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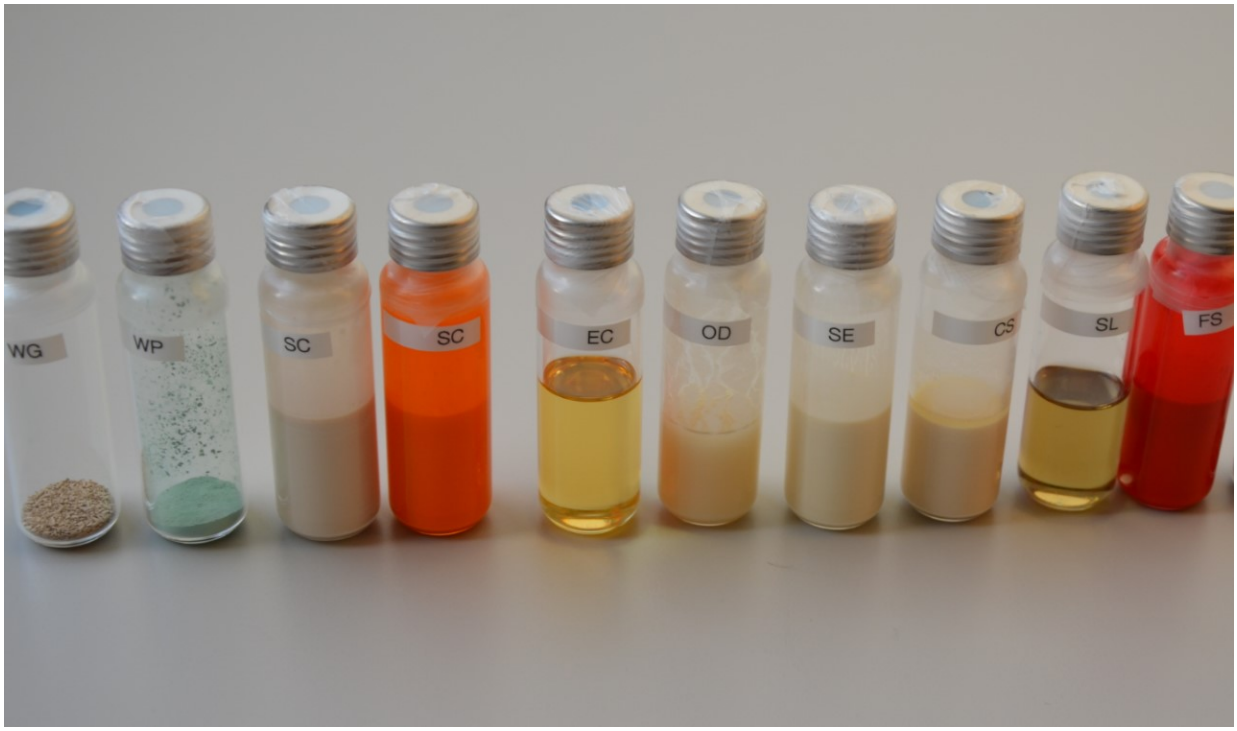
Co-formulants in plant protection products

Initial study on the risk assessment of co-formulants in plant protection products



Project report on behalf of the FSVO

Ulrich Schaller and Marianne Balmer

03/2018

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Project report dated 29.03.2018 (German)

https://www.blv.admin.ch/dam/blv/de/dokumente/lebensmittel-und-ernaehrung/lebensmittelsicherheit/stoffe-im-fokus/bericht-beistoffe-in-pflanzenschutzmitteln.pdf.download.pdf/Bericht_Vorstudie_Beistoffe_in_Pflanzenschutzmitteln_DE.pdf

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Samples of various plant protection product formulations (U. Schaller, Agroscope)

Contents

1 Summary

This initial study analysed and estimated the quantities of co-formulants in Swiss plant protection products. The study was based on the sales figures of plant protection products (PPP) in 2015 and the exact compositions of the formulations.
A list ranking the individual co-formulants or co-formulant groups by quantity was produced. Even after chemically similar co-formulants were grouped, over 90 different co-formulants/co-formulant groups remained and were assessed in this study. The five most important and common formulation types of plant protection products were analysed individually. On average, the co-formulants accounted for just over 20 % of the formulations, although this percentage varied considerably depending on the formulation type. Based on the estimated quantities of co-formulants sold and their grouping, individual substances can now be prioritised for follow-up investigations in respect of their potential for residues in foodstuffs.

2 Introduction

A plant protection product (PPP) consists of one or more active substances, possibly a synergist or a safener, and co-formulants. While the contents of the active substance and synergist/safener are declared on every pack of a PPP, co-formulants and their concentrations do not need to be publicly disclosed. A plant protection product can contain numerous different co-formulants.

The Swiss Plant Protection Products Ordinance (PlantPPO)[1] defines residues as one or more substances present in, or on, plants or plant products, edible animal products, drinking water or elsewhere in the environment and resulting from the use of a PPP, including their metabolites, breakdown or reaction products. The PlantPPO further specifies that residues of plant protection products must not produce any harmful effects on human or animal health or on groundwater.

In practice, the risk assessment and the regulation of residues are limited exclusively to the active substances in the plant protection products and their metabolites and breakdown or reaction products. Annex 2 of the Swiss PestRO[2], for example, only lists maximum residue levels for active substances in plant protection products. Co-formulants of PPPs are not considered. The possibility that co-formulant residues may be present on foodstuffs treated with PPPs cannot be ruled out. At present, it is not possible to assess the resulting risk. The level of exposure is not known. Moreover, the co-formulants are often inadequately characterised in terms of toxicology.

In Switzerland, several hundred different plant protection products with varying compositions and formulation types are authorised, including solid and liquid (water-based or solvent-based) PPPs. Some plant protection products can be applied directly, while many others first have to be diluted with water and stirred to form a spray mixture. The number of different co-formulants that can be introduced into the environment through the use of PPPs and possibly lead to residues is considerable. Neither the identity nor the level of co-formulant residues in foodstuffs is known.

[1] Ordinance on the Placing on the Market of Plant Protection Products (Plant Protection Products Ordinance, PlantPPO) of 12 May 2010 (version: 1 November 2016)
[2] FDHA Ordinance on the Maximum Residue Levels for Pesticides in or on Products of Plant and Animal Origin (PestRO) of 16 December 2016 (version: 1 May 2017)

This initial study is designed to identify co-formulants that are applied to agricultural crops in large quantities and that could lead to consumers being exposed. Once the co-formulants that potentially lead to residues in foodstuffs are identified, these residues can then be measured in follow-up investigations and subjected to risk assessments.

3 Aim of the initial study and any follow-up studies

This preliminary study aims to identify the quantitatively most important PPPs co-formulants that are applied to agricultural crops and that could potentially lead to residues in foodstuffs based on their method of application and substance properties (e.g. persistence).

The toxicological properties of the co-formulants will not be considered at this initial stage, rather those co-formulants overall that potentially contribute most to (chronic) exposure will be analysed. The initial study is designed to form the basis for further studies that will enable the co-formulant exposure of consumers through foodstuffs to be estimated and any resulting risk to human health to be regulated accordingly in future.

4 Results

An initial analysis of sales figures (Table 1) resulted in the following distribution via the sales channels.

Table 1: Sales volumes and percentages of plant protection products by sales channel in 2015

Product	Sales figures for 2015 (t)	Proportion (%)
Original authorisation	5290	77 %
Sales permit	1268	18 %
From parallel import	353	5 %
Total	6912	100 %

The sales figures shown here relate to products and should not be confused with previously published sales figures for active substances in plant protection products (annually around 2200 tonnes of plant protection product active substances (http://2016.agrarbericht.ch/de/umwelt/wasser/einsatz-von-pflanzenschutzmitteln).

It emerged that the products used for this initial study, with an original authorisation or sales permit issued by the Swiss authorities, accounted for 95 % of plant protection products sold. According to the notified sales figures, the proportion of parallel-imported plant protection products is small compared to the total. Only products with an original authorisation or sales permit will be considered in the subsequent analysis, since the co-formulants of parallel-imported products are not known to the Swiss authorities. In view of the small percentage involved, the exclusion of parallel-imported products from the subsequent analysis is unlikely to lead to any distortion of the results.

