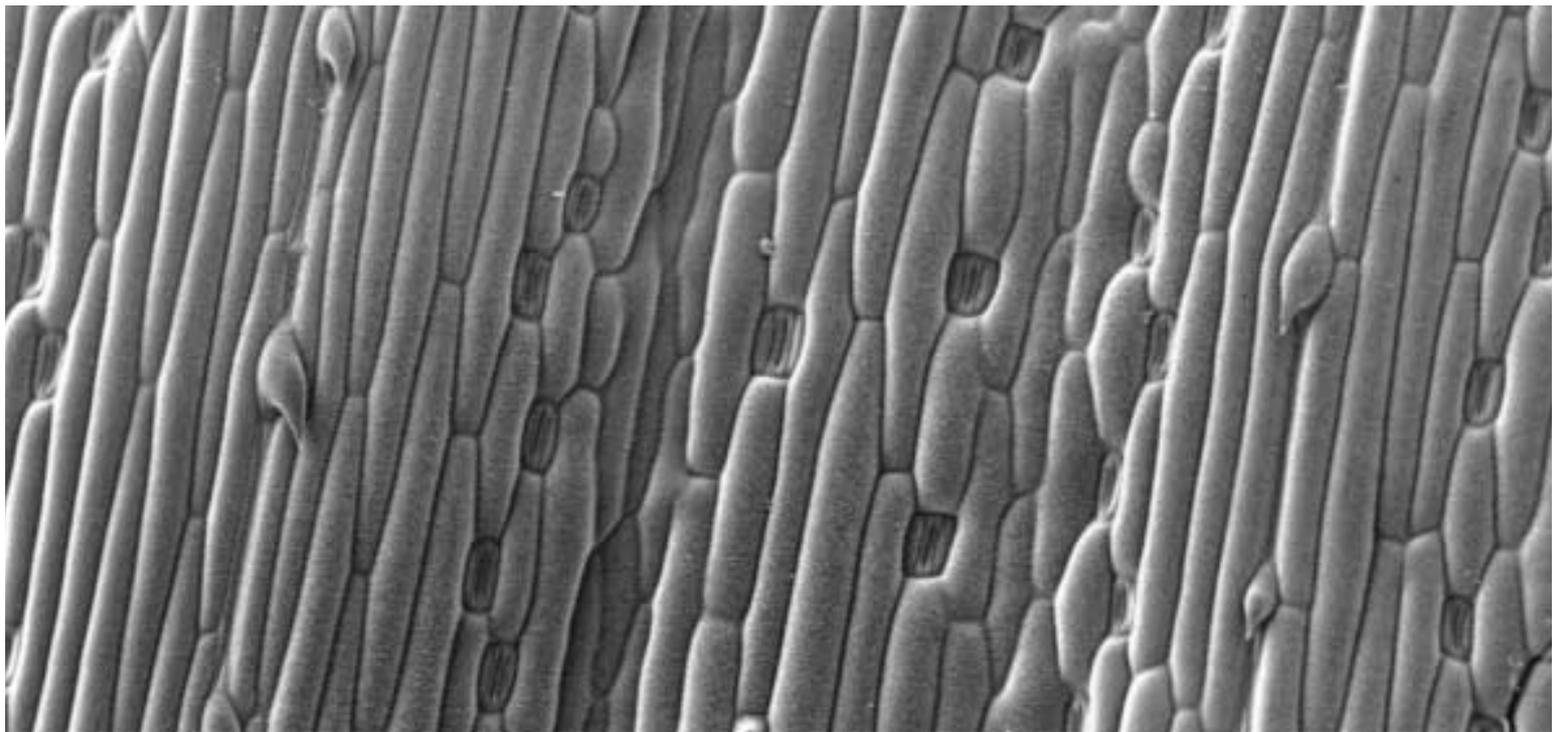




# Foliar absorption of crop protection agents: influence of cpa properties, formulation and plant species

A literature study for the Dutch Research Programme Pesticides and the Environment (DWK-359) theme B-2

Hans de Ruiter, Corné Kempenaar & Greet Blom







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Hans de Ruiter<sup>1</sup>, Corné Kempenaar<sup>2</sup> & Greet Blom<sup>2</sup>

<sup>1</sup> SURfaPLUS b.v., Costerweg 5, Wageningen, The Netherlands

<sup>2</sup> Plant Research International, P.O. Box 16, Wageningen, The Netherlands

