Research Article

Residues of pesticide co-formulants in lettuce and parsley: Identification of decline processes using field trials in different cropping systems

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Abstract

BACKGROUND: Although co-formulants constitute a substantial portion of the total plant protection product (PPP) mass applied to crops, data on residue formation and the behaviour of these substances on plants are scarce. In an earlier study we demonstrated that co-formulants commonly used in PPPs can form considerable residues, i.e., in the low to medium mg/kg range, but normally decline rapidly within few days. In the field trial reported here, we aimed to identify the major decline processes of co-formulants. Residues of co-formulants were therefore monitored in parsley and lettuce grown in an open field as well as under foil tunnels equipped with either an overhead or a drip irrigation system.

RESULTS: Dissipation of three anionic surfactants was markedly faster when crops (parsley and lettuce) were exposed to natural rainfall or irrigation from above compared to drip irrigation. In contrast, the decline of three volatile organic solvents was not affected by rain or irrigation, but was dependent on the crop, with much shorter half-lives in lettuce than in parsley. Furthermore, dilution through plant growth contributed significantly to the reduction of residues over time.

CONCLUSION: In this work we substantiate earlier findings on the magnitude and dissipation of residues of anionic surfactants and solvents representing the most important co-formulant classes. The chosen experimental setup allowed differentiation between decline processes and we confirm that foliar wash-off is a major dissipation process for anionic surfactants. For volatile organic solvents, dissipation appears to depend on the properties not only of the substance but also of the plant (surface).
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Supporting information may be found in the online version of this article.

Keywords: pesticide co-formulants; residues in food; vegetable; wash-off; volatilisation; field trial

1 INTRODUCTION

Plant protection products (PPPs) contain one or more active substances, occasionally a safener or a synergist, and usually several co-formulants. When PPPs are applied to agricultural crops, residues on the treated plants are to be expected, including in the edible part of the plant. However, today regulation, enforcement and monitoring of PPP residues in plants and plant commodities solely focus on active substances.[1] Consequently, information on co-formulants, including their use, occurrence and behaviour in the environment, and formation of residues in plants is scarce. However, co-formulants, excluding water, roughly account for 20% of the total mass of PPPs sold.[2] In two studies, dissipation of selected co-formulants from fruit or vegetables was studied under laboratory conditions,[3,4] while the behaviour in the field has thus far received very little attention. In a previous study we therefore examined the formation and subsequent dissipation of residues of four different co-formulants after PPP application on various vegetable crops and on apples under realistic field conditions.[5] Together with two further studies published around the same time,[6,7] this was the first instance when measured data on co-formulant residues on plants grown under field conditions was published. Our study demonstrated that co-formulants can form considerable amounts of residues directly after treatment in the field, i.e., in the low mg/kg range, but in general decline rapidly with half-lives of few days, with wash-off and volatilisation as the most probable major dissipation processes. Based on the results of this field trial we further suggested a simple approach for estimation of potential co-formulant residues using publicly available residue data for active substances to be applied, for

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example, in future assessments of the exposure of consumers to co-formulants in a regulatory framework.[5]

In the present study we aimed to obtain a deeper insight into the occurrence and behaviour of PPP co-formulants on vegetables to distinguish and quantify the impact of different dissipation processes and to confirm the applicability of the earlier proposed worst-case estimation approach. We therefore carried out a field trial where we investigated co-formulant residues in parsley (*Petroselinum crispum convar. crispum*) and oak leaf lettuce (*lactuca sativa var. crispa*) in three different cropping systems. The criteria for selection of co-formulants were the same as elucidated earlier,[5] namely, the representativeness for important co-formulant classes, viability of a robust and sensitive analytical method including access to reference material, and the availability of PPPs containing the respective co-formulants in sufficient amounts. The investigated co-formulants were di-2-ethylhexyl sulfosuccinate (docusate), sodium dodecyl sulfate (SDS) and linear alkylbenzene sulfonate (LAS), all representing anionic surfactants, as well as N,N-dimethyldecanamide (DMDA), octylpyrrolidone and 1- and 2-methylnaphthalene (components of solvent naphtha), representing solvents (chemical structures shown in Fig. 1). Solvents and surfactants were identified as the major classes of co-formulants.[2,8] To complement the data on co-formulants and to allow for a direct comparison, spiroxamine and tebuconazole, active substances in three of the applied fungicides, were also monitored. Docusate, SDS, DMDA and spiroxamine were also investigated in the previous field trial.[5]

Parsley and lettuce were selected (i) to represent crops that are frequently treated with PPP close to harvest and (ii) to confirm some of the findings from our previous field trial. To distinguish possible dissipation processes and to assess the importance of wash-off, three cropping systems were tested in parallel: (i) a foil tunnel equipped with a drip irrigation system to exclude potential wash-off, (ii) a foil tunnel equipped with an overhead irrigation system and (iii) open-field conditions exposed to rainfall.

2 MATERIAL AND METHODS

2.1 Field trials and sampling procedure

Field trials were conducted on three adjacent fields (two covered with foil tunnels and one open field), located in Wädenswil, Switzerland (47°13′20.0′′N 8°40′07.3′′ E, altitude 510 m). Parsley (Grüne Perle, curly variety) and oak leaf lettuce (Kisheri F1) were each planted on four test plots (1.5 × 12 m) and two untreated control plots (1.5 × 4 m) per field (Supporting Information S2, Table SI 1.1). Planting dates were June 2 for parsley and June 21, 2020 for lettuce.