4.1 Number of products and sales volumes per formulation type

The number of authorised plant protection products per formulation type is presented in the following graph for the year 2017.

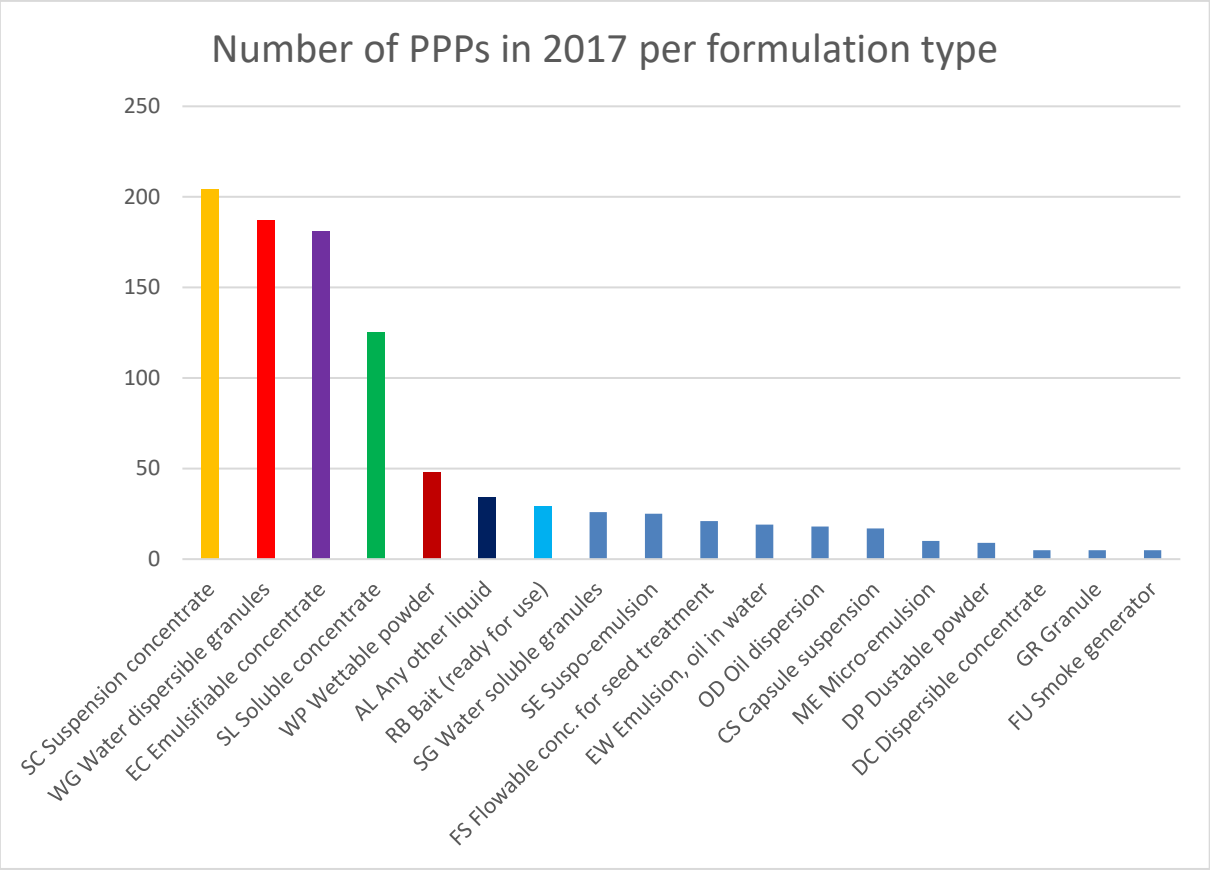


Figure 1: Number of plant protection products authorised in 2017 by formulation type. Only formulation types with at least five products are shown.

In 2017 approx. 1,000 different plant protection products were authorised in Switzerland. The formulation types SC, WG, EC, SL and WP account for the largest number of authorised products. Special formulation types for which only one to four products were registered are not shown on this graph.

The same analysis was also carried out for the year 2015 for those products that were commercially available according to the sales figures.

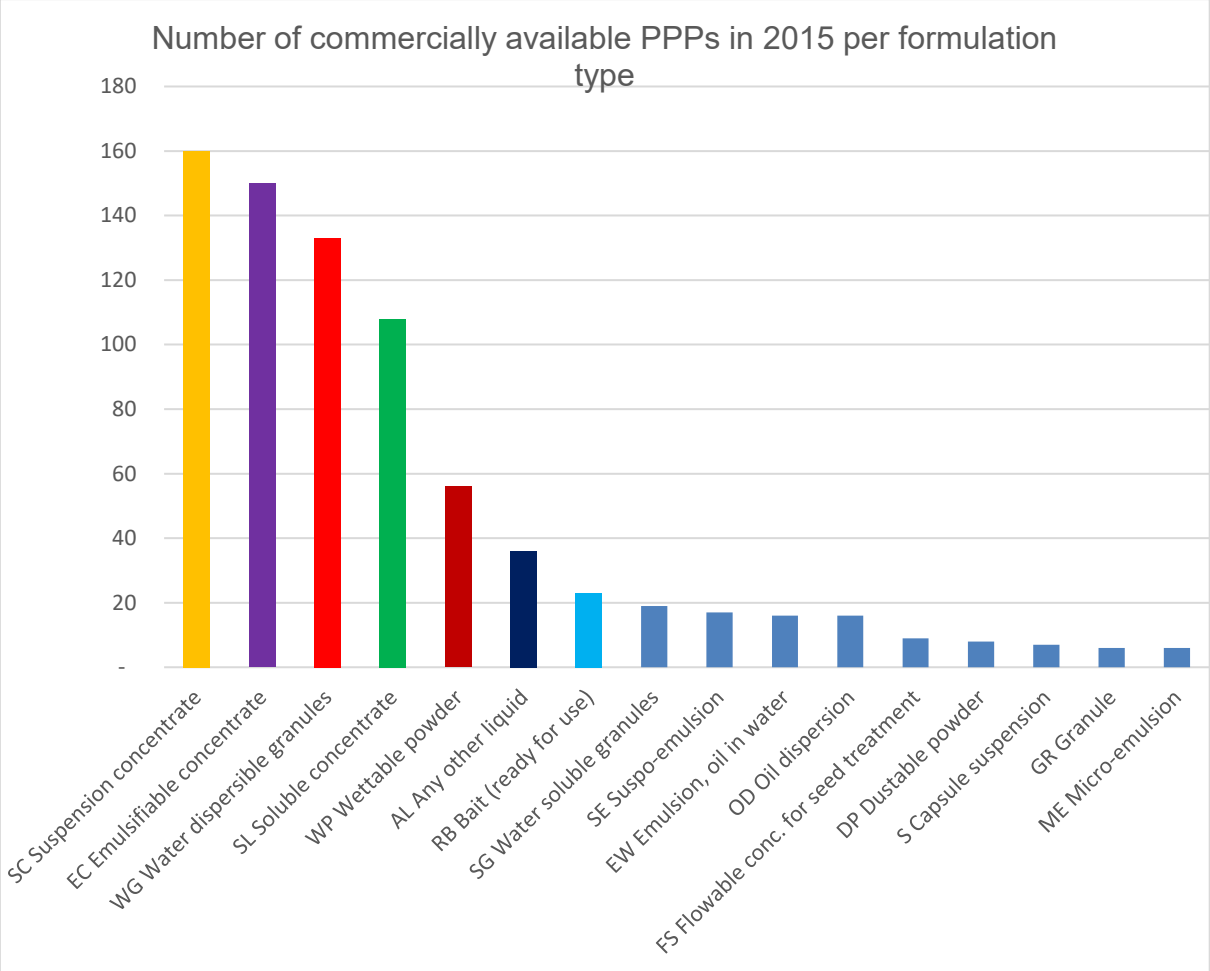


Figure 2: Number of commercially available plant protection products per formulation type in 2015. Only formulation types with at least five products are shown.