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# 1. Introduction

After the application of cpa's (cpa is crop protection agent) over plants, volatilization of the cpa may occur both from the soil (Jansma & Linders, 1995; Smit *et al.*, 1997) and from the leaf surface (Jansma & Linders, 1995; Smit *et al.*, 1998). After landing of drops on the leaf surface, most but often not all water evaporates within 10-40 minutes depending on the climatic conditions. After this period a drop residue containing cpa, formulation constituents and often water remains on the leaf surface for hours and sometimes days. Evidence exists that the volatilization from the leaf surface of several cpa's can amount to several tens percents of the applied amount (Jansma & Linders, 1995; Smit *et al.*, 1997; Smit *et al.*, 1998; De Ruiter *et al.*, 2003). It can be argued that the micro-climate in the foliage, the vapour pressure of the cpa, its solubilization in the drop residue, the chemical stability of the cpa to UV-light and the sink-function of the plant determine the actual volatilization of a cpa from the leaf surface. The sink-function of the plant is influenced by the property of the (chloroform) soluble epicuticular (surface) and cuticular waxes to sorb cpa (Baker *et al.*, 1992; Bukovac *et al.*, 1990; Devine *et al.*, 1993; Schreiber & Schönherr, 1992) and the permeability of the leaf cuticle (Chamel, 1986; Schönherr & Baur, 1994). After passing across the leaf cuticle, cpa's enter the leaf tissue (Baker *et al.*, 1992; Stevens & Baker, 1987) and further transport in the plant may occur depending on the cpa involved. This sink-function reduces the availability of the cpa for volatilization from the leaf surface. The foliar penetration can be enhanced to a high extent by formulation constituents or adjuvants (Schönherr & Baur, 1994). Influence of the plant's sink function on the emission of cpa's has not been subject of a study as far we know. In this survey of the literature an effort is made to quantify the potential of the sink-function to reduce volatilization of cpa's from the leaf surface.

Factors influencing the foliar penetration of cpa's are: the lipophilicity (octanol/water partition coefficient) of the cpa (Baker *et al.*, 1992; Kerler & Schönherr, 1988), the melting point (Baker *et al.*, 1992), the properties of added formulation constituents or adjuvants (Stock *et al.*, 1993), the ion-strength in the drop residue (Schönherr & Baur, 1994) and the plant properties as mentioned above. The dependence on the plant properties makes that uptake of cpa's is species-dependent (Baker *et al.*, 1992; Price & Anderson, 1985; Stevens & Baker, 1987). In this study we use published foliar uptake kinetics of cpa's to calculate or to estimate the number of hours required for an uptake of 50 (FUP<sub>50</sub>) of the amount applied on the leaf surface. Thereby FUP is Foliar Uptake Period. The correlation of the FUP<sub>50</sub> values with the factors determining foliar penetration as mentioned above, will be investigated. The ultimate objective is to demonstrate relations that can be used to estimate the actual volatilization of cpa from the leaf surface. A second objective is to indicate whether this volatilization can be reduced by improving the foliar uptake enhancing property of the formulation constituents.



## **2. Development of database as provided in the Supplement**

Only those reports were selected where it was possible to calculate more or less accurately the  $FUP_{50}$ . In many studies the uptake curves were such that a  $FUP_{90}$  could not be calculated or estimated and therefore we left out any  $FUP_{90}$  value. In a small number of studies, only three time points (for instance 24, 48 and 72 h) were used to measure foliar uptake. Those studies were used for estimation of  $FUP_{50}$  if the uptake substantially increased in the periods between the time points.



### 3. Influence of cpa properties and adjuvants/formulations on foliar uptake

#### 3.1 Influence of lipophilicity and melting point on foliar uptake

To develop insight in the possible influence of lipophilicity ( $K_{o/w}$ ) and the melting point on the foliar uptake, we extracted data from the Supplement. Only those data were used where unformulated cpa was applied. Presence of adjuvant or formulation components have such a substantial influence on foliar uptake that these data were not included. Twenty-three observations were extracted and in 16 of these observations foliar uptake did not attain the 50% level. This outcome demonstrates that cpa's are absorbed poorly by the leaves without support of formulations and/or adjuvants. The number of remaining observations (Figure 1) is not sufficient for statistically sound conclusions. There is a strong indication that liquid and more lipophilic cpa's are absorbed better by the leaves. The 16 observations not attaining the 50% uptake level comprised one observation with a liquid cpa (2,4-D iso-ocyl ester), and the remaining seven data comprised four observations with liquid cpa (2,4-D iso-ocyl ester, 2,4-D butoxyethyl ester and sethoxydim). The relevance of a liquid state seems obvious because cpa molecules fixed in a solid structure are not well available for foliar uptake. The relevance of the melting point (Baker *et al.*, 1992) and that of the lipophilicity (Baker *et al.*, 1992; Kerler & Schönherr, 1988) have been mentioned previously.

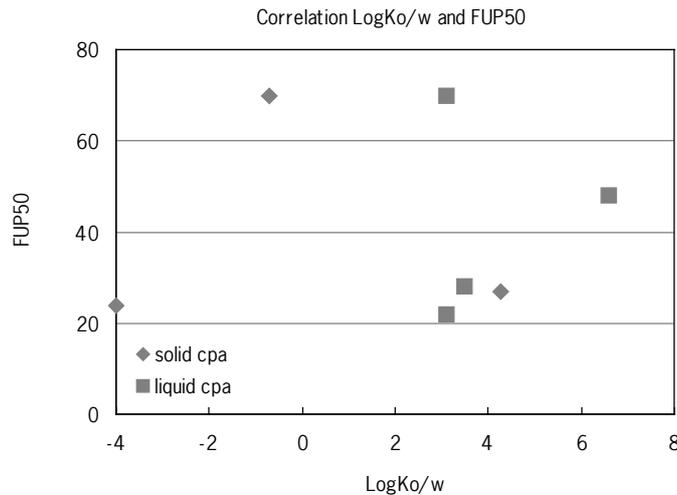


Figure 1. Influence of lipophilicity and physical state of cpa's on the  $FUP_{50}$ .