Crop cultivation (i.e., irrigation, pest management and fertilisation) was done according to normal agricultural practice (Supporting Information S2, Table SI 1.2). Notably, PPPs used on the crops before the start of the residue trial did not contain any of the substances investigated in this study. All fields were irrigated as necessary using an overhead irrigation system until day 0 (July 6, 2020, day of PPP treatment). Starting from day 0, overhead irrigation was maintained in the open field and in one of the two foil
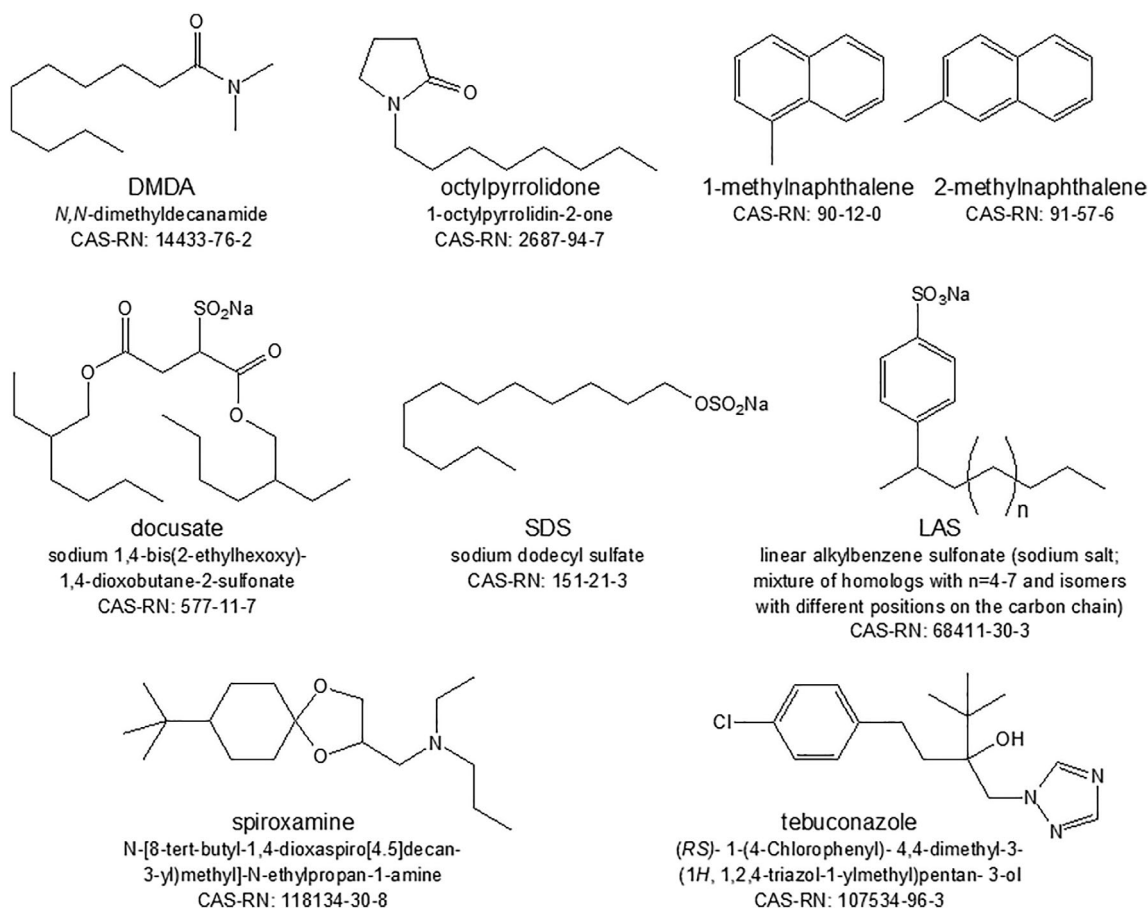

Figure 1. IUPAC names, CAS-RN and chemical structures of substances assessed in the residue field trials.

tunnels, whereas in the second tunnel a drip irrigation system was used to distinguish wash-off from other decline processes.

Four different fungicides that contained one to three of the investigated co-formulants were applied in each cropping system to one separate plot of parsley (BBCH 43-45) and lettuce (BBCH 41-42) with the application rates typically used on these or similar crops (Table 1).

A meteorological station within 800 m of the test site recorded daily mean air temperatures between 11.7 and 30.3 °C with an overall mean of 19.9 °C in the open field (day 0 to day 21). The temperatures in the foil tunnels varied between 10.2 and 40.2 °C with an overall mean of 22.1 °C. No rain was recorded on the first 3 days after treatment. A total of 87.7 mm of rainfall was measured over the entire sampling period. The open-field plots were additionally irrigated if necessary. The total amount of artificial irrigation was in the same order of magnitude as natural precipitation (about 90 mm over the 21-day sampling period). In the foil tunnels, the crops were irrigated on a daily basis to allow normal plant growth, starting after day 1 sampling. The amount of irrigation water corresponded to precipitation of about 280 mm for the overhead system and 210 mm for the drip irrigation system (Supporting Information S2, Table SI 1.3a and b).

From each treated plot 12 individual plants were randomly collected for a sample within about 1 h after treatment to allow for complete drying of the spray deposited on the plants (day 0), as well as 1, 2, 3, 7, 14 and 21 days after treatment. Control samples were randomly collected on the day before treatment over all plots and separately for the cropping systems (12 plants each). The samples were weighed, packed into plastic bags and frozen within less than 2 h after sampling. The samples were stored at −20 °C until processed for analysis.