In 2015 approx. 800 different plant protection products authorised in Switzerland were commercially available. Some products were sold under several trade names since sales permits existed for these products. There is also a large number of PPPs which, although authorised, have not, or not yet, been placed on the market by the respective companies. Therefore, the absolute number here is smaller than that in the analysis for 2017.

The distribution pattern is similar to that in Figure 1, apart from the fact that the formulation types EC and WG have swapped places 2 and 3. Since no major differences are apparent, it can be assumed that the sales figures for 2015 are also representative of the situation in 2017. The actual quantities of PPPs can be analysed on the basis of the available sales figures. These are shown in Figure 3.

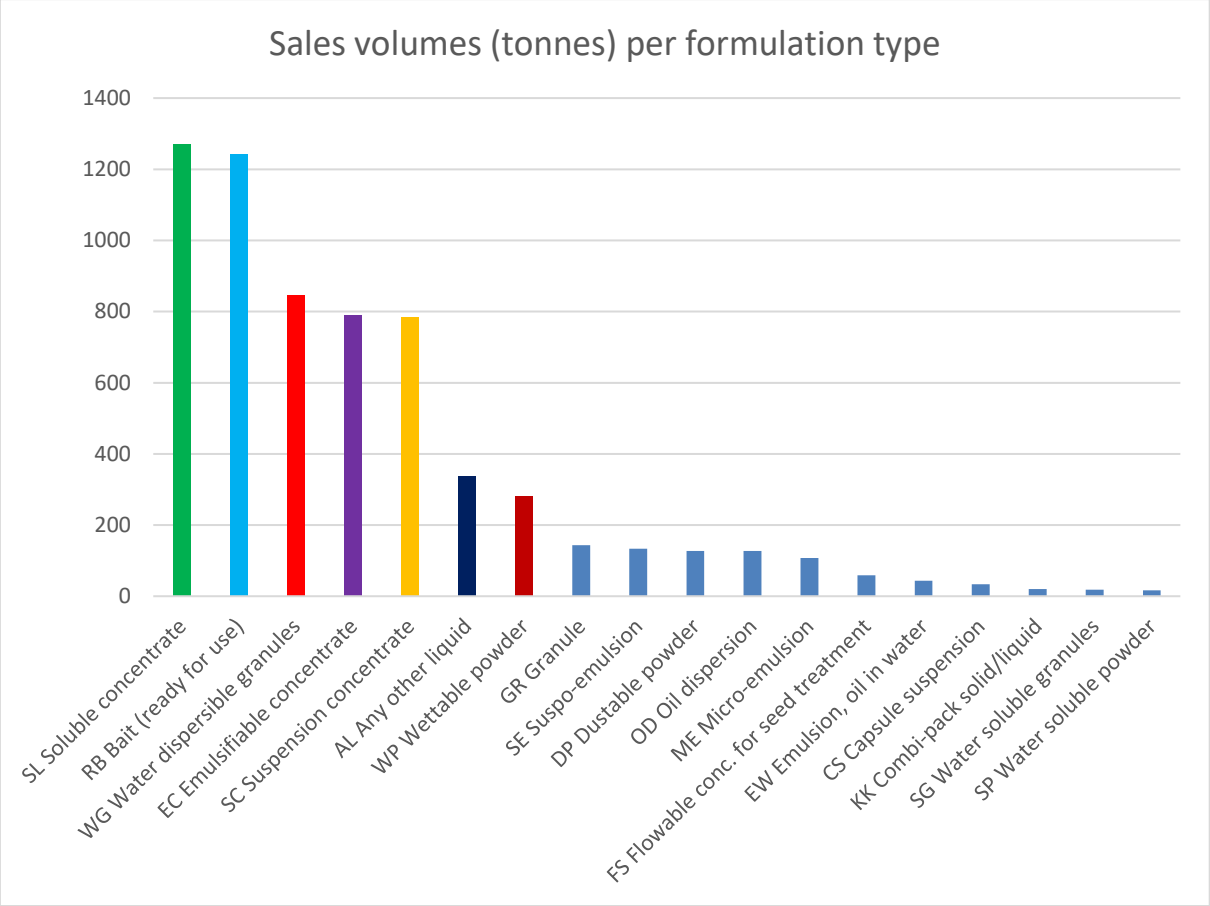


Figure 3: Sales volumes of plant protection products per formulation type in 2015. Only those formulation types for which more than 10 tonnes of products were sold are shown.

The order has changed significantly compared to Figure 2. Large quantities of baits (ready for use) (RB), any other liquids (AL) and the soluble concentrates (SL) are sold.

Note that baits (ready for use) are almost exclusively slug pellets. In addition to the active substance, these mainly consist of flour (the percentage of flour in the formulation can be as high as 97 %). Therefore they only contain very small quantities of other co-formulants (typically less than 3 % of the formulation) and are not important for the remit of this initial study. Moreover, slug pellets do not normally come into contact with the crop.

Any other liquids (AL) are used primarily as domestic garden products and do not need to be diluted before they are applied to crops. Since they contain a lot of water (up to 99.9 %), but only very small amounts of active substance (normally << 1 %) and very small amounts of co-formulants, they are not included in this study.

This leaves the five formulation types SL, WG, EC, SC and WP, which are relevant for the subject of co-formulants and co-formulant components and which are also sold in fairly large quantities (> 280 t per year).

4.2 Composition of frequently used formulation types

The various formulation types of plant protection products contain widely differing quantities of active substances and co-formulants. Chemically, the co-formulants differ considerably and perform specific functions in the formulation. To provide a rough overview, an average composition is listed in this section for the five most common formulation types. This was determined on the basis of the sales volumes of 10 selected products and their compositions.
These are the liquid formulations SL (soluble concentrate) and SC (suspension concentrate), which are mostly water-based, followed by the solid formulations WG (water dispersible granules) and WP (wettable powder), and the solvent-based liquid formulation EC (emulsifiable concentrate). Plant protection products of these five formulation types must be diluted with water to produce a homogeneous spray mixture before they can be applied. The volume of water required for dilution in the individual case can be found on the permit and the label. Typically, approx. 1.5 kg to 6 kg of product is added to 1000 litres of water, which means that the concentration of the products in the mixture is usually less than 1%.

Formulation type	Substance, substance group	Proportion (%)
SL Soluble concentrate	Active substance Water (or other solvents) Surfactant (wetting agent) Poss. foam inhibitor, preservative, frost protection	45 % 50 % **4 %**
SC Suspension concentrate	Active substance Water Surfactant (dispersant) Frost protectant Poss. preservative, foam inhibitor, thickening agent	40 % 50 % **5 %** **4 %**
WG Water dispersible granules	Active substance Surfactant (dispersant, lignosulphonate) Carrier (stone flour) Surfactant (wetting agent) Poss. foam inhibitor, anti-caking agent	60 % **20 %** **10 %** **5 %**
WP Wettable powder	Active substance Surfactant (dispersant) Carrier (stone flour) Poss. foam inhibitor, wetting agent	85 % **7 %** **6 %**
EC Emulsifiable concentrate*	Active substance Solvent Surfactant (emulsifiers) Poss. wetting agent, stabiliser, synergist	15 % **70 %** **14 %**

* Emulsifiable concentrates with oils, fatty acids or fatty acid methyl esters as the active substance are not considered here

Although the average composition presented here is a rough generalisation, it is useful to have an overview of the co-formulant groups and their proportions. Individual plant protection products can vary considerably from the average composition shown here.

Because a risk assessment has already been conducted and the residues have already been regulated for the active substances in plant protection products in the authorisation procedure, and since no further attention needs to be paid to water, only those substance groups highlighted in blue are relevant for further analysis.

In respect of the co-formulants, the emulsifiable concentrates stand out among these five formulation types because, on average, these contain a high percentage of solvents (70 %) as well as a substantial proportion of surfactants (14%). The water dispersible granules are also noticable because their co-formulants account for 35 to 40 %. For the other three formulation types (SL, SC, WP) the average co-formulant percentage is less than 15 %, and even as low as 4 – 5 % for SL.

4.3 Quantities of individual co-formulants per formulation type

For each of the five chosen formulation types, approx. 10 products were selected based on their high sales volumes and authorised applications in fruit, berry or vegetable growing, i.e. they can potentially lead to residues.