#### 3.2 Improvement of foliar uptake by adjuvants/formulations

Adjuvant effects on the  $FUP_{50}$  (Table 3.1) were extracted from the database (Supplement). The extracted data demonstrate an obvious improvement of foliar uptake by an appropriate formulation or inclusion of adjuvants. We have to comment that there are a few more reports demonstrating a positive effect of adjuvants on foliar uptake. In these studies, uptake did not attain the 50% level or uptake was measured at one point in time. In this study, we selected those data allowing us to calculate the  $FUP_{50}$  value. The adjuvant effect was also observed with commercially formulated cpa's (Table 1). This is not unknown for those familiar with formulations; commercial formulations are often compromises meeting several needs and are therefore not necessarily the most effective formulations for foliar uptake. Without extra adjuvant, an uptake level of 50% is not reached ( $n=21$ ) or the  $FUP_{50}$  is 36 h ( $n=9$ ;  $SE=8.9$ ).

With inclusion of extra adjuvant, the average FUP<sub>50</sub> is 15 h (n=28; SE=4). Thus adjuvants have the potency to get at least 50% of the intercepted cpa into the plant within 15 h. Due to the influence of cpa properties, plant properties and the agricultural conditions for a certain application, we recommend optimization in a case-by-case approach. The positive effect of adjuvants on foliar uptake has been recognized in previous reports (Stevens & Bukovac, 1987; Baker *et al.*, 1992; Stock *et al.*, 1993; Schönherr & Baur, 1994).

Table 3.1. Influence of adjuvants on the period required for 50% uptake of cpa's into plants.

cpa	Formulated (F) or Unformulated (U) <sup>1</sup>	FUP <sub>50</sub> cpa without extra adjuvant (h)	FUP <sub>50</sub> cpa plus most effective adjuvant (h)	Species <sup>2</sup>	Reference
2,4-D	F	>> <sup>3</sup>	6	pear (isolated cuticle)	Schönherr & Baur, 1994
2,4-D	F	>>	1	<i>Stephanotis</i> (isolated cuticle)	Schönherr & Baur, 1994
2,4-D butoxyethylester	F	14	2	oat	Gauvrit & Dormoy, 1995
2,4-D butoxyethylester	U	28	18	aspen poplar (detached leaves)	Sharma & Van den Born, 1970
2,4-D triethanolamine	U	>>	48	black nightshade	De Ruiter <i>et al.</i> , 1993
2,4-D triethanolamine	U	70	26	pea	De Ruiter <i>et al.</i> , 1993
2,4-D Na-salt	U	>>	6	wild oat	Holloway & Edgerton, 1992
2,4-D Na-salt	U	>>	19	field bean	Holloway & Edgerton, 1992
Bentazone	F	>>	8	bean	Liu & Zabkiewicz, 2001
Bentazone	F	>>	>>	velvetleaf	Levene & Owen, 1994
Diclobutrazol	F	>>	6	wheat	Holloway <i>et al.</i> , 1992
Difenzoquat	F	>>	14	wild oat	Clipsham, 1985
Ethirimol	F	>>	28	wheat	Holloway <i>et al.</i> , 1992
Diclofop-methyl	F	72	15	rye grass	Gauvrit & Dufour, 1990
Diclofop-methyl	F	>>	3	maize	Urvoy & Gauvrit, 1991
Fluazifop-butyl ester	F	>>	<24	oat	Nalewaja & Skrzypczak, 1986
Fluazifop-butyl ester	F	18	8	green foxtail	Grafstrom & Nalewaja, 1988

cpa	Formulated (F) or Unformulated (U) <sup>1</sup>	FUP <sub>50</sub> cpa without extra adjuvant (h)	FUP <sub>50</sub> cpa plus most effective adjuvant (h)	Species <sup>2</sup>	Reference
Gibberellic acid	U	>> <sup>3</sup>	108	sour cherry (detached leaves)	Knoche & Bukovac, 1992
Glyphosate	U	>>	4	winter wheat	De Ruiter <i>et al.</i> , 1994
Glyphosate	U	>>	8	oat	Van Toor <i>et al.</i> , 1994
Glyphosate	U	>>	26	field bean	Van Toor <i>et al.</i> , 1994
Haloxypop-methyl	F	>>	1	giant foxtail	Novereske <i>et al.</i> , 1992
Phenmedipham	U	>>	2	pea	Serre <i>et al.</i> , 1993
Phenmedipham	U	>>	21	cleavers	Serre <i>et al.</i> , 1993
Phenmedipham	U	>>	8	barley	Serre <i>et al.</i> , 1993
Quizalofop-ethyl	U	27	8	pea	Serre <i>et al.</i> , 1993
Quizalofop-ethyl	U	>>	7	barley	Serre <i>et al.</i> , 1993
Sethoxydim	U	70	4	johnsongrass	Scott <i>et al.</i> , 1998
Sethoxydim	U	22	3	soybean	Scott <i>et al.</i> , 1998
Sethoxydim	F	6	4	wild oat	Smith & Van den Born, 1992

<sup>1</sup> Formulated: commercial formulation or cpa plus an adjuvant which is used as background in all treatments. Unformulated is cpa alone.

<sup>2</sup> Whole plant study unless indicated otherwise.

<sup>3</sup> Uptake of 50% is not attained in the uptake period.