2.2 Sample preparation and analysis

Stored and frozen samples were homogenized and then processed as described in Balmer et al.,[5] according to the QuEChERS multimethod,[9] using acetonitrile [for liquid chromatography–tandem mass spectrometry (LC-MS/MS) analysis of DMDA, octylpyrrolidone, docusate, SDS and LAS as well as the active substances spiroxamine and tebuconazole] and ethyl acetate [for gas chromatography–mass spectrometry (GC-MS) analysis of 1- and 2-methylnaphthalene] as extractants. Two subsamples of each homogenate (replicates) were processed and analysed independently in separate series on two consecutive days. Fortified samples were included in each series for quality control. Details of the analytical methods are provided in Supporting Information S2, Section SI 2.

2.3 Quantification

The test substances were quantified using external standards prepared in acetonitrile for LC-MS/MS analysis and blank parsley or lettuce extract for GC-MS analysis (for reference materials, see Table SI 2.2). The calibration ranges were different for the different substances, starting from 0.001 mg kg^{-1} for docusate, DMDA, octylpyrrolidone, tebuconazole and spiroxamine, from 0.005 mg kg^{-1} for 1- and 2-methylnaphthalene, and from 0.01 mg kg^{-1} for SDS and LAS (equivalent to fresh plant weight; Supporting Information S2, Table SI 2.3). Residues of docusate and SDS are expressed as sodium salts. For spiroxamine, residues are expressed as the sum of its two diastereomers, assuming equal response. The quantification of LAS residues was based on the peak area of undecylalkylbenzene sulfonate, as the most abundant component in spray solution and initial residues, but concentrations are expressed as the total amount of alkylbenzene sulfonic acid sodium salts in the reference mixture. Thus, the composition of LAS residues is not precisely known and concentrations should therefore be considered as semiquantitative only. More details are reported in Supporting Information S2, Section SI 2.

3 RESULTS AND DISCUSSION

3.1 Performance of the analytical method

For each analyte, recoveries were determined at three to six fortification levels in both lettuce and parsley, in 18 to 24 independent

Table 1. Fungicides containing the co-formulants and active substances applied to parsley and lettuce in the open-field and tunnel systems

Fungicide trade name (formulation code)	Amount of fungicide (water) (kg or L ha^{-1})	Co-formulant or active substance	Function	Measured (declared) content in fungicide (g kg^{-1})	Amount of test substance applied (g ha^{-1})
Armicarb (SP)	5 (400)	Docusate	Surfactant	88	440
		SDS	Surfactant	62	310
		KHCO$_3$[a]	Fungicide	(850)	(4250)
Input (EC)	1.25 (400)	DMDA	Solvent	433	541
		Spiroxamine	Fungicide	(300)	(375)
		Prothioconazole[a]	Fungicide	(160)	(200)
Pronto Plus (EW)	1.5 (400)	DMDA	Solvent	328	492
		Octylpyrrolidone	Solvent	84	126
		LAS	Surfactant	35	53
		Spiroxamine	Fungicide	(250)	(375)
		Tebuconazole	Fungicide	(133)	(200)
Slick (EC)	0.5 (400)	1-methylnaphthalene	Solvent[b]	31	16
		2-methylnaphthalene	Solvent[b]	62	31
		Difenoconazole[a]	Fungicide	(250)	(125)

Abbreviation: DMDA, N,N-dimethyldecanamide; LAS, linear alkylbenzene sulfonate; SDS, sodium dodecyl sulfate.
[a] Substances not monitored.
[b] Components of the co-formulant "solvent naphtha".
Formulation types: water-soluble powder (SP), emulsifiable concentrate (EC), emulsion oil in water (EW).

samples each. Mean recoveries over all spike levels and both crops were acceptable for all test substances at 100% (for spiroxamine), 105% (tebuconazole) 103% (docusate), 101% (octylpyrrolidone), 102% (DMDA), 94% (SDS), 100% (LAS), 86% (1-methylnaphthalene) and 83% (2-methylnaphthalene). More details are reported in Supporting Information S2, Table SI 2.5.

The precision of the analytical method, determined as the relative deviation of residual concentrations from the mean of two replicates, was <5% for ~70% of samples, <10% for ~90% of samples and >25% for only ~1% of samples (Supporting Information S2, Fig. SI 2.3). For 1- and 2-methylnaphthalene, analytical precision was only evaluated in parsley but not in lettuce, where concentrations were below the limit of quantification (LOQ). The values detailed for each sample are reported in Supporting Information S1.

The storage stability of docusate, DMDA, SDS and spiroxamine in homogenised samples at −20 °C over several months was demonstrated in our earlier study.[5] The storage stability of the remaining test substances was determined by comparing the concentrations in freshly homogenized samples to those in homogenate of the same samples after storage at −20 °C during 60–240 days, and was found to be 96%, 90% and 97% for octylpyrrolidone, LAS and tebuconazole, respectively (mean of both parsley and lettuce), and 91% and 99% for 1- and 2-methylnaphthalene, respectively, in parsley. No storage stability tests were performed for 1- and 2-methylnaphthalene in lettuce (due to concentrations below LOQ; Supporting Information S2, Table SI 2.4).

LOQs were 0.001 mg kg^{-1} for docusate and octylpyrrolidone, 0.01 mg kg^{-1} for SDS (arbitrarily determined from the lowest standard concentration), 0.005 mg kg^{-1} for spiroxamine, 0.01 mg kg^{-1} for DMDA and 1-methylnaphthalene, 0.02 mg kg^{-1} for 2-methylnaphthalene and tebuconazole, and 0.2 mg kg^{-1} for LAS (all based on background

concentrations in blank and untreated control samples). Recovery samples were analysed in each series to ensure continuous performance of the analytical procedure.