The precise compositions of these selected products that are already known to the authorities from the authorisation procedure were used to calculate the individual co-formulant quantities, taking account of the sales volumes. These are stated separately in the following tables 2 to 6 for each of the five selected formulation types. The quantity of each co-formulant was also extrapolated to the total sales volume of the respective formulation type.

4.3.1 SL Soluble concentrate

Table 2: Co-formulant and active substance quantities in SL formulations for the selected products with extrapolation to all SL products sold

Co-formulant or active substance	Function	CAS no.	Tonnes	Extrapolation Tonnes all SLs
Active substances			166.28	557.03
Water	Solvent		195.48	654.86
1-Methoxy-2-propanol	Solvent	000107-98-2	4.71	15.79
Dimethyl sulphoxide	Solvent	67-68-5	0.02	0.08
N-methyl-2-pyrrolidone (NMP)	Solvent	872-50-4	0.02	0.08
Dodecanol	Solvent	000112-53-8	0.25	0.85
Propylene glycol	Frost protection	000057-55-6	2.17	7.26
Decyl octyl glucoside (oligomer)	Surfactant	068515-73-1	6.24	20.89
Tristyrylphenol ethoxylated sulphate, ammonium salt	Emulsifier	119432-41-6	0.002	0.01
Ether amine oxide, ethoxylated	Wetting agent	226563-63-9	1.57	5.25
Alkylbenzene sulphonate, TEA salt, n-C10-C13	Wetting agent	68411-31-4	0.21	0.72
Alcohols, C9-11, ethoxylated	Wetting agent	068439-46-3	1.07	3.60
Bis(2-hydroxyethyl)(coconut oil alkyl)amine	Surfactant/wetting agent	061791-31-9	0.07	0.24
2-methyl-isothiazolone, 5-chloro-2-methyl-isothiazolone	Preservation	002682-20-4; 026172-55-4	0.0003	0.001
Methylparaben	Preservation	5026-62-0	0.01	0.03
Polydimethylsiloxane	Foam inhibitor	63148-62-9	0.06	0.22
Pectin, hydrolysed	Stabiliser	9046-38-2	0.04	0.14
Xanthan gum	Thickener	011138-66-2	0.04	0.14
Sodium chloride	Salt	7647-14-5	0.07	0.23
Liquitint colourant	Colour		0.003	0.01
Glycerol		56-81-5	0.42	1.40
Potassium sorbate		024634-61-5	0.01	0.03

11 SL products were analysed. The sales volumes of these 11 products are equivalent to 30 % of the total SL sales volume.

The proportion of active substances in the formulations of the 11 analysed products is 44 % by weight of the sold quantity, while water accounts for 52 %. Therefore, the other co-formulants in the SLs only account for 4.5 %.

4.3.2 SC Suspension concentrate

Table 5: Co-formulant and active substance quantities in SC formulations for the selected products with extrapolation to all SC products sold

Co-formulant or active substance	Function	CAS no.	Tonnes	Extrapolation Tonnes all SCs
Active substances			58.49	307.68
Water	Solvent		71.20	374.53
Ethylene glycol	Frost protection	107-21-1	3.31	17.40
Propylene glycol	Frost protection	57-55-6	3.82	20.11
Tristyrylphenol ethox phosphate	Dispersant	105362-40-1	1.81	9.51
Acrylic graft copolymer	Dispersant	119724-54-8	0.27	1.41
Copolymer butanol PO/ EO	Dispersant	9038-95-3	0.27	1.40
Block polymer propylene oxide/ ethylene oxide	Dispersant	106392-12-5; 9003-11-6	0.32	1.69
Tristyrylphenol ethoxylated	Dispersant	99734-09-5	0.90	4.75
Tristyrylphenol ethox. phosphate, K	Dispersant	163436-84-8	0.34	1.77
Lignosulphonic acid, sodium salt	Dispersant	8061-51-6	0.05	0.27
Alcohols C16-18, ethoxylated	Emulsifier	068439-49-6	0.62	3.26
Tristyrylphenol ethoxylated sulphate, ammonium	Emulsifier	119432-41-6	0.11	0.56
Sodium alkyl benzene sulphonate	Emulsifier		0.08	0.43
5-Chloro-2-methyl-isothiazolone	Preservation	055965-84-9	0.004	0.02
1,2-Benzisothiazolin-3-one	Preservation	002634-33-5	0.06	0.31
1,3,5-Triazine-1,3,5(2H,4H,6H)-triethanol	Preservation	004719-04-4	0.03	0.17
2-Hydroxymethylaminoethanol	Preservation	34375-28-5	0.01	0.04
Copolymer acrylate-isopropyl acetate	Wetting agent	052880-57-6	0.18	0.96
Polydimethylsiloxane	Foam inhibitor	63148-62-9	0.33	1.71
Xanthan gum	Thickener	011138-66-2	0.33	1.71
Magnesium aluminium silicate	Thickener	1302-78-9	0.55	2.91
Silicate (Na Al)	Thickener	001344-00-9	1.94	10.22
Attapulgite, Al Mg Fe SiO2	Thickener	12174-11-7	0.08	0.43
Formaldehyde		50-00-0	0.07	0.34
Citric acid		77-92-9	0.04	0.21
Copolymer maleate / acrylate		52255-49-9	0.17	0.88
Urea		000057-13-6	0.62	3.26

11 SC products were analysed. The sales volumes of these 11 products are equivalent to 19 % of the total SC sales volume.

The proportion of active substances in the formulations of the 11 evaluated products is 40 % by weight of the sold quantity, while water accounts for 49 %. Therefore, the other co-formulants in the SCs only account for 11 %.

4.3.3 WG Water dispersible granules

Table 3: Co-formulant and active substance quantities in WG formulations for the selected products with extrapolation to all WG products sold

Co-formulant or active substance	Function	CAS no.	Tonnes	Extrapolation Tonnes all WGs
Active substances			237.84	601.73
Lignosulphonate Na, Ca, NH_4	Dispersant	008061-53-8	54.51	137.91
Lignosulphonate ethoxylated, Na	Dispersant	068611-14-3	0.07	0.19
Tristyrylphenol ethoxylated	Dispersant	099734-09-5	2.14	5.41
Sodium alkyl naphthalene sulphonate	Wetting agent	105864-15-1	0.43	1.08
Sodium di(2-ethylhexyl) sulphosuccinate	Wetting agent	000577-11-7	0.43	1.08
Sodium dodecyl sulphate	Wetting agent	151-21-3	0.06	0.14
Sodium diisobutyl naphthalene sulphonate	Wetting agent	25417-20-3	0.10	0.25
Butylated polyvinylpyrrolidone	Surfactant	026160-96-3	0.02	0.05
Kaolin	Carrier	001332-58-7	10.67	26.99
Kaolinite	Carrier	001318-74-7	8.90	22.52
Silicate	Carrier		1.35	3.42
Urea-formaldehyde polymer	Carrier	009011-05-6	1.46	3.70
Phonolite, vulcanite	Anti-caking agent		1.35	3.43
Polydimethylsiloxane	Foam inhibitor	063148-62-9	0.91	2.30
Water			2.26	5.71
Sodium/calcium sulphate			2.93	7.41
Ammonium bicarbonate		001066-33-7	0.02	0.05
Corn starch			0.88	2.23

10 WG products were analysed. The sales volumes of these 10 products are equivalent to 40 % of the total WG sales volume.

The proportion of active substances in the formulations of the 10 analysed products is 73 % by weight of the sold quantity; the co-formulant share is 27 %, of which 17 % is attributable to lignosulphonate, 8 % to stone flours/carriers and just 2.7 % to the other co-formulants.

