 0.013     | 0.012 | 0.012 0.74 |
| 1            | 4.3       | 4.2   | 4.3 0.45 | 0.009     | 0.012 | 0.010 13 |
| 2            | 4.5       | 4.4   | 4.5 1.0 | 0.012     | 0.012 | 0.012 0.9 |
| 3            | 0.44      | 0.49  | 0.47 6.0 | 0.006     | 0.005 | 0.006 5.8 |
| 7            | 0.11      | 0.11  | 0.11 0.29 | 0.002     | 0.002 | 0.002 3.0 |
| 14           | 0.009     | 0.009 | 0.009 1.0 | 0.002     | 0.002 | 0.002 1.5 |
| leaf lettuce |           |       |                          |           |       |                          |
| QC [%] (spike level) | 91 (0.064)| 91 (0.014)| 91 | 111 (0.054)| 111 (0.055)| 111 |
| -1           | <0.001    | <0.001 | <0.001                  | <0.001    | <0.001 | <0.001                  |
| 0            | 7.5       | 7.6   | 7.5 0.70 | 4.8       | 4.8   | 4.8 0.21 |
| 1            | 5.9       | 5.8   | 5.8 0.65 | 6.7       | 5.9   | 6.3 6.2 |
| 2            | 4.7       | 5.2   | 5.0 4.4 | 5.4       | 5.2   | 5.3 1.3 |
| 3            | 0.59      | 0.56  | 0.57 3.1 | 0.43      | 0.44  | 0.44 1.2 |
| 7            | 0.081     | 0.094 | 0.087 7.9 | 0.23      | 0.24  | 0.24 2.1 |
| 14           | 0.001     | 0.001 | 0.001 1.5 | 0.057     | 0.061 | 0.059 3.5 |
| rondini      |           |       |                          |           |       |                          |
| QC [%] (spike level) | 79 (0.11) | 85 (0.11) | 82 |           |       |           |
| -1           | <0.001    | <0.001 | <0.001                  | <0.001    | <0.001 | <0.001                  |
| 0            | 6.5       | 6.4   | 6.5 1.2 | 6.3       | 6.3   | 6.3 2.1 |
| 1            | 6.2       | 6.4   | 6.3 2.1 | 6.4       | 6.4   | 6.4 1.2 |
| 2            | 6.4       | 6.3   | 6.4 1.2 | 0.56      | 0.54  | 0.55 1.7 |
| 3            | 0.56      | 0.54  | 0.55 1.7 | 0.16      | 0.14  | 0.15 6.1 |
| 7            | 0.045     | 0.039 | 0.042 7.1 |           |       |           |
| parsley      |           |       |                          |           |       |                          |
| QC (quality control): Homogenates of samples from untreated plots were fortified, processed and analysed in each series for the control of method performance. The table represents the recoveries in % and the levels of fortification (spike level) in mg/kg in brackets.
Table SI 3.2: Crop parameters used for generic calculation of day 0-residues and resulting $C_{0,\text{gen}}$ values (assuming a standard application rate of 1 kg/ha)

| crop       | no. of plants per hectare | weight of individual plant (g) | total plant mass per ha (kg) | crop soil coverage (-) | application rate (kg/ha) | $C_{0,\text{gen}}$ (mg/kg) |
|------------|---------------------------|--------------------------------|------------------------------|------------------------|--------------------------|---------------------------|
| leaf lettuce | 95238                     | 171                            | 16311                        | 0.580                  | 1                        | 36                        |
| head lettuce | 95238                     | 237                            | 22546                        | 0.738                  | 1                        | 33                        |
| parsley    | 71429                     | 158                            | 11317                        | 0.469                  | 1                        | 41                        |
| celery     | 71429                     | 688                            | 49143                        | 0.747                  | 1                        | 15                        |

**Notes to table:**
The number of plants per hectare was calculated from the actual cropped area of a plot, thus excluding the tractor tracks between plots. The weight of an individual plant was determined as mean of the weight of 6 individual plants sampled on day 0 (before treatment), with exception of celery where the weight was determined as mean of 24 plants sampled on the day before treatment (day -1). These two numbers were used to estimate the total plant mass per hectare at the time of treatment.

Crop soil coverage is the portion of soil (referring to the actual cropped area of a plot) that was covered by plants. It was determined from photographs (top view) taken of the crops the day before treatment (day -1). The pictures were analysed with the online tool as described by Rasmussen and co-authors\(^3\). «IMAGING Crop Response Analyser» (Version 0.4) is available at [https://www.imaging-crops.dk](https://www.imaging-crops.dk). See also pictures in Fig. SI 3.1 below.

Based on these parameters the generic initial residues $C_{0,\text{gen}}$ for leaf lettuce, head lettuce, parsley and celery were estimated for a standard application rate of 1 kg/ha, using the formula presented in the main text.