3.2 Initial residues

All co-formulants investigated were detected in concentrations well above the respective LOQs in parsley and lettuce collected directly after spraying (day 0 samples) from all cropping systems, with the exception of 1- and 2-methylnaphthalene in lettuce, where residues were below LOQs (tunnels and the open field). The concentrations that were measured in these day 0 samples were overall lowest for 1- and 2-methylnaphthalene (0.043–0.12 mg kg^{-1} in parsley), followed by LAS (2.3–4.5 mg kg^{-1}), octylpyrrolidone (1.2–4.2 mg kg^{-1}), SDS (5.4–12 mg kg^{-1}), DMDA (3.8–20 mg kg^{-1}) and docusate (13–31 mg kg^{-1}) in parsley and lettuce. The ascending order of co-formulant residues was overall consistent with the application rates, which were lowest for 1- and 2-methylnaphthalene (16 and 31 g ha^{-1}, respectively) and still comparably low for LAS and octylpyrrolidone (55 and 110 g ha^{-1}) compared to about 250 g ha^{-1} for SDS and 400–500 g ha^{-1} for DMDA and docusate. Day 0 residues of the active substances spiroxamine and tebuconazole were 7.9–26 and 15–23 mg kg^{-1}, respectively, and thus were consistent with the application rates of 375 and 200 g ha^{-1} (Table 2).

The initial residues of DMDA and spiroxamine, which were applied with two different PPPs, were similar in terms of a crop/cropping system combination, indicating that for these two products formulation type (emulsifiable concentrate and emulsion oil in water, respectively; Table 1) is not a dominant factor for the formation of residues, consistent with observations reported by Maclachlan and Hamilton.[10]

Excluding possible losses during spraying or between spraying and sampling (e.g., due to volatilisation), initial residues are expected to mainly be determined by the application rate, but

Table 2. Initial residues in parsley and lettuce sampled immediately following application (day 0), measured (C_0) and scaled to a standard application rate of 1 kg ha^{-1} ($C_{0,norm}$)

	Parsley, tunnel, drip (mg kg^{-1})		Parsley, tunnel, overhead (mg kg^{-1})		Parsley, open field (mg kg^{-1})		Lettuce, tunnel, drip (mg kg^{-1})		Lettuce, tunnel, overhead (mg kg^{-1})		Lettuce, open field (mg kg^{-1})	
	C_0[a]	$C_{0,norm}$[b]	C_0[a]	$C_{0,norm}$[b]	C_0[a]	$C_{0,norm}$[b]	C_0[a]	$C_{0,norm}$[b]	C_0[a]	$C_{0,norm}$[b]	C_0[a]	$C_{0,norm}$[b]
Anionic surfactants												
Docusate	24	56	31	72	22	49	22	50	24	54	13	29
SDS	9.1	29	12	40	9.9	32	6.1	20	7.2	23	5.4	17
LAS	4.5	86	3.7	70	3.0	58	3.4	65	3.4	64	2.3	44
Solvents												
DMDA (Input)[c]	16	30	20	37	15	27	11	21	15	27	3.7	6.9
DMDA (Pronto Plus)[c]	14	29	17	35	11	22	11	23	8.1	17	4.6	9.3
Octylpyrrolidone	3.5	28	4.2	33	2.6	21	3.1	24	2.2	17	1.2	9.5
1-methylnaphthalene	0.052	3.3	0.096	6.2	0.043	2.8	<LOQ	–	<LOQ	–	<LOQ	–
2-methylnaphthalene	0.077	2.5	0.12	3.8	0.058	1.9	<LOQ	–	<LOQ	–	<LOQ	–
Active substances												
Spiroxamine (Input)	10	27	14	37	9.0	24	24	65	25	66	13	34
Spiroxamine (Pronto Plus)	9.9	26	11	30	7.9	21	26	69	18	47	12	32
Tebuconazole	23	114	23	114	16	81	23	117	19	95	15	77