4.3.4 WP Wettable powder

Table 6: Co-formulant and active substance quantities in WP formulations for the selected products with extrapolation to all WP products sold

Co-formulant or active substance	Function	CAS no.	Tonnes	Extrapolation Tonnes all WPs
Active substances			163.04	234.78
Calcium lignosulphonate (ammonium)	Dispersant	008061-52-7	13.11	18.87
Naphthalenesulfonic acid, polymer with formaldehyde, sodium salt	Dispersant	9084-06-4	0.28	0.41
Diisopropylnaphthalenesulphonic acid, Na	Dispersant	001322-93-6	0.09	0.13
Vinyl carboxylate acetate copolymer, sodium	Surfactant	67906-92-7	0.004	0.01
Polyvinyl alcohol	Surfactant	25213-24-5	0.33	0.48
Sodium dodecylbenzene sulphonate	Wetting agent	25155-30-0	0.04	0.06
Polydimethylsiloxane	Foam inhibitor	63148-62-9	0.06	0.09
Silica (SiO_2)	Filler	061790-53-2	2.02	2.90
Kaolin	Filler	001332-58-7	7.13	10.27
Calcium carbonate	Filler	471-34-1	0.12	0.17
Sodium bicarbonate, carbonate, sulphate	Filler		2.88	4.14
Magnesium oxide	Filler	1309-48-4	0.003	0.004
Brilliant blue	Colourant	003844-45-9	0.003	0.004
Pigment blue 27	Colourant	025869-00-5	0.21	0.31
Water			1.12	1.61
Sucrose octaacetate		000126-14-7	0.01	0.01
Sorbitol		50-70-4	0.10	0.14
Hydroxyethyl cellulose		009004-62-0	0.33	0.48
Cell wall			1.76	2.54
Formic acid-silica		64-18-6	0.27	0.38
Tannins		001401-55-4	0.07	0.10
Saponins			0.04	0.05

9 WP products were analysed. The sales volumes of these 9 products are equivalent to 69 % of the total WP sales volume.

The proportion of active substances in the formulations of the 9 analysed products is 84 % by weight of the sold quantity; the co-formulant share is 16 %, of which 6.8 % is attributable to lignosulphonate, 6.3 % to stone flours/carriers and just 2.4 % to the other co-formulants.

4.3.5 EC Emulsifiable concentrate

According to the sales figures, 800 tonnes of emulsifiable concentrates were sold in total. Of these 800 tonnes, approx. 300 tonnes were attributable to plant protection products with oils, fats or fatty acid methyl esters as the active substance. This is a special group of emulsifiable concentrates with compositions that do not correspond to the usual composition of ECs. These products are not considered in the analysis because they contain very small amounts of co-formulants (high active substance contents of up to 100 %).

Table 4: Co-formulant and active substance quantities in EC formulations for the selected products with extrapolation to all EC products sold

Co-formulant or active substance	Function	CAS no.	Tonnes	Extrapolation Tonnes all ECs
Active substance			17.60	71.50
Calcium dodecylbenzene sulphonate	Emulsifier, anionic	26264-06-2	3.35	13.60
Tristyrylphenol sulphate ethoxylated, ammonium	Emulsifier, anionic	119432-41-6	0.19	0.76
Alcohols C16-C18 ethoxylated	Emulsifier, neutr.	68920-66-1	2.88	11.71
Alcohols C12-C15 ethoxylated/propoxylated	Emulsifier, neutr.	068551-13-3	0.64	2.59
Oleate ethoxylated	Emulsifier, neutr.	9004-96-0	1.61	6.54
Sorbitan trioleate ethoxylated	Emulsifier, neutr.	9005-70-3	2.51	10.22
Tristyrylphenol ethoxylated	Emulsifier, neutr.	99734-09-5	0.13	0.53
Butanol	Solvent	000071-36-3	0.30	1.21
Cyclohexanone	Solvent	108-94-1	5.08	20.63
Dipropylene glycol methyl ether	Solvent	034590-94-8	33.64	136.77
Dimethyl sulphoxide	Solvent	67-68-5	1.56	6.35
Isobutyl alcohol	Solvent	78-83-1	1.49	6.07
Methyl octanoate	Solvent	111-11-5	2.11	8.57
N,N-Dimethyldecanamide	Solvent	14433-76-2	2.21	8.98
Octanol	Solvent	203-917-6	1.41	5.75
Oleyl alcohol	Solvent	143-28-2	2.11	8.60
Rapeseed oil	Solvent	008002-13-9	14.74	59.93
Solvent naphtha	Solvent	64742-94-5	13.06	53.10
Xylene	Solvent	001330-20-7	4.91	19.97
Castor oil ethoxylated	Wetting agent	61791-12-6	6.39	25.97
Nonyl aldehyde	Stabiliser	124-19-6	0.04	0.16
Sesame oil	Synergist	8008-74-0	2.51	10.22
Lubricating oils C17 to C32	Carrier material	101316-70-5	2.60	10.58

10 EC products were analysed. The sales volumes of these 10 products are equivalent to 25 % of the total EC sales volume of 500 tonnes.

The proportion of active substances in the formulations of the 10 analysed products is 14 % by weight of the sold quantity, which means that the other co-formulants in the ECs still account for 86 %.

4.3.6 Co-formulants for formulation types SL, WG, EC, SC, WP

The active substance and co-formulant quantities listed in tables 2 to 6 were merged to provide a general overview, and the proportions of the respective co-formulants were calculated. The individual co-formulants were sorted by quantity (according to the extrapolation). This produces a good overview showing which co-formulants are of greater relevance relative to their sales volumes and which are only used in small amounts. In order to obtain a better overview, the co-formulants were combined into groups insofar as possible. Nevertheless, this still left approx. 90 different co-formulants/co-formulant groups in Table 7.

Table 7: Co-formulant and active substance quantities in SL, WG, EC, SC and WP formulations

Co-formulant or active substance	Function	CAS no.	Tonnes Extrapolation	Proportion (%)
Active substances			1772.72	48.7%
Water			1036.70	28.5%
Lignosulphonate Na, Ca, NH4	Dispersant	008061-51-6	157.06	4.3%
Dipropylene glycol methyl ether	Solvent	034590-94-8	136.77	3.8%
Rapeseed oil	Solvent	008002-13-9	59.93	1.6%
Kaolin	Carrier	001332-58-7	59.78	1.6%
Solvent naphtha ND	Solvent	64742-94-5	53.10	1.5%
Propylene glycol	Frost protection	000057-55-6	27.37	0.8%
Castor oil ethox.	Wetting agent	61791-12-6	25.97	0.7%
Alcohols C9-18, ethox. propox.	Emulsifier, neutr.	068551-13-3	21.15	0.6%
Decyl octyl glucoside (oligomer)	Surfactant	068515-73-1	20.89	0.6%
Cyclohexanone	Solvent	108-94-1	20.63	0.6%
Xylene	Solvent	001330-20-7	19.97	0.5%
Ethylene glycol	Frost protection	107-21-1	17.40	0.5%
1-Methoxy-2-propanol	Solvent	000107-98-2	15.79	0.4%
Silicate (Na Al)	Thickener	001344-00-9	13.63	0.4%
Alkyl benzene sulphonate, calcium	Emulsifier, anionic	26264-06-2	13.60	0.4%
Tristyrylphenol ethoxylated	Dispersant	099734-09-5	10.69	0.3%
Lubricating oils C17 to C32	Carrier material	101316-70-5	10.58	0.3%
Sesame oil	Synergist	8008-74-0	10.22	0.3%
Sorbitan trioleate ethoxy.	Emulsifier, neutr.	9005-70-3	10.22	0.3%
Tristyrylphenol ethox phosphate	Dispersant	105362-40-1	9.51	0.3%
N,N-Dimethyldecanamide	Solvent	14433-76-2	8.98	0.2%
Oleyl alcohol	Solvent	143-28-2	8.60	0.2%
Methyl octanoate	Solvent	111-11-5	8.57	0.2%
Sulphate Na/Ca			7.41	0.2%
Oleate ethox.	Emulsifier, neutr.	9004-96-0	6.54	0.2%
Dimethyl sulphoxide	Solvent	67-68-5	6.43	0.2%
Isobutyl alcohol	Solvent	78-83-1	6.07	0.2%
Octanol	Solvent	203-917-6	5.75	0.2%
Ether amine oxide, ethoxylated	Wetting agent	226563-63-9	5.25	0.1%
Polydimethylsiloxane	Foam inhibitor	63148-62-9	4.31	0.1%
Sodium bicarbonate, carbonate, sulphate	Filler		4.14	0.1%
Urea-formaldehyde polymer	Carrier	009011-05-6	3.70	0.1%
Phonolite, vulcanite	Anti-caking		3.43	0.1%
Urea		000057-13-6	3.26	0.1%
Magnesium aluminium silicate	Thickener	1302-78-9	2.91	0.1%
Silica (SiO_2)	Filler	061790-53-2	2.90	0.1%
Cell wall			2.54	0.1%
Corn starch			2.23	0.1%
Xanthan gum	Thickener	011138-66-2	1.85	0.1%