## 4. Influence of plant species on foliar uptake

Without taking into account the cpa and the experimental conditions, the  $FUP_{50}$  values with a  $FUP_{50} \leq 6$  h and those  $\geq 6$  h were listed (Table 4.1). There was a rather equal distribution of species over the low and high  $FUP_{50}$  values; 21 species with a low value and 25 species with a high value. Within the class of monocotyledons there were 12 species with a low  $FUP_{50}$  and 9 with a high  $FUP_{50}$ . Within the class of dicotyledons there were 9 species with a low  $FUP_{50}$  and 16 with a high  $FUP_{50}$ . It cannot be excluded that the difference between mono- and dicotyledons is accidental due to the method of data sampling. The outcome may also indicate that, within the dicotyledons, relatively more species have a leaf cuticle with a low permeability for formulated cpa's.

Table 4.1. List of plant species with a low ( $\leq 6$  h) and a high ( $\geq 6$  h)  $FUP_{50}$  using formulated cpa's.<sup>1,2,3</sup>

Species	$FUP_{50} \leq 6$ h	$FUP_{50} \geq 6$ h
Monocotyledons	giant foxtail, SETFA johnsongrass, SORHA (2x) maize oats, AVESA rye grass, LOLMU wheat (3x) wild oat, AVEFA (2x) yellow foxtail, SETLU	barley (2x) barnyardgrass, ECHCG giant foxtail, SETFA green foxtail, SETVI (2x) perennial ryegrass, LOLPE quackgrass, AGRRE wild oat, AVEFA
Dicotyledons	pea peanut pear <sup>4</sup> prickly sida, SIDSP sicklepod, CASOB soybean (2x) <i>Stephanotus</i> sunflower	aspen poplar bean black nightshade, SOLNI Canada thistle, CIRAR cleaver, GALAP common cocklebur, XANST field bean (2x) field bindweed, CONAR hemp dogbane, APCCA pea (2x) poplar sour cherry tomato <sup>3</sup> velvetleaf, ABUTH

<sup>1</sup> Based on references in Supplement plus Wilcut et al., 1989.

<sup>2</sup> The best formulation was selected for a certain cpa in a certain reference.

<sup>3</sup> The Bayer code of weeds is added to the common name in order to prevent misunderstanding with regard to the use of American common names.

<sup>4</sup> Studies with isolated cuticles.

Table 4.2. List of plant species regarding uptake of cpa and tested within one study.

Species	cpa	Reference
<i>Xanthium pennsylvanicum</i> (XANST) and Maize>orange and apple	10 formulated cpa's	Price & Anderson, 1985
Soybean>peanut, sicklepod and prickly sida>Florida beggarweed	chlorimuron	Wilcut <i>et al.</i> , 1990
Barley>green foxtail	glufosinate (formulated)	Mersey <i>et al.</i> , 1990
Ryegrass>wheat	diclofop-methyl EC without and with adjuvant	Gauvrit & Dufour, 1990
Rape and strawberry>sugar beet>maize	26 cpa's without and with adjuvant	Baker <i>et al.</i> , 1992
Wild oat>field bean	2,4-D Na-salt with adjuvant	Holloway & Edgerton, 1992
Wheat>field bean	methylglucose, phenylurea and cyanazine with adjuvant <sup>2</sup>	Stock <i>et al.</i> , 1993
Wheat>field bean	methylglucose with adjuvant	Stock <i>et al.</i> , 1993
Wheat>field bean	phenylurea with adjuvant	Stock <i>et al.</i> , 1993
Wheat>field bean	cyanazine with adjuvant	Stock <i>et al.</i> , 1993
Wheat<field bean	permethrin	Stock <i>et al.</i> , 1993
Pea>black nightshade	2,4-D TEA and 2,4-D iso-octyl ester without and with adjuvant	De Ruiter <i>et al.</i> , 1993
Pea>barley>cleavers	phenmedipham without and with adjuvant	Serre <i>et al.</i> , 1993
Oat>field bean	glyphosate without and with adjuvant	Van Toor <i>et al.</i> , 1994
Giant foxtail>barnyard grass>velvetleaf>common lambsquarters	glufosinate (formulated)	Steckel <i>et al.</i> , 1997
Johnsongrass>soybean	sethoxydim without and with adjuvant	Scott <i>et al.</i> , 1998
Pea>black nightshade	bromoxynil K-salt without and with adjuvant	De Ruiter <i>et al.</i> , 2001
Pea and strawberry>nine other species	2,4-D and procloraz with surfactant	Stevens & Baker, 1987

<sup>1</sup> Note that absolute uptake values and not  $FUP_{50}$  values are used here for ranging species.

<sup>2</sup> Similar uptake values in wheat and field bean were measured with permethrin.

A next step was to take into account the cpa and the environmental conditions (Table 4.2). This may facilitate to verify the suggestion in the previous sub-section that monocotyledons tend to absorb formulated cpa's better than dicotyledons. We found 11 observations where mono- and dicotyledons were involved. In eight of them, the monocotyledon had a higher uptake of the cpa concerned. In one study the monocotyledon was the second-best out of three (Serre *et al.*, 1993), in one study the monocotyledon (maize) had the lowest uptake (Baker *et al.*, 1992) and in one study with permethrin, the uptake into field bean 5 DAT was higher than the uptake into wheat leaves (Stock *et al.*, 1993). Pea was included in five observations and demonstrated a relatively high uptake.