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\(^3\) Rasmussen J, Nørremark M and Bibby BM, Assessment of leaf cover and crop soil cover in weed harrowing research using digital images. *Weed Research* 47:299-310 (2007).
Table SI 3.3a: Results from kinetic fitting of decline over time-curves of co-formulants and active substances in vegetables and apples from field trials, applying SFO (single first order) kinetics

| SFO fit parameter | leek | leaf lettuce | head lettuce | parsley | celery | apple |
|-------------------|------|---------------|--------------|---------|--------|-------|
| DMDA              |      |               |              |         |        |       |
| DT50 (d)          | 0.299| 0.211         | 0.184        | 6.24    | 7.26   | -     |
| $\chi^2$ (%)      | 3.84 | 1.6           | 0.65         | 9.85    | 18.1   |       |
| $r^2$             | 0.9997| 0.9999       | 1.0000       | 0.9076  | 0.7295 |       |
| visual            | acceptable | good       | good         | acceptable | poor  |       |
| docusate          |      |               |              |         |        |       |
| DT50 (d)          | 1.45 | 1.20          | 0.982        | 1.54    | 1.86   | 0.552 |
| $\chi^2$ (%)      | 16.9 | 22.2          | 13.6         | 27.9    | 22.9   | 24.8  |
| $r^2$             | 0.9604| 0.9350       | 0.9800       | 0.8856  | 0.8934 | 0.9748|
| visual            | acceptable | poor       | acceptable   | poor    | poor   | poor  |
| SDS               |      |               |              |         |        |       |
| DT50 (d)          | 1.25 | n.a.          | n.a.         | 1.37    | 1.51   | 0.564 |
| $\chi^2$ (%)      | 15.4 |                |              | 24.8    | 27.7   | 21.1  |
| $r^2$             | 0.9645|                 | 0.9158       | 0.8871  | 0.9821 |       |
| visual            | acceptable | poor       | acceptable   | poor    | poor   | poor  |
| DBNS              |      |               |              |         |        |       |
| DT50 (d)          | 1.93 | 1.38          | 1.16         | 1.49    | 2.14   | n.a.  |
| $\chi^2$ (%)      | 28.1 | 17.2          | 17.3         | 26.7    | 40.8   |       |
| $r^2$             | 0.8830| 0.9515       | 0.9617       | 0.8939  | 0.7300 |       |
| visual            | poor | acceptable   | acceptable   | poor    | poor   | poor  |
| spiroxamine       |      |               |              |         |        |       |
| DT50 (d)          | 1.93 | 1.51          | 0.976        | 2.04    | 2.66   |       |
| $\chi^2$ (%)      | 7.17 | 12.4          | 9.30         | 8.73    | 12.2   |       |
| $r^2$             | 0.9926| 0.9715       | 0.9892       | 0.9795  | 0.9468 |       |
| visual            | good | acceptable   | good         | acceptable | acceptable |       |
| trifloxystrobin   |      |               |              |         |        |       |
| DT50 (d)          | 2.71 | 1.77          | 1.67         | 2.20    | 2.44   | 12.4  |
| $\chi^2$ (%)      | 23.0 | 28.1          | 24.7         | 36.0    | 41.2   | 14.3  |
| $r^2$             | 0.8972| 0.8629       | 0.8978       | 0.7659  | 0.6933 | 0.7510|
| visual            | acceptable | poor       | poor         | poor    | poor   | poor  |

**Notes to table:**
For fitting of the decline curves of co-formulants and the two monitored a.s. in vegetables and apples the program CAKE (Version 3.4) was used (available at [https://www.tessella.com/showcase/computer-assisted-kinetic-evaluation](https://www.tessella.com/showcase/computer-assisted-kinetic-evaluation)). The kinetic model has two fitting parameters (initial residue and degradation rate = ln2/DT50); initial residues were not fixed. Residue values <LOQ were set to 0.5 x LOQ for the first time point with a concentration level <LOQ, consecutive time points were not considered then. SFO fits were run for all available co-formulant/crop combinations, provided there where at least five data points available. Examples see Figure SI 3.2.

n.a.: not available (no fits could be run because there were not enough values >LOQ available).

$\chi^2$ (Chi-square) and $r^2$ are measures for the deviation between observed and predicted values, as described in the respective EU Guidance. Further, the quality of the fits was checked and qualified (good, acceptable, or poor) by visual examination.

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FOCUS (2006): «Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration» Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference Sanco/10058/2005 version 2.0, 434 pp, available at [https://esdac.jrc.ec.europa.eu/projects/degradation-kinetics](https://esdac.jrc.ec.europa.eu/projects/degradation-kinetics)
Table SI 3.3b: Results from kinetic fitting of decline of co-formulants and trifloxystrobin in apples from field trials, applying bi-exponential kinetics (DFOP).

| apples       | DFOP fit | DT50 (days) | DT50 (d) | DT90 (d) | fit quality |
|--------------|----------|--------------|----------|----------|-------------|
|              | fast phase | slow phase | g^a      |          |             |
| docusate     | 0.0309   | 16.8        | 0.859    | 0.387    | 8.38        | 7.66        | 0.9959       | good        |
| SDS          | 0.350    | 12.9        | 0.869    | 0.429    | 5.09        | 6.55        | 0.9973       | good        |
| trifloxystrobin | 1.09    | 32.4        | 0.460    | 5.22     | 78.9        | 6.17        | 0.9670       | good        |

\(^a\) g is the fraction of residues at time 0 which is subject to fast degradation

**Notes to table:**

The decline curves of docusate, SDS, and trifloxystrobin in apples were well described by bi-exponential kinetics (DFOP: double first order in parallel, Figure SI 3.2), assuming a substance is applied to two compartments with fast and slow decline, respectively. Further information and reference, see Notes to table SI 3.3a.

Decline curves of co-formulants and actives in vegetables did not exhibit a clear bi-phasic behaviour. Kinetics other than SFO were, therefore, not applied.

Figure SI 3.2: Example fits of residue data with SFO (top row) and DFOP (bottom row). Dashed lines in bottom panels indicate SFO fits for comparison.