Co-formulant or active substance	Function	CAS no.	Tonnes Extrapolation	Proportion (%)
Tristyrylphenol ethox. phosphate, K	Dispersant	163436-84-8	1.77	0.05%
Block polymer PO/EO	Dispersant	106392-12-5; 9003-11-6	1.69	0.05%
Acrylic graft copolymer	Dispersant	119724-54-8	1.41	0.04%
Glycerol		56-81-5	1.40	0.04%
Copolymer butanol PO/EO	Dispersant	9038-95-3	1.40	0.04%
Tristyrylphenol ethox sulphate	Emulsifier	119432-41-6	1.33	0.04%
Butanol	Solvent	000071-36-3	1.21	0.03%
Di(2-ethylhexyl) sulphosuccinate	Wetting agent	000577-11-7	1.08	0.03%
Sodium alkyl naphthalene sulphonate	Wetting agent	105864-15-1	1.08	0.03%
Polymer acrylate-isopropyl acetate	Wetting agent	052880-57-6	0.96	0.03%
Copolymer maleate / acrylate		52255-49-9	0.88	0.02%
Dodecanol	Solvent	000112-53-8	0.85	0.02%
Alkylbenzene sulphonate, TEA salt	Wetting agent	68411-31-4	0.72	0.02%
Hydroxyethyl cellulose		009004-62-0	0.48	0.01%
Polyvinyl alcohol		25213-24-5	0.48	0.01%
Sodium alkyl benzene sulphonate	Emulsifier, anionic		0.43	0.01%
Al Mg Fe SiO2, attapulgite	Thickener	12174-11-7	0.43	0.01%
Poly alkyl naphthalene sulphonate	Dispersant	9084-06-4	0.41	0.01%
Formic acid-silica		64-18-6	0.38	0.01%
Formaldehyde		50-00-0	0.34	0.01%
1,2-Benzisothiazolin-3-one	Preservation	002634-33-5	0.31	0.01%
Pigment blue 27	Colourant	025869-00-5	0.31	0.01%
Sodium diisobutylnaphthalene sulphonate	Wetting agent	25417-20-3	0.25	0.01%
Bis(2-hydroxyethyl)(coconut oil alkyl)amine	Surfactant/wetting agent	061791-31-9	0.24	0.01%
Sodium chloride	Salt	7647-14-5	0.23	0.01%
Citric acid		77-92-9	0.21	0.01%
Lignosulphonate ethoxylated, Na	Dispersant	068611-14-3	0.19	0.01%
1,3,5-Triazine-1,3,5(2H,4H,6H)-triethanol	Preservation	004719-04-4	0.17	0.005%
Calcium carbonate	Filler	471-34-1	0.17	0.005%
Nonyl aldehyde	Stabiliser	124-19-6	0.16	0.004%
Pectin, hydrolysed	Stabiliser	9046-38-2	0.14	0.004%
Sodium dodecyl sulphate	Wetting agent	151-21-3	0.14	0.004%
Sorbitol		50-70-4	0.14	0.004%
Diisopropylnaphthalenesulphonic acid	Dispersant	001322-93-6	0.13	0.004%
Tannins		001401-55-4	0.10	0.003%
N-methyl-2-pyrrolidone (NMP)	Solvent	872-50-4	0.076	0.002%

Co-formulant or active substance	Function	CAS no.	Tonnes Extrapolation	Proportion (%)
Sodium dodecylbenzene sulphonate	Wetting agent	25155-30-0	0.064	0.002%
Saponins			0.051	0.001%
Ammonium bicarbonate		001066-33-7	0.051	0.001%
Butylated polyvinylpyrrolidone		026160-96-3	0.046	0.001%
2-Hydroxymethylaminoethanol	Preservation	34375-28-5	0.041	0.001%
Potassium sorbate		024634-61-5	0.028	0.001%
Methylparaben	Preservation	5026-62-0	0.028	0.001%
5-Chloro-2-methyl-isothiazolone	Preservation	055965-84-9	0.021	0.001%
Liquitint colourant	Colour		0.0088	0.0002%
Sucrose octaacetate		000126-14-7	0.0077	0.0002%
Polyvinyl carboxylate acetate		67906-92-7	0.0062	0.0002%
Magnesium oxide		1309-48-4	0.0040	0.0001%
Brilliant blue	Colourant	003844-45-9	0.0038	0.0001%
2-methyl-isothiazolone; 5-chloro-2-methyl-isothiazolone	Preservation	002682-20-4; 026172-55-4	0.0010	0.00003%
Total			**3640.63**	**100.00%**

In addition to the five formulation types used in the analysis, a small number of other formulation types also potentially involve residues when applied to crops (in the spray mixture). In relation to the total quantity of co-formulants however, these play a minor role.

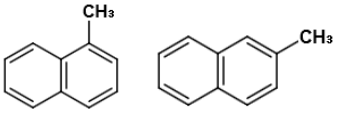
Surprisingly, only five co-formulants account for more than 1 % of the quantity of PPPs sold, while 38 still account for at least 0.1 %. However, most co-formulants are used in smaller quantities (maximum of 0.05 % of the quantity sold).

The co-formulants rapeseed oil, kaolin, silicate (sodium or aluminium silicate), sesame oil, magnesium aluminium silicate and silica listed on the first page of Table 7 are either already authorised as active substances according to Swiss PlantPPO[1], Annex 1, or similar active substances are authorised. Stone flours and various oils that are used both as active substances and as carrier materials or as solvents, respectively, have already undergone a risk analysis during the authorisation process.

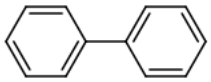
4.4 Physical and chemical properties of the selected co-formulants

For some of the selected co-formulants listed in the upper part of Table 7, various physical and chemical properties from the safety data sheets (section 9) were compiled. The safety data sheets used were either submitted during the authorisation process or are freely available online. The information varies in terms of quality and completeness, and are only intended to serve as initial pointers; subsequent investigations will need to research and check the plausibility of the substance parameters in greater detail.

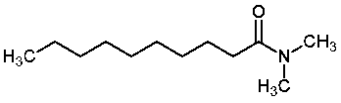
4.4.1 Solvent naphtha

Solvesso 200 ND; Hydrocarbons, C10-C13, aromatics, <1% naphthalene;		Hydrocarbons, aromatic, C10 to C13, e.g. 
CAS no.	64742-94-5	
Molecular weight (g/mol)	variable	
Boiling point/range	200°C - 310°C	
Vapour pressure	< 0.1 kPa (0.75 mm Hg) at 25°C	
Relative vapour density	> 1	
Relative density	0.951 – 1.051 g/cm³, at 15 °C	
Water solubility	negligible	

4.4.1.1 Biphenyl (co-formulant component of Solvent naphtha)

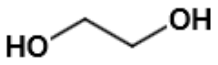
CAS no.	92-52-4	
Molecular weight (g/mol)	154.21	
Crystalline, light yellow		
pH	5.5	
Melting point/range:	68 - 70 °C	
Initial boiling point and boiling range	255 °C	
Vapour pressure	0.04 hPa at 20 °C (5.5 hPa at 100 °C)	
Relative density	0.992 g/cm3	
Water solubility	0.0075 g/l at 15 °C	
Partition coeff.: n-octanol/water log POW:	4.008 at 25 °C	

4.4.2 Dimethyldecanamide

CAS no.	14433-76-2	
Molecular weight (g/mol)	199.338	
Liquid, yellowish		
pH	10	
Melting point	-11 to -7 °C	
Initial boiling point and boiling range	291 °C at 1,013 hPa	
Vapour pressure	0.001 hPa at 20 °C	
Relative density	0.88 g/cm3 at 20 °C	
Water solubility	0.34 g/l at 20 °C	
Partition coeff.: n-octanol/water log POW:	3.44	