Abbreviation: DMDA, *N,N*-dimethyldecanamide; LAS, linear alkylbenzene sulfonate; LOQ, limit of quantification; SDS, sodium dodecyl sulfate.
[a] Mean values of two subsamples, processed separately on consecutive days.
[b] $C_{0,norm}$ was calculated using the application rates listed in Table 1.
[c] Two different plant protection products (Pronto Plus and Input), both containing DMDA as co-formulant and spiroxamine as active substance were applied on different subplots, yielding separate values.
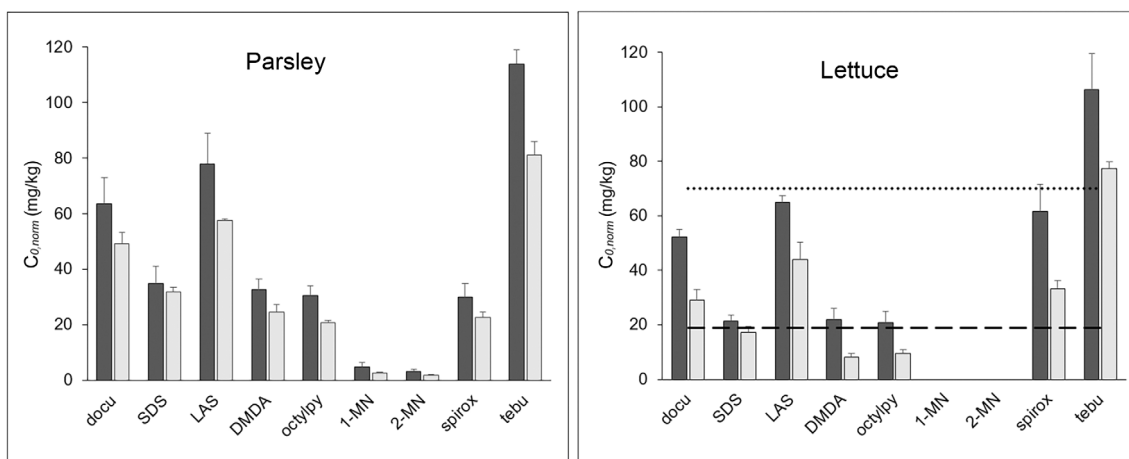
Figure 2. Day 0 residues (measured directly after application) scaled to an application rate of 1 kg ha^{-1} ($C_{0,norm}$) for the co-formulants docusate (docu), sodium dodecyl sulfate (SDS) and linear alkylbenzene sulfonate (LAS) (representing anionic surfactants) and *N,N*-dimethyldecanamide (DMDA), octylpyrrolidone, and 1- and 2-methylnaphthalene (1-MN and 2-MN; solvents) as well as spiroxamine and tebuconazole (spirox and tebu; active substances) in parsley and oakleaf lettuce under foil tunnels (dark grey columns) and open-field conditions (light grey), respectively. Combined values for both tunnel systems are shown. The values for DMDA and spiroxamine are mean values from two subplots treated separately with different plant protection products containing the respective compound. Error bars indicate the standard deviation from replicate measurements. For comparison, day 0 residues in leaf lettuce as reported by Mclachlan and Hamilton[11] are indicated (median, dashed line; 90th percentile, dotted line).

presumably are influenced by crop-specific factors such as growth stage, plant habitus and surface, or planting density. Thus, initial concentrations are expected to be similar for all co-formulants in a specific crop and cropping system when normalised for a standard application rate. We therefore scaled the residues measured in day 0 samples to an application rate of 1 kg ha^{-1} to yield a calculated and normalised concentration ($C_{0,norm}$). These normalised residues were in a comparably narrow range for the surfactants docusate, SDS and LAS in parsley (29–85 mg kg^{-1}) and lettuce (17–65 mg kg^{-1}) for both the tunnel and open-field conditions. The normalised initial concentrations of the solvents 1- and 2-methylnaphthalene, DMDA and octylpyrrolidone were clearly lower when compared to the surfactants and were in the range of 1.9–6.2 mg kg^{-1} for 1- and 2-methylnaphthalene in parsley and 21–36 mg kg^{-1} and 7–27 mg kg^{-1} for DMDA and octylpyrrolidone in parsley and lettuce, respectively. These lower $C_{0,norm}$ values for these solvents may be attributed to partial volatilisation from the plant surface between application and sampling or even during spraying before reaching the target, consistent with the comparably high vapour pressures (7 and 9 Pa for 1- and 2-methylnaphthalene, 0.11 and 0.03 Pa for DMDA and octylpyrrolidone, respectively). This finding confirms the results from our earlier work, where considerably lower $C_{0,norm}$ values were observed for DMDA in five different vegetables grown under open-field conditions when compared to $C_{0,norm}$ values for other co-formulants (surfactants, considered to be nonvolatile) in the respective samples[5] (Table 2 and Fig. 2).

We further observed that $C_{0,norm}$ values for all co-formulants were lowest in lettuce from the open-field system. Initial residues in crops that are sprayed from above may also be estimated using a simple approach assuming these crops to act as filter for the applied PPP. The approach assumes the residues to be proportional to the portion of the sprayed area covered by the crop (i.e., crop soil coverage) and inversely proportional to the total plant weight in the respective area (i.e., yield).[5] In fact, generic initial concentrations estimated accordingly ($C_{0,gen}$) were lower for lettuce in the open field than in the tunnels (40 and 83 mg kg^{-1}, respectively, for a standard application rate of 1 kg ha^{-1}) based on higher total plant weight (3.5 t/ha compared to 2.4 t/ha) in

combination with a lower crop soil coverage (0.14 compared to 0.2) under open-field conditions than in the tunnel systems at the time of application. Different crop weights and soil coverage at the time of application presumably were due to different conditions with respect to irrigation, rainfall, temperature and sunlight. However, similar crop weight and crop soil coverage were observed in both tunnels, in agreement with equal conditions from planting to the time of application. In contrast to lettuce, the estimated $C_{0,gen}$ values for parsley were similar for open-field and tunnel conditions (100 and 84 mg kg^{-1}, respectively). More details are provided in Supporting Information S2, Section SI 3.

The above-described effect of lower initial concentrations in lettuce under open-field conditions compared to the tunnel systems was most pronounced for the solvents DMDA and octylpyrrolidone. This indicates that in lettuce volatilisation might be more important under open-field conditions (overlaying with the effect of crop weight and soil coverage). Again, locally deviating environmental conditions in the open field, such as higher wind speed or solar irradiation, may have facilitated volatilisation from plant surfaces during drying of the spray solution.

The scaled initial residues for all investigated substances that were detected in parsley and lettuce under open-field and tunnel conditions were in the range of 2–85 mg kg^{-1}, with the exception of tebuconazole, where higher residues were found (up to 117 mg kg^{-1}). These $C_{0,norm}$ values are consistent with the range of scaled values for numerous publicly available day 0 residue data as compiled by Maclachlan and Hamilton,[11] who reported a median day 0 residue of 19 mg kg^{-1} and a 90th percentile day 0 residue of 70 mg kg^{-1} for leaf lettuce (no data provided for parsley). Furthermore, the $C_{0,norm}$ values determined in this trial were in good agreement with normalised initial residues of the same co-formulants (docusate, SDS and DMDA) in our earlier field trial.[5] The $C_{0,gen}$ values estimated on the basis of crop parameters were higher but of the same order of magnitude and were suitable to explain the observed differences between the cropping systems.