Although the number of observations is low, we conclude that there is an indication that monocotyledons and dicotyledons like pea, rape and strawberry have a leaf surface more permeable to formulated cpa's.

## 5. Role of epicuticular leaf waxes in foliar uptake

It has been recognized that plants with obvious presence of waxes on the leaf surface (pea, rape and strawberry) absorb chemicals more easily than plants with little surface waxes (Silcox & Holloway, 1986a; Stevens & Baker, 1987; Baker *et al.*, 1992; De Ruiter *et al.*, 1993). The waxy plants are difficult to wet whereas the non-waxy plants have an easily wettable leaf surface. From the biological point of view, plants need protection for evaporation of water from the plant but also for leaching of valuable chemicals due to run-off during rainfall. Either waxes on the leaf surface or a more impermeable leaf cuticle prevent contact between rainwater and the apoplast of plants. Thus from this point of view, a waxy plant may have a more permeable leaf cuticle.

In several studies, sorption of cpa's by epicuticular waxes is not considered as foliar uptake. Methods like cellulose-acetate film stripping (Price & Anderson, 1985; Silcox & Holloway, 1986b; Holloway & Edgerton, 1992; De Ruiter *et al.*, 1993) and washing with chloroform (Baker *et al.*, 1992) are used to exclude this sorption. Sorption of 2,4-D (applied as 2,4-D triethanolamine salt and 2,4-D *iso*-octyl ester) by pea epicuticular waxes was 1.4% (n=40; SD=1.8) of the applied amount when averaged over all treatment combinations (De Ruiter *et al.*, 1993). Baker *et al.* (1992) tested 26 chemicals on four species and found that less than 5% of the applied amount was recovered from the surface waxes by the majority of the treatments. In 38 of the 612 treatment combinations this recovery exceeded 10%. Due to possible diffusion from the leaf cuticle to solvents during the application of the stripping and washing methods, the real sorption by epicuticular waxes may be over-estimated. Application of the cellulose acetate stripping method on black nightshade (no surface waxes) supports this view (De Ruiter *et al.*, 1993).

A study on conifer needles (Schreiber & Schönherr, 1993) demonstrates that the sorption of organics by surface waxes is reversible. Thus sorbed chemicals may diffuse to the drop deposit, to the air and to the leaf cuticle. Diffusion and partition coefficients in and between the different compartments determine the fate of the sorbed chemical. Taking into account the level of this sorption as indicated in the previous paragraph and the limitation in tools to reduce this sorption, I suggest not to pay much attention to this sorption.



## **6. Concluding remarks and recommendations**

### **6.1 Concluding remarks**

Generally, unformulated crop protection agents are absorbed very poorly by leaves. The literature search indicates that lipophilic cpa's being a liquid at ambient temperatures are most likely an exception. Chemicals added to crop protection agents, either to enable the application ("formulation constituents") or to improve targeting ("adjuvants") can promote the foliar uptake of cpa's into plants to a large extent. As a consequence the volatilization of cpa's from the drop deposits on the leaf surface can be reduced.

The study indicates that monocotyledons and a few dicotyledons like pea, rape and strawberry have a leaf surface more permeable to formulated cpa's.

Formulation and plant species have such a substantial influence on uptake and as a consequence on volatilization of the cpa from the leaf surface, that these factors have to be included in a model that predicts volatilization from the leaf surface. Climatic conditions (not included in this study) influence volatilization directly and indirectly by influencing foliar uptake.

### **6.2 Recommendations**

When a model to predict the volatilization from the leaf surface will be constructed, I suggest a step-by-step approach. Starting with a small number of cpa applications. After validation of the model by quantitative measurements, the model can be improved further. I estimate that the abundant volatilization that may occur after application merits attention on this subject.

Formulations and adjuvants are essential vehicles for fast and substantial entry of cpa's into plants. Fast and substantial entry reduces the loss of cpa by volatilization. It depends on the mode of action of the cpa whether fast and substantial foliar entry is a benefit for efficacy. In those applications where foliar uptake is required, registration authorities may request a time course of foliar uptake.

A drastic alternative regarding volatilization of herbicides is the use of glyphosate-resistant crops if available. Glyphosate is a salt and non-volatile.

