Bayer CropScience

Title:

Imidacloprid Residue Movement in Plants Following Foliar Applications and the Implications for Potential Bee Exposure

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1 BACKGROUND

On 16 September 2008, Bayer CropScience Deutschland GmbH received letters from BVL which communicated concerns about the potential impact on bees for imidacloprid products that can be applied as a foliar spray to outdoor plants. Because imidacloprid is known to exhibit systemic behavior following seed or soil treatments, questions have been raised about the potential for imidacloprid residues resulting from foliar sprays to move throughout a plant into nectar and /or pollen for some weeks after pre-flowering applications are made. In addition, potential exposure to bees by nectar and/or pollen of plants exposed by spray drift is also questioned.

2 OBJECTIVE

The objectives of this paper are:

1) to summarize available information concerning the systemicity and translocation of imidacloprid in plants to demonstrate that imidacloprid residues in nectar or pollen will be negligible following foliar sprays made to crops or ornamental plants according to label directions and
2) to summarize key studies that can be used in risk assessment to address potential bee exposure from off-crop drift.

3 TRANSLOCATION OF IMIDACLOPRID IN PLANTS

3.1 THEORY

Systemic properties of a molecule are mainly determined by its water solubility, its octanol/ water-partition coefficient (log Pow) and its acid constant (pKa). Following the simulation model of Briggs et al. 1982 a good membrane penetration and a high xylem mobility would be predicted for imidacloprid (log Pow = 0.51). The high pKa of 14 indicates that imidacloprid remains in a non-ionised state in the plant and therefore has the potential to diffuse within the plant transportation system independent of pH (pH value phloem = 8.0 and xylem= 5.0). However, since bulk flow in the xylem system is faster by a factor of 50 to 100 than in the phloem tubes (Bromilow and Chamberlain 1989), imidacloprid in leaves will become "trapped" by the counter-current principle within the leaf, with only minute amounts redistributed to the plant stem.

Similar log P values have been established for 4 known plant metabolites of imidacloprid which, like parent substance, do not have an acidic proton and therefore remain un-ionized in the plant. These data suggest the metabolites are also expected to be xylem but not phloem mobile. A fifth metabolite, imidacloprid olefin, does show pH dependency with respect to LogP values and has an acidic proton, but the resulting acidic properties are fairly weak, making potential phloem mobility rather unlikely according to the model of Kleier (1988).

3.2 REGULATORY PLANT METABOLISM AND RESIDUE FINDINGS REPORTED IN THE 91/414 DAR

The systemic behavior of imidacloprid has been studied in numerous crops after different types of application: foliar, soil and seed treatment (for an overview see [redacted] 2003). The studies show that imidacloprid is mainly acropetally transported in the xylem and rapidly metabolized; therefore significant residues would not be expected to move into nectar or pollen.

In addition, a number of studies have also been conducted to quantify parent and 2 metabolite residue levels in flowering crops and plants grown in fields previously treated with imidacloprid as well as planted during the test year with treated seeds (see table below). The lack of significant residues in nectar and pollen further supports that neither imidacloprid nor its metabolites are highly phloem mobile.

Aged soil residue mg/kg	Limit of quantification			Residue concentrations (mg/kg)				Reference
				Imidacloprid		Metabolites		
	Parent	5-OH	Olefin	Nectar	Pollen	Nectar	Pollen	
Sunflower crops								
0.0157	B	B	A	n.d.	n.d.	n.d.	n.d.	[redacted] (1999) SXR/AM 007 BIE2003-218
0.0127	B	B	A	n.d.	n.d.	n.d.	n.d.	
0.0143	B	B	A	n.d.	n.d.	n.d.	n.d.	
Seed rate 52 g/ha	B	B	A	n.d.	n.d.	n.d.	n.d.	
0.0178	B	B	A	n.d.	n.d.	n.d.	n.d.	[redacted] (1999) SXR/AM 006 BIE2003-219
<0.006	B	B	A	n.d.	n.d.	n.d.	n.d.	
Seed rate 45 g/ha	B	B	A	n.d.	n.d.	n.d.	n.d.	
Rape crops								
0.0157	B	B	A	n.d.	n.d.	n.d.	n.d.	[redacted] (1999) SXR/AM 008 BIE2003-222
0.0127	B	B	A	n.d.	<LOQ	n.d.	n.d.	
0.0143	B	B	A	n.d.	<LOQ	n.d.	n.d.	
Seed rate 33.5 g/ha	B	B	A	<LOQ	n.d.	n.d.	n.d.	
0.0178	B	B	A	n.d.	n.d.	n.d.	n.d.	[redacted] 999); SXR/AM 010 BIE2003-223
<0.006	B	B	A	n.d.	n.d.	n.d.	n.d.	
Seed rate 72 g/ha	B	B	A	<LOQ	<LOQ	n.d.	n.d.	
Clover crops and nearby wildflowers (soil residue aging period approx. 28 months)								
0.025	C	C	C	n.d.	n.d.	n.d.	n.d.	[redacted] (2002)
0.014	C	C	C	n.d.	n.d.	n.d.	n.d.	
0.024	C	C	C	n.d.	n.d.	n.d.	n.d.	
0.017	C	C	C	n.d.	n.d.	n.d.	n.d.	