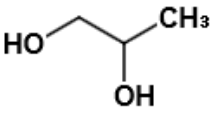
4.4.3 Ethylene glycol

CAS no.	107-21-1
Molecular weight (g/mol)	62.07
Liquid, colourless	
pH	7
Melting point	- 16 °C
Boiling point/range	188 °C
Vapour pressure	0.186 hPa
Relative vapour density	2.62
Relative density	1.11 g/cm³, at 20 °C
Water solubility at 20 °C	soluble



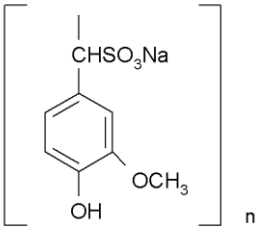
4.4.4 Propylene glycol

CAS no.	57-55-6
Molecular weight (g/mol)	76.09
Liquid, colourless	
pH	6 – 8
Melting point	- 60 °C
Boiling point/range	187 °C
Vapour pressure	0.11 hPa, at 20 °C
Relative vapour density	2.6
Relative density	1.03 g/cm³, at 20 °C
Water solubility at 20 °C	soluble
Partition coeff.: n-octanol/water log POW:	-0.9 to -1.07 (20 °C)



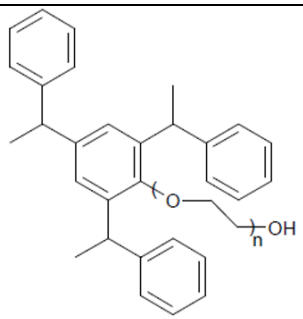
4.4.5 Lignosulphonate

CAS no.	8061-51-6
Molecular weight (g/mol)	variable
Fine powder, light brown.	
pH:	8
Melting point:	>130° , degradation.
Density:	500 kg/m³
Water solubility:	good, approx. 600 g/L.



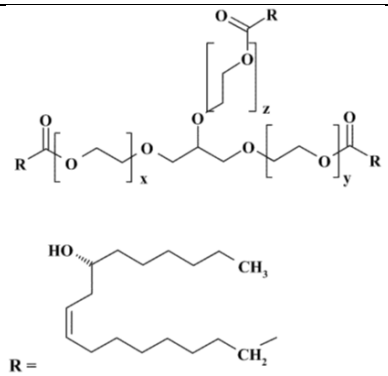
4.4.6 Tristyrylphenol ethoxylate

CAS no.	99734-09-5
Molecular formula	C30H30O-(C2H4O)n
Molecular weight (g/mol)	variable
Solid, yellow	
pH	9 – 11 (50 g/L)
Solidification point	55 °C (initial solidification)
Relative density	1.085 g/cm³, at 60 °C
Water solubility at 50 °C	soluble



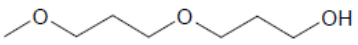
4.4.7 Castor oil ethoxylated

Castor oil, ethoxylated	
CAS no.	61791-12-6
Molecular weight (g/mol)	variable
Yellow wax	
pH	5 - 7
Melting point	22 – 26 °C
Relative density	1.04 g/cm³, at 50 °C
Water solubility at 20 °C	soluble



4.4.8 Dipropylene glycol methyl ether

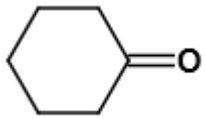
1(or 2)-(2-methoxymethylethoxy)-propanol	
CAS no.	34590-94-8
Molecular weight (g/mol)	148.2
Liquid, colourless	
pH	6 – 7, at 200 g/l, 20 °C
Melting point,	< -50 °C
Boiling point/range	184 °C, at 1.013 hPa
Vapour pressure	0.75 hPa, at 25 °C
Relative vapour density	5.14
Relative density	0.95 g/cm³, at 20 °C
Water solubility at 20 °C	soluble
Partition coeff.: n-octanol/water log POW:	< 0.001 (25 °C)



and other isomers

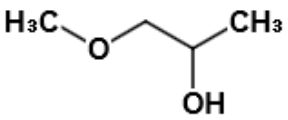
4.4.9 Cyclohexanone

CAS no.	108-94-1
Molecular weight (g/mol)	98.15
clear, liquid, colourless	
Melting point/freezing point:	-47 °C
Initial boiling point and boiling range	155 °C
Vapour pressure	4.5 hPa at 20 °C, 13.3 hPa at 38.7 °C
Vapour density	3.39 - (air = 1.0)
Relative density	0.947 g/cm3 at 25 °C
Water solubility	86 g/l at 20 °C
Partition coeff.: n-octanol/water log POW:	0.81



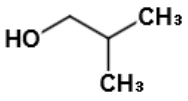
4.4.10 1-Methoxy-2-propanol

CAS no.	107-98-2
Molecular weight (g/mol)	90.12
liquid, clear, colourless	
Initial boiling point and boiling range	118 - 119 °C
Vapour pressure	14.5 hPa at 25 °C
Vapour density	3.11 - (air = 1.0)
Relative density	0.916 g/cm3 at 25 °C
Water solubility	fully miscible



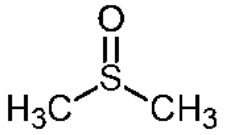
4.4.11 Isobutyl alcohol

CAS no.	78-83-1
Molecular weight (g/mol)	74.12
Appearance/form:	liquid
Melting point/freezing point:	-108 °C
Initial boiling point and boiling range	108 °C
Evaporation rate	0.6
Vapour pressure	8 hPa at 20 °C
Vapour density	2.55
Relative density	0.803 g/cm3 at 25 °C
Water solubility	70 g/l at 20 °C
Partition coeff.: n-octanol/water log POW:	1 at 25 °C



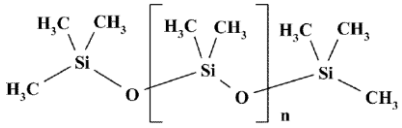
4.4.12 Dimethyl sulphoxide (DMSO)

CAS no.	67-68-5
Molecular weight (g/mol)	78.13
Appearance/form:	liquid, clear
Melting point/freezing point	18.4 °C
Initial boiling point and boiling range	189 °C at 1.013 hPa
Vapour pressure	0.55 hPa at 20 °C
Vapour density	2.70 - (air = 1.0)
Relative density	1.1 g/cm3
Water solubility	fully miscible
Partition coeff.: n-octanol/water log POW:	-2.03



4.4.13 Polydimethylsiloxane

CAS no.	63148-62-9
Molecular weight (g/mol)	variable
Appearance/form:	viscous, colourless
Melting point/freezing point	-54.99 °C
Initial boiling point and boiling range	> 140 °C at 0.003 hPa
Vapour pressure	< 7 hPa at 25 °C
Water solubility	slightly soluble



4.4.14 Influence of physical/chemical properties on residue formation

It is often difficult to predict the potential for residue formation on crops on the basis of the physical and chemical properties of the substances. Moreover, information on the physical and chemical properties is not readily obtainable for various co-formulants or co-formulant groups (e.g. the polymers).

Nevertheless, it can be assumed that substance properties such as volatility and water solubility influence residue formation. Thus, for example, solvents with a low boiling point tend to evaporate fairly quickly (e.g. dimethylsulphoxide, isobutanol, 1-methoxy-2-propanol, cyclohexanone, dipropylene glycol methyl ether…), whereas solvents with a higher boiling point (solvent naphtha, N,N-dimethyldecanamide) probably remain on the surface of the crop longer. Solvents with poor water solubility are not as greatly affected by rainfall as other co-formulants. The two co-formulants ethylene glycol and propylene glycol (frost protectant), many ethoxylated surfactants and lignosulphonate are readily soluble in water but not volatile. Their fate on the crop probably depends greatly on the weather (rain).

Biphenyl can be considered as a special case. Residues of biphenyl have been measured on crops in individual cases. Biphenyl used to be authorised as a pesticide active substance and is therefore often also included in investigations on PPP residues. Although it is no longer authorised as an active substance, low concentrations of biphenyl have been found in

parsley (0.01 to 0.12 mg/kg) and other kitchen herbs [3, 4]. It has been suggested that biphenyl reaches the crops via the air. But biphenyl is also a co-formulant component of solvent naphtha, which is used as a solvent in various plant protection products of the formulation type emulsifiable concentrate (EC). This could also be a possible source. However, the significance of plant protection products for biphenyl residues has not been investigated to date.