Overall, the results confirm that both approaches – the use of publicly available residue data reported by Maclachlan and Hamilton,[11] as well as the generic estimation based on crop

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parameters – may provide useful first estimates for initial residues of co-formulants in situations where measured residue concentrations are not available. The latter approach is, by nature, limited to crops which are sprayed from above, where the consumable parts are equal to the aerial parts of the plants and the respective crop parameters are available (i.e., not valid for vertical crops, fruits or root vegetables).

3.3 Decline of residues over time

The concentrations of all co-formulants decreased over time in both crops and in all three cropping systems. However, the decline rates differed depending on type of co-formulant, crop and system. The concentrations of the anionic surfactants (docusate, SDS and LAS) declined to roughly 5–65% of the initial residues in samples that were collected 3 days after application and to <1–15% in samples from day 14, with the highest remaining residues in the tunnel with drip irrigation. The concentrations measured on day 14 were 3.5, 1.8 and 0.6 mg kg^{-1} in parsley and 0.5, 0.2 and <0.2 mg kg^{-1} in lettuce for docusate, SDS and LAS, respectively, under drip irrigation but <0.2 mg kg^{-1} for all surfactants in all samples grown under overhead irrigation or in the open field. Qualitatively, the decline patterns of all surfactants were similar in both parsley and lettuce, i.e., fairly rapid dissipation in the open field and foil tunnel with overhead irrigation *versus* clearly slower dissipation in the tunnel with drip irrigation (Fig. 3).

The behaviour of the solvents was markedly different from that of the anionic surfactants. The decline was slower in parsley compared to lettuce and there was no apparent difference between the decline in the tunnel with drip irrigation and that in the other two cropping systems. In parsley, concentrations were in the range of 43–65% and 9–19% of the initial residues on days 3 and 14, respectively. Concentrations were 2.0–3.4 mg kg^{-1} for DMDA and 0.3–0.4 mg kg^{-1} for octylpyrrolidone on day 14. A similar behaviour was observed for 1- and 2-methylnaphthalene in parsley with a decline to about 50–80% of initial residues within 3 days after application. In contrast, a faster decline was observed for DMDA and octylpyrrolidone in lettuce, with remaining residues of less than 2% of the initial concentrations in day 3 samples irrespective of the cropping system. The decline of 1- and 2-methylnaphthalene in lettuce is not discussed, as all residues were below the LOQ.

For the two active substances spiroxamine and tebuconazole a continuous decline occurred to about 2–12% (0.3–3 mg kg^{-1}) and 0.2–3% (0.02–0.7 mg kg^{-1}) of the initial concentrations in parsley and lettuce sampled on day 14, respectively.

Various factors account for the decline of residues in plants, among which volatilisation, wash-off, dilution by plant growth, plant metabolism and (photo)chemical degradation are the most important. The trial setup and the selection of the co-formulants were intended to minimise the influence of some factors on the decline in specific subplots and thus
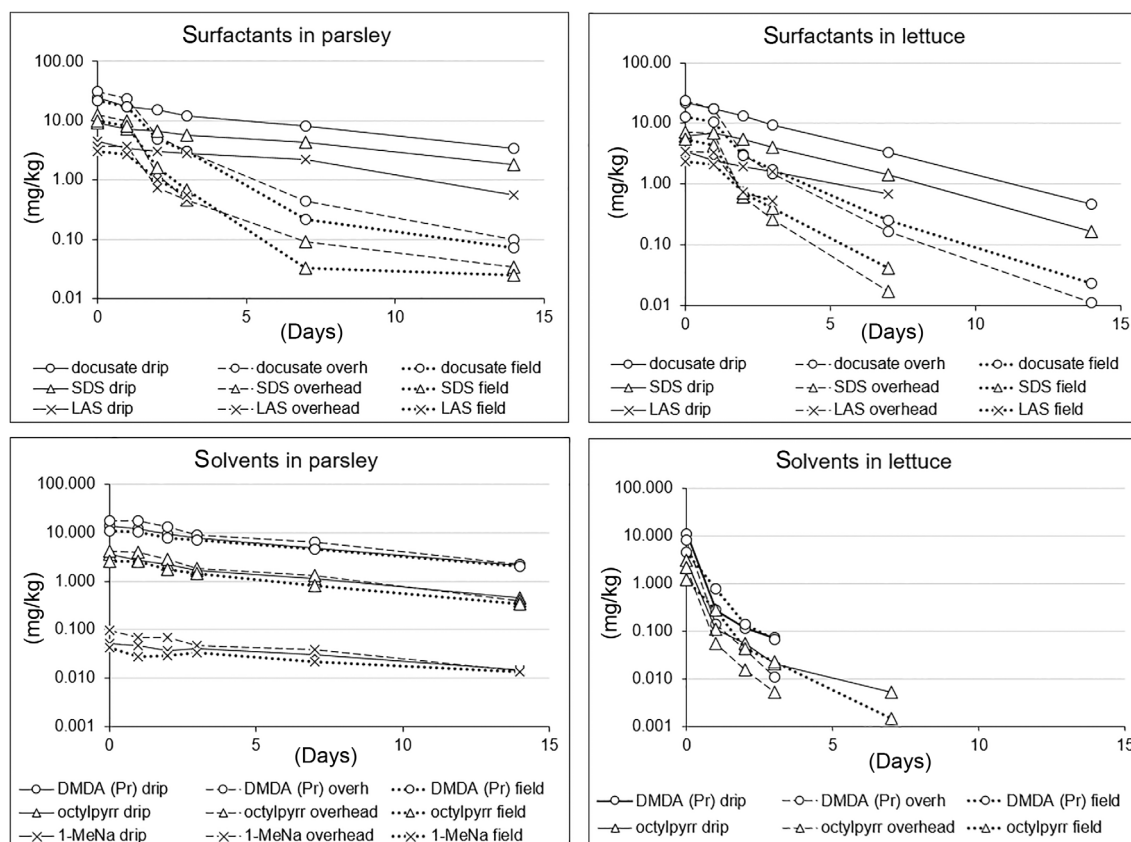