### **6.3 Acknowledgments**

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## **Appendix I.**

### **Supplement with data from foliar uptake studies**

cpa	Log Ko/w at pH of treatment solution <sup>1</sup>	m.p. <sup>1</sup> (°C)	Species	Concentration cpa in treatment solution	Formulation Adjuvants <sup>3</sup>	FUP <sub>50</sub> <sup>2</sup> (h)	Reference
2,4-D	0.5 to -0.72 <sup>9</sup>	140.5	pear <sup>7</sup>	0.025-0.05 mM	0.1 M AMS	>>	Schönherr & Baur, 1994
2,4-D					0.1 M AMS + 0.15% Tween 80	6	
2,4-D					0.1 M AMS + 0.5% Tween 80	7	
2,4-D					0.1 M AMS + 1.5% Tween 80	9	
2,4-D			<i>Stephanotus</i> <sup>7</sup>	0.025-0.05 mM	0.1 M AMS	>>	
2,4-D					0.1 M AMS + 0.15% Tween 80	12	
2,4-D					0.1 M AMS + 0.01% Genapol C-050	12	
2,4-D					0.1 M AMS + 0.025% Genapol C-050	2	
2,4-D					0.1 M AMS + 0.05% Genapol C-050	1.5	
2,4-D					0.1 M AMS + 0.1% Genapol C-050	1	
2,4-D					0.1 M AMS + 0.2% Genapol C-050	1	
2,4-D butoxyethyl ester	>3 <sup>4</sup>	liquid	aspen poplar	1.7 mM	cpa alone	28	Sharma & Van den Born, 1970
2,4-D butoxyethyl ester	0 <sup>4</sup>	85-87	aspen poplar	18.8 mM	1% blend of non-ionics commercial formulation	18	
2,4-D DMA					commercial F + 1% blend of non-ionics	>>	
2,4-D DMA					commercial formulation	>>	
2,4-D butoxyethylester	>3 <sup>4</sup>	liquid	oats	12.4 mM	CF + 1.3% mineral oil	14.4 h	Gauvrit & Dormoy, 1995
2,4-D butoxyethylester	0 <sup>4</sup>	85-87	sunflower	100 mM	commercial formulation	2.4 h	
2,4-D DMA		60-65 <sup>10</sup>	sunflower	100 mM	commercial formulation	2	Que Hee & Sutherland, 1973
2,4-D dodecylamine salt	0 <sup>4</sup>	solid	wild oat	20.6 mM	commercial formulation	0.5	
2,4-D Na-salt					cpa alone	>>	Holloway & Edgerton, 1992
2,4-D Na-salt					0.01% C13-C15 polyoxyethylene (10) 1-alkanol	>>	
2,4-D Na-salt					0.05% C13-C15 polyoxyethylene (10) 1-alkanol	>>	
2,4-D Na-salt					0.1% C13-C15 polyoxyethylene (10) 1-alkanol	>>	

cpa	Log Ko/w at pH of treatment solution <sup>1</sup>	m.p. <sup>1</sup> (°C)	Species	Concentration cpa in treatment solution	Formulation Adjuvants <sup>3</sup>	FUP <sub>50</sub> <sup>2</sup> (h)	Reference
2,4-D Na-salt					0.2% C13-C15 polyoxyethylene (10) 1-alkanol	12	
2,4-D Na-salt					0.5% C13-C15 polyoxyethylene (10) 1-alkanol	6	
2,4-D Na-salt			field bean	20.6 mM	cpa alone	>>	
2,4-D Na-salt					0.01% C13-C15 polyoxyethylene (10) 1-alkanol	>>	
2,4-D Na-salt					0.05% C13-C15 polyoxyethylene (10) 1-alkanol	>>	
2,4-D Na-salt					0.1% C13-C15 polyoxyethylene (10) 1-alkanol	>>	
2,4-D Na-salt					0.2% C13-C15 polyoxyethylene (10) 1-alkanol	72	
2,4-D Na-salt					0.5% C13-C15 polyoxyethylene (10) 1-alkanol	19	
2,4-D triethanolamine	-0.72 <sup>9</sup>	142-144	black nightshade	11.3 mM	cpa alone	>>	De Ruiter <i>et al.</i> , 1993
2,4-D triethanolamine					0.5% tallowamine 12PO-5EO (blocks)	48	
2,4-D triethanolamine			pea	11.3 mM	cpa alone	70	
2,4-D triethanolamine					0.5% tallowamine 12PO-5EO (blocks)	26	
2,4-D iso-octylester	6.6 <sup>5</sup>	liquid	black nightshade	11.3 mM	cpa alone	>>	
2,4-D iso-octylester		liquid			0.5% tallowamine 12PO-5EO (blocks)	>>	
2,4-D iso-octylester			pea	11.3 mM	cpa alone	48	
2,4-D iso-octylester					0.5% tallowamine 12PO-5EO (blocks)	>>	

cpa	Log Ko/w at pH of treatment solution <sup>1</sup>	m.p. <sup>1</sup> (°C)	Species	Concentration cpa in treatment solution	Formulation Adjuvants <sup>3</sup>	FUP <sub>50</sub> <sup>2</sup> (h)	Reference
bentazone	0.77 to -0.55	139.4-141	bean ( <i>Vicia faba</i> )	2.1 mM	CF bentazone sodium salt	>>	Liu & Zabkiewicz, 2001
bentazone					CF + 0.5% C13/C15 polyoxyethylene (5) alkanol	8 h	
bentazone					CF + 0.5% C13/C15 polyoxyethylene (10) alkanol	14 h	
bentazone					CF + 0.5% C13/C15 polyoxyethylene (14) alkanol	22 h	
bentazone			velvetleaf	20 mM	CF (Basagran)	>>	Levene & Owen, 1994
bentazone					CF + 1% COC	>>	
clethodim	4.18	liquid	yellow foxtail	?	herbicide plus adjuvant emulsion	3	Culpepper <i>et al.</i> , 1999
diclofop-methyl	4.58	39-41	rye grass	6.3 mM	EC formulation	72 h	Gauvrit & Dufour, 1990
diclofop-methyl					EC + mix of adjuvants	15 h	
diclofop-methyl			wheat	6.3 mM	EC formulation	>>	
diclofop-methyl					EC +mix of adjuvants	>>	
diclofop-methyl	4.58	39-41	maize	2.9 mM	EC formulation	>>	Urvoiy & Gauvrit, 1991
diclofop-methyl					EC plus emulsifier used for oil	21 h	
diclofop-methyl					EC + emulsified methyloleate	3 h	
diclofop-methyl					EC + emulsified trioleine	8	
diclobutrazol	3.2	165-166	wheat	1.9 mM	SC formulation	>>	Holloway <i>et al.</i> , 1992
diclobutrazol					SC F + C13/C15 polyoxyethylene (7)	>>	
diclobutrazol					1-alkanol 0.1%		
diclobutrazol					SC F + C13/C15 polyoxyethylene (7)	>>	
diclobutrazol					1-alkanol 0.2%		
diclobutrazol					SC F + C13/C15 polyoxyethylene (7)	>>	
diclobutrazol					1-alkanol 0.5%		
diclobutrazol					SC F + C13/C15 polyoxyethylene (7)	6	
diclobutrazol					1-alkanol 1%		