4.5 Co-formulants that occur in most products

The composition shows that only the foam inhibitor polydimethylsiloxane, from which a spray mixture is prepared, occurs in almost all plant protection products. However, the quantity of foam inhibitor in the individual products is very small. Although it is frequently used, Table 7 shows that polydimethylsiloxane plays a minor role in respect of quantity. The proportion is around 0.1 % polydimethylsiloxane in those plant protection products that were included in the analysis.

All other co-formulants or co-formulant components are used in just one or a small number of specific formulation types.

[3] EFSA, 2010. Modification of the existing MRLs for biphenyl in various commodities. EFSA Journal 8(10), 1855.
[4] FiBL Research Institute of Organic Agriculture, 2017, Report, Residues of biphenyl in herbs – Literature study on occurrence, potential causes and measures to avoid them, B. Speiser, R. Bickel, (in German) www.fibl.org/fileadmin/documents/de/schweiz/forschung/Biphenyl-2017-01-20.pdf

5 Summary and conclusion

Based on the analysis of 50 PPPs, the sales volumes of the individual co-formulants were estimated for Switzerland based on the precise composition of the formulations. In those formulation types included in the analysis, it emerged that almost half of the plant protection product consisted of active substance and a further 30 % of water. Accordingly, the total co-formulants accounted for over 20 % of the formulations on average, although the co-formulant quantities differed considerably depending on the formulation type of the plant protection product. Emulsifiable concentrates have on one hand the largest proportion of co-formulants because they contain large quantities of solvents and emulsifiers. On the other hand their active substance content is relatively low.

In this initial study, the numerous co-formulants in the plant protection products in Switzerland were grouped together and identified. Then, on the basis of the sales figures available for PPPs, the quantities of co-formulants sold in 2015 were estimated and ranked in a list. The five most important formulation types were analysed separately. This study therefore creates a good basis for selecting specific co-formulants and plant protection products for future investigations.

6 Appendix

6.1 Procedure

The analysis was based on the sales figures for plant protection products in 2015 and the Federal Office for Agriculture (FOAG) database of authorised plant protection products (GIAPP) and the compositions of selected PP products. Companies are required to submit the sales of plant protection products each year to the FOAG. No newer sales figures were available at the time this project started.

Sales volume by sales channel
The sales figures were initially analysed by the channels original authorisation, sales permit and parallel import, and their proportions in relation to the total volume sold were calculated.

Authorised PPPs in 2017
In order to be able to assess whether the situation in 2017 (project management) was comparable with that in 2015 (available sales figures), all of the products approved in Switzerland in September 2017 were selected. Next, products of the following types were ruled out of the study (deleted) since they do not usually contain co-formulants: living organisms, micro-organisms, fungi, larvae, ova, mycelia, pheromones, gases, insecticide nets.
The PPPs were then sorted by formulation type and analysed in order to produce Fig. 1 (Number of authorised products per formulation type).

Commercially available PP products in 2015
The products authorised in 2015 were selected from the GIAPP database. The selection of authorisations in 2015 was supplemented with the sales figures for 2015. As a result, the sales volume, formulation type, scientific name and the active substances and their concentrations could be assigned to the individual products. Then the sales figures for products with a sales permit were assigned to the original product.
Next, products of the following types were ruled out of the study (deleted) since they do not usually contain co-formulants: living organisms, micro-organisms, fungi, larvae, ova, mycelia, pheromones, gases, insecticide nets.
Parallel-imported products were also disregarded since the co-formulants contained in these products are not known.
The PPPs were then sorted by formulation type and analysed in order to produce Fig. 2 (Number of commercially available products per formulation type).

Sales volumes in 2015
The resulting table was also used to determine the sales volumes for each formulation type, which are presented in Figure 3.

Co-formulant quantities per formulation type
The subsequent analysis of co-formulant quantities only considered plant protection products of formulation types soluble concentrate (SL), suspension concentrate (SC), water dispersible granules (WG), wettable powder (WP) and emulsifiable concentrate (EC). These are the most common types and most relevant to the study remit. Taken together, these formulation types account for the largest proportion by far of the products sold (see section 4).

Supplementary remark: Of the emulsifiable concentrates (EC), a total of 800 tonnes of PPPs are available on the market. Of these, however, 300 tonnes of PPPs with active substances in the form of "oils", "fats", "fatty acid methyl esters" were not considered in subsequent analyses. These products only contain very small proportions of co-formulants because their active substance contents are almost 100 %. They were therefore considered as a special group of emulsifiable concentrates.

For each of the five chosen formulation types, approx. 10 products were selected based on their high sales volumes and authorised applications in fruit, berry or vegetable growing. For any residue formation, the use of these products in these crops is very important since they are only applied shortly before harvesting and the withholding period can be short. The fact that the edible plant parts are treated directly is also crucial. Moreover, the expected residues are higher with short withholding periods (time between the last treatment and harvesting). Based on these criteria, those products that might potentially lead to co-formulant residues were selected for the subsequent analyses (Expert Judgement). Most of these products are fungicides, insecticides and, in isolated cases, herbicides. The selected products account for a significant proportion of quantities sold (per formulation type) (see section 4).

For each of the selected products, the composition was taken from the confidential documents that are reviewed in connection with the authorisation procedure for plant protection products in Switzerland by Plant Protection Chemistry. These contain the exact percentages for each co-formulant in the formulation. Chemically similar co-formulants in the products were combined into groups. The groups were formed on the basis of an identical CAS number or an expert judgement. This step was essential in producing a clearer overview. As can be seen in Table 7, this still leaves approx. 90 different co-formulants/co-formulant groups.

For each of the selected products, the quantity of co-formulant in tonnes was calculated on the basis of the sales figures and the co-formulant percentage in the composition.

Extrapolation
The quantity of each co-formulant was then also extrapolated to the sales volumes of the selected products and the total sales volume of the respective formulation type.

Example: Extrapolation factor for water dispersible granules WG:
$Factor_{WG}$ = sales volume of all WG products / sales volumes of selected WG products
$Factor_{WG}$ = 2.5
This means that the selected WG products account for 40 % of the total amount sold.

Tables 2 to 6 present the calculated and extrapolated co-formulant quantities for each of the five selected formulation types.

Combination of extrapolated co-formulant quantities
Finally, the extrapolated co-formulant quantities for the five investigated formulation types were combined and sorted by quantity in a table (Table 7).

Average composition
To produce the overview of the average compositions of the formulation types presented in section 4.2, the co-formulant quantities in Tables 2 to 6 were sorted according to the most

important functions and totalled. The substance groups of active substance, water, surfactant (wetting agent, dispersant, emulsifier), frost protectant and carrier were quantitatively analysed. The functions of the other substance groups, which only occur in small quantities in the respective type, were listed without their quantities.

Physical/chemical properties
The physical and chemical properties of individual co-formulants were taken from the safety data sheets (section 9) that had been submitted during the authorisation process or that are freely available online.

6.2 Abbreviations and explanations

AL	Formulation type: Any other liquid
FOAG	Federal Office for Agriculture
CAS no.	Chemical Abstract Service number
EC	Formulation type: Emulsifiable concentrate
PPP	Plant protection product. A plant protection product consists of one or more active substances, possibly a synergist or a safener, and co-formulants.
PlantPPO	Plant Protection Products Ordinance
RB	Formulation type: Bait (ready for use)
SC	Formulation type: Suspension concentrate
SL	Formulation type: Soluble concentrate
Sales permit	An approved plant protection product can be placed on the market with a sales permit under the name of the holder of the sales permit and under a trade name that differs from that of the approved plant protection product. The sales permit only applies to the uses listed in the authorisation. The sales permit is granted if the authorisation holder has consented accordingly. The composition of the product on the sales permit is identical to that on the original authorisation.
Water	Although water is, by definition, also a co-formulant in a PPP, in this initial study water was listed separately and not counted as a co-formulant.
WG	Formulation type: Water dispersible granules
WP	Formulation type: Wettable powder