Figure 3. Residue decline over time in parsley and lettuce grown in tunnels with drip irrigation and overhead irrigation, respectively, and in the open field sampled after treatment with PPPs for selected co-formulants. Only time points where both replicates were above the limit of quantification are shown (mean values). Note the semilogarithmic scale. Decline curves of all substances are shown in Supporting Information S2, Fig. SI 3.1. Abbreviation: DMDA (Pr), *N*,*N*-dimethyldecanamide (applied with Pronto Plus); LAS, linear alkylbenzene sulfonate; SDS, sodium dodecyl sulfate; 1-MeNa, 1-methylnaphthalene.

allowed to qualitatively assess the importance of selected decline processes: (i) potential wash-off of any substance was prevented by the tunnel in combination with drip irrigation; (ii) volatilisation was not expected to be a significant decline process for anionic surfactants (nonvolatile compounds, in contrast to the solvents, which are considered to be volatile), and (iii) the monitoring of plant weight throughout the trials allowed the estimation of residue decline due to plant growth.

To describe and compare the residue decline of the different co-formulants in the different crops and conditions, we fitted the experimental residue data to a simple exponential kinetic model (single first order, SFO). This simple approach was previously recommended as the most appropriate way to describe the decline of plant residues of PPP active ingredients, particularly within a regulatory framework[12,13] and was also used in our earlier study.[5]

In the corresponding equation used to fit the experimental data, C_0 is the initial concentration, t is the time between application and sampling, and k is the decline rate (DT$_{50}$, the corresponding half-life of the residues):

$$C_t = C_0 \times e^{-kt} \text{ and } DT_{50} = \ln 2 / k$$

All surfactant decline curves from the drip irrigation systems were well described by SFO kinetics and corresponding DT$_{50}$ values were in a narrow range for all three surfactants investigated (4.1–6.1 days in parsley and 2.5–3.8 days in lettuce). In contrast, under overhead irrigation or in the open field the decline of the surfactants was considerably faster, yielding DT$_{50}$ in the range of 1.0–1.5 days. Although the latter decline curves could not be adequately described by first-order kinetics, we consider the derived DT$_{50}$ as indicative (Table 3). The distinctly faster decline

in the open field and overhead irrigation plots demonstrates that wash-off is an important process for the removal of readily water-soluble co-formulants (such as anionic surfactants) provided the crops are exposed to rain and/or irrigation from above. This confirms the findings in our previous field trial, where anionic surfactants applied as PPP co-formulants were subject to fast decline in five different vegetables, likely driven by an intense rainfall event few days after treatment.[5]

The decline of the solvents DMDA and octylpyrrolidone in both crops and in all systems was well described by SFO kinetics. The DT$_{50}$ values for both solvents were in a narrow range for each crop, independent of the irrigation system, indicating that wash-off is not a main dissipation process for these compounds. However, DT$_{50}$ values were considerably longer in parsley (3.9–5.7 days) than in lettuce (0.16–0.46 days). The DT$_{50}$ values of 1- and 2-methylnaphthalene in parsley were similar (about 5–8 days), but could not be investigated in lettuce as the residues in all samples were below the LOQ. The different dissipation behaviour of the solvents in parsley compared to lettuce was in agreement with the previously observed behaviour of DMDA: in our earlier field trial half-lives of approximately 6 days in parsley and 0.2 days in head and leaf lettuce were observed.[5] The fast dissipation from lettuce can presumably be attributed to volatilisation from the plant surface (based on the relatively high vapour pressures of these solvents). The slower decline in parsley substantiates the conclusion from our previous trial that residues of co-formulants that are both volatile and lipophilic need specific consideration as their behaviour may not solely be driven by volatilisation, but may also depend on specific plant surface properties.

An increase in plant weight over the course of the trial also leads to the (apparent) decline of monitored residues. This dilution of

Table 3. DT$_{50}$[a] values resulting from SFO fitting of residue decline over time

DT$_{50}$ (days)	Parsley, tunnel, drip	Parsley, tunnel, overhead	Parsley, open field	Lettuce, tunnel, drip	Lettuce, tunnel, overhead	Lettuce, open field
Anionic surfactants						
Docusate	4.1	(1.1)	(1.2)	2.5	(1.0)	(1.2)
SDS	6.1	(1.0)	(1.1)	3.8	(1.1)	(1.1)
LAS	5.6	(1.3)	(1.5)	2.8	(1.4)	(1.5)
Solvents						
DMDA (Pronto Plus)	4.4	4.2	5.3	0.19	n.a.	0.39
DMDA (Input)	5.7	5.1	4.7	0.16	0.17	0.39
Octylpyrrolidone	3.8	3.4	3.9	0.21	0.19	0.46
1-methylnaphthalene	7.8	4.9	(8.2)	n.a.	n.a.	n.a.
2-methylnaphthalene	8.3	(5.1)	7.6	n.a.	n.a.	n.a.
Active substances						
Spiroxamine (Pronto Plus)	(1.6)	(1.8)	(1.6)	1.7	1.6	1.4
Spiroxamine (Input)	(2.1)	(1.6)	(1.3)	2.0	1.8	(0.98)
Tebuconazole	4.3	(1.8)	(1.7)	1.7	(1.4)	(1.4)
Theoretical dilution by plant growth[b]	13	7.2	20	4.2	3.4	4.9