cpa	Log Ko/w at pH of treatment solution <sup>1</sup>	m.p. <sup>1</sup> (°C)	Species	Concentration cpa in treatment solution	Formulation Adjuvants <sup>3</sup>	FUP <sub>50</sub> <sup>2</sup> (h)	Reference
ethirimol	2.3	159-160	wheat	2.4 mM	SC formulation	>>	
ethirimol					SC F + C13/C15 polyoxyethylene (11) 1-alkanol 0.02%	>>	
ethirimol					SC F + C13/C15 polyoxyethylene (11) 1-alkanol 0.1%	106	
ethirimol					SC F + C13/C15 polyoxyethylene (11) 1-alkanol 0.5%	28	
ethirimol					SC F + C13/C15 polyoxyethylene (11) 1-alkanol 1%	28	
difenoquat	-0.62	150-160	wild oat	5.3 mM	commercial formulation	>>	Clipsham, 1985
difenoquat					CF + polyoxyethylene (8) nonylphenol 1.65%	14 h	
fluazifop-butyl	4.5	13	oats	?	% and POE-1-alkanol 1.65%	>>	Nalewaja & Skrzypczak, 1986
fluazifop-butyl					commercial formulation	<24	
fluazifop-butyl			green foxtail	?	commercial F + Petroleum oil 11N	18	Grafstrom & Nalewaja, 1988
fluazifop-butyl					commercial formulation	8	
gibberellic acid		223-225	sour cherry leaves <sup>8</sup>	0.5 mM	commercial F + oil Atplus 411F	>>	Knoche & Bukovac, 1992
gibberellic acid					cpa alone	>>	
gibberellic acid					+ 0.0625% Ortho-X-77 (free fatty acids and isopropanol)		
gibberellic acid					+0.25% Regulaid (POE polypropoxypropanol, alkyl 2-ethoxyethanol)	108	
glyphosate acid					+AMS 0.75% and polyoxyethylene (8) nonylphenol 0.5%	4	
glyphosate acid			winter wheat	16 mM	+POE (15) C16/C18 1-alkanol 0.54%	22	Laerke & Streibig, 1995
glyphosate acid				16 mM	+ POE (25) C16/C18 1-alkanol 0.27%	>>	

cpa	Log Ko/w at pH of treatment solution <sup>1</sup>	m.p. <sup>1</sup> (°C)	Species	Concentration cpa in treatment solution	Formulation Adjuvants <sup>3</sup>	FUP <sub>50</sub> <sup>2</sup> (h)	Reference
glyphosate mono-ammonium			winter wheat	14.6 mM	+ Trimethylaminoethanol + 8 PO 0.27%	>>	
glyphosate ipa salt	<-3.2	189.5	poplar <sup>7</sup>	4.4 or 8.8 mM	-70% RH (finite dose)	35 h	Schönherr, 2002
glyphosate ipa salt					-80 % RH (finite dose)	22 h	
glyphosate ipa salt					-100% RH (finite dose)	11 h	
glyphosate ipa salt			winter wheat	1.3 mM	cpa alone	>>	De Ruiter <i>et al.</i> , 1994
glyphosate ipa salt					polyoxyethylene (8) nonylphenol 0.05%	>>	
glyphosate ipa salt					polyoxyethylene (8) nonylphenol 0.5%	>>	
glyphosate ipa salt					polyoxyethylene (15) tallowamine 0.05%	24	
glyphosate ipa salt					polyoxyethylene (15) tallowamine 0.5%	15	
glyphosate ipa salt					+AMS 0.75%	13	
glyphosate ipa			oat	2.1 mM	cpa alone	>>	Van Toor <i>et al.</i> , 1994
glyphosate ipa					+ 0.1% C13/C14- polyoxyethylene (6)	>>	
glyphosate ipa					aliphatic primary alcohol		
glyphosate ipa					+ 0.1% C13/C14- polyoxyethylene (20) aliphatic primary alcohol	8	
glyphosate ipa			field bean	2.1 mM	cpa alone	>>	
glyphosate ipa					+ 0.5% C13/C14- polyoxyethylene (15) aliphatic primary alcohol	26	
glyphosate ipa			field bean	4.2	cpa alone	>>	
glyphosate ipa					+ 0.5% C13/C14- polyoxyethylene (15) aliphatic primary alcohol	20	
glyphosate ipa			perennial ryegrass	12.6 mM	cpa alone	>>	
glyphosate ipa					+organosilicone (Silwet L77) 0.1% (v/v)	45 h	Field & Bishop, 1988
glyphosate ipa			field bindweed	71 mM	cpa alone(HLLH)	>>	Sherrick <i>et al.</i> , 1986

cpa	Log Ko/w at pH of treatment solution <sup>1</sup>	m.p. <sup>1</sup> (°C)	Species	Concentration cpa in treatment solution	Formulation Adjuvants <sup>3</sup>	FUP <sub>50</sub> <sup>2</sup> (h)	Reference
glyphosate ipa					+polyoxyethylene tallow amine (MON 0818) 1% (w/v) (HLLH)	80 h	
glyphosate ipa					+oxysorbic (20 POE) (Tween 20) 1% (w/v) (HLLH)	>>	
glyphosate ipa			quackgrass	26 mM	+MON 0818 0.8%	40 h	Sprankle <i>et al.</i> , 1975
glyphosate ipa			hemp dogbane (upperleaf)	11 mM	+ MON-0818 1% and NH <sub>4</sub> HCO <sub>3</sub> 0.1 N	55 h	Schultz & Burnside, 1980
glyphosate ipa			hemp dogbane (lowerleaf)		+ MON-0818 1% and NH <sub>4</sub> HCO <sub>3</sub> 0.1 N	210 h	
glyphosate ipa			Canada thistle	3.3 mM	cpa alone low RH	>>	Gottrup <i>et al.</i> , 1976
glyphosate ipa					+ Tween 20 0.5% low RH	>>	
glyphosate ipa					cpa alone high RH	24	
glyphosate ipa					+ Tween 20 0.5% high RH	20	
haloxyfop-methyl	4	55-57	large crabgrass	0.3 mM	CF + petroleum oil concentrate	0.7 h	Peregoy <i>et al.</i> , 1990
haloxyfop-methyl			johnsongrass			0.7 h	
haloxyfop-methyl			giant foxtail	2 mM	EC-formulation	>>	Novereske <i>et al.</i> , 1992
haloxyfop-methyl					EC + 1.25% crop oil concentrate	1 h	
NAA	2-4 <sup>4</sup>	134-135	tomato <sup>7</sup>	0.1 mM	NAA in citrate buffer pH 3.2	20 h	Knoche & Bukovac, 2001
phenmedipham	3.59	143-144	pea	10 mM	cpa alone in 95% acetone	>>	Serre <i>et al.</i> , 1993
phenmedipham					+ 10 mM butyloleate	2 h	
phenmedipham			cleaver	10 mM	cpa alone in 95% acetone	>>	
phenmedipham					+ 10 mM butyloleate	21 h	
phenmedipham			barley	10 mM	cpa alone in 95% acetone	>>	
phenmedipham					+ 10 mM butyloleate	8 h	
quizalofop-ethyl	4.28	91.7-92.1	pea	10 mM	cpa alone in 95% acetone	27 h	
quizalofop-ethyl					+ 10 mM octylololeate	8 h	
quizalofop-ethyl			barley	10 mM	cpa alone in 95% acetone	>>	
quizalofop-ethyl					+ 10 mM octylololeate	7 h	
quizalofop-P-ethyl	4.66	76.1-77.1	yellow foxtail	0.3 mM	herbicide plus crop oil concentrate	3	Culpepper <i>et al.</i> , 1999

cpa	Log Ko/w at pH of treatment solution <sup>1</sup>	m.p. <sup>1</sup> (°C)	Species	Concentration cpa in treatment solution	Formulation Adjuvants <sup>3</sup>	FUP <sub>50</sub> <sup>2</sup> (h)	Reference
sethoxydim	1.65-4.51	liquid	johnsongrass	0.76 mM	cpa alone	70	Scott <i>et al.</i> , 1998
sethoxydim			soybean	0.76 mM	+ 0.5% crop oil concentrate cpa alone	4 22	
sethoxydim			soybean		+ 0.5% crop oil concentrate	3	
sethoxydim			wild oat	1.8 mM	commercial formulation CF + 2% AMS	6 4	Smith & Van den Born, 1992

<sup>1</sup> Sources: BCPC Pesticide Manual (reference Tomlin, 2000) and WSSA Herbicide Handbook (reference Ahrens, 1994).

<sup>2</sup> Period required for foliar uptake of 50% of the applied amount.

<sup>3</sup> CF=commercial formulation; F=formulation.

<sup>4</sup> Estimation based on known values of similar compounds.

<sup>5</sup> Calculated according to the Hansch and Leo approach (personal communication 1993, dr. R. S. Tsai, University of Lausanne).

<sup>6</sup> >> means that 50% uptake is not attained in the uptake period of the study concerned.

<sup>7</sup> Isolated leaf cuticles were used for the experiments.

<sup>8</sup> Detached leaves were used for the experiments.

<sup>9</sup> Based on BCPC Pesticide Manual (reference Tomlin, 2000) and De Ruiter *et al.*, 1995.

<sup>10</sup> Based on Que Hee & Sutherland, 1973.