Abbreviation: DMDA, *N,N*-dimethyldecanamide; LAS, linear alkylbenzene sulfonate; LOQ, limit of quantification; n.a., not applicable (not enough time points with residue concentrations above LOQ available); SDS, sodium dodecyl sulfate; SFO, single first order.
[a] For curve fitting the program CAKE (version 3.4)[14] was used, applying SFO kinetics to the experimental data (more details in Supporting Information S2, Section SI 3). DT$_{50}$ values from SFO fits that did not adequately describe the respective decline curves are reported in parentheses and should be considered as indicative only.
[b] Estimated (theoretical) decline due to dilution of the residues by plant growth (assuming no other decline process occurs). SFO kinetics were fitted to a 'decline curve' as calculated from the weight of plants in the different cropping systems (weight at day 0/weight at day *t*).

residues due to plant growth superimposes with other decline processes. To quantify the contribution of plant growth to the observed overall decline we also monitored plant weights. In fact, a considerable increase in plant weight was recorded between days 0 and 14 (a factor of about 2–4 for parsley and a factor of 6–10 for lettuce, respectively; for details see Supporting Information S2, Table SI 3.1). The dilution of residues caused by plant growth alone would result in an apparent DT_{50} of 7.2–20 days in parsley and 3.4–4.9 days in lettuce (applying SFO kinetics). These dilution half-lives are in the same order of magnitude as the overall observed half-lives for certain co-formulant/system combinations, and plant growth is the driving factor for residue decline in these cases: For the anionic surfactants, dilution due to plant growth contributed most in the drip irrigation system (about 30–50% for parsley and 60–90% for lettuce), but less in the overhead irrigation and open-field system (less than 20% for parsley and about 20–40% for lettuce). For the solvents, plant growth contributed about 20–70% to the overall decline in parsley (all cropping systems) but was of minor importance in lettuce (<10%).

For the active substance spiroxamine DT_{50} values in the range of 1–2 days were derived, again in good agreement with previously observed behaviour.[5] The half-lives for tebuconazole were 1.3–1.8 days with the exception of a somewhat longer half-life in parsley under drip irrigation (4.3 days). For both active substances the contribution of plant growth to the overall decline was in the range of <10 to ~50%.

Furthermore, the half-lives derived in this study were well below the worst-case DT_{50} values of 8–12 days that were derived from publicly available residue data for PPP active substances as discussed previously.[5]

4 CONCLUSION

This study was designed as follow-up of a previous field trial, where for the first time data on PPP co-formulant residues on vegetable and fruit crops grown under realistic field conditions were published. With this second field trial we extended the database on co-formulant residue formation in plants and were able to identify the most important dissipation processes as well as quantifying their contribution to the observed overall decline over time. We confirmed that compounds representing the two most important co-formulant classes (anionic surfactants and solvents) form considerable residues in/on parsley and lettuce when applied as components of commercially available PPPs and according to normal agricultural practice. The initial residues of all investigated co-formulants were in the low mg/kg range and thus in the same order of magnitude as previously detected in a variety of vegetable crops and in good agreement with publicly available data for PPP active substances.

The investigation and comparison of the residue behaviour in different cropping systems, i.e., tunnels with drip and overhead irrigation as well as open-field conditions, showed a markedly faster dissipation of three different anionic surfactants when they were exposed to irrigation from above and/or precipitation compared to drip irrigation. These results substantiated our previous interpretation and clearly demonstrate that foliar wash-off is a major dissipation process for water-soluble co-formulants. In contrast, the behaviour of three solvents did not significantly vary between cropping systems, thus supporting the assumption that wash-off is not a key process for this class of co-formulants. Residues of the investigated solvents declined very rapidly in lettuce (half-life of few hours), in agreement with their volatility and

consistent with earlier observations. However, the decline of these solvents was consistently slower in parsley than in lettuce. This behaviour, again, strongly supports our previously formulated hypothesis that the behaviour of volatile, lipophilic co-formulants is not only driven by volatilisation but may also be governed by plant surface properties. Dilution of residue concentrations due to plant growth contributed substantially to the overall decline in certain cases. This can be attributed to the fact that in our field trial treatment was carried out at plant stages, where the final leaf mass was not reached yet. If PPPs are applied at a later stage (i.e., closer to commercial harvest), dilution by plant growth may be less important.

Given the vast number of co-formulants present in PPPs on the market and their often complex nature (along with analytical challenges) and regarding the absence of information on their use, measured residue data may not be available for most of these substances in the foreseeable future. Therefore, robust estimation methods will have to be used as substitute in cases where consumer exposure, e.g., in a regulatory context, needs to be evaluated. Our data suggest that worst-case estimation of co-formulant residues on plants based on publicly available residue data for pesticide active substances or, alternatively, on crop parameters are feasible approaches.

DATA AVAILABILITY STATEMENT
The data that supports the findings of this study are available in the supplementary material of this article

SUPPORTING INFORMATION
Supporting information may be found in the online version of this article.

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