LOQ values: A=0.01 mg/kg; B=0.005 mg/kg; C=0.002 mg/kg
n.d. = not detected

3.3 TRANSLOCATION EXPERIMENTS AFTER FOLIAR APPLICATION

In three publications by Nauen et. al., the translocation of imidacloprid in three diverse crops, cotton, cabbage and hops, following application to leaves is examined.

In two studies in cotton (1999 and 2001), radiolabelled imidacloprid was applied in droplets to the upper sides of the first true leaf of a two to three leaf stage cotton plant and its translocation examined by autoradiography as well as measured by combustion analysis of different plant fractions 1 day (both studies) and 7 days (2001 study) after application . In the first study, the translocation behavior of the olefin metabolite was also investigated.

The findings 1 day after application for parent compound were consistent across both studies. Between 65 and 70% of total radioactivity was recovered from the leaf surface, and more than 30% was found in the first true leaf tissue at or above the application site. After 7 days, nearly 50% of total applied radioactivity was still unabsorbed, with almost 46% in the first (treated) leaf.

The findings for imidacloprid olefin one day after application were similar to those found for parent (see table below).

Distribution of radioactivity in cotton after leaf application of 14-C-imidacloprid or 14-C-olefin

% of total applied radioactivity					
Experiment 1 (1999)			Experiment 2 (2001)		
Fraction	Olefin 1 DAT	Imidacloprid 1 DAT	Fraction	Imidacloprid 1 DAT	Imidacloprid 7 DAT
Leaf surface	67.7	65.0	Leaf surface	68.3	48.8
Application site	28.8	27.9	Application site	18.8	24.9
Leaf above appl. site	2.94	5.12	1st true leaf	12.2	21.0
Cotyledons	0.03	0.05	Remainder of plant	0.7	5.3
2nd leaf	0.06	0.18			
New shoot tip	0.05	0.20			
Stem	0.47	1.46			
Root	0.03	0.09			

It is clear from the distribution of radioactivity that there is very little basipetal translocation of either imidacloprid or the olefin metabolite in cotton. For both imidacloprid and it olefin, the major part of the radioactivity taken up by the plant within 1 day remained at the site of application, and of the fraction of radioactivity that was translocated, the majority moved acropetally. In addition, it was seen that most of the radioactivity which was detected away from the site of application was related to slower moving metabolites which are more polar than the compounds examined based on TLC analysis (Nauen 1999). Uptake of imidacloprid into cotton leaves does increase with time; at 7 days after application almost 20% more penetration was observed compared to 1 day after application. However, ca. 90% of the radioactivity taken up after 7 days still remained in the treated leaf.

Also in the 2001 study, foliar penetration and short-term translocation was examined in cabbage. Radiolabelled imidacloprid was applied as droplets to the upper surface of the first true leaf of a Savoy cabbage plant having two nearly expanded true leaves and a third approximately a quarter of its final size. Although nearly twice as much imidacloprid penetrated into cabbage leaves as into cotton, translaminar behavior was similar, with acropetal translocation indicating imidacloprid's good xylem mobility. Even 7 days after application, no significant quantities of radiolabel were detected in other plant parts (see table below).

Distribution of radioactivity in cabbage after leaf application of 14-C-imidacloprid

% of total applied radioactivity		
Fraction	Imidacloprid 1DAT	Imidacloprid 7 DAT
Leaf surface	23.1	22.4
Application site	15.9	7.4
1st true leaf	60.8	69.3
Remainder of plant	0.2	1.0

In a third study (2003), the systemic properties and translaminar bioavailability of imidacloprid SL formulation with or without additive was investigated in hop leaves 1 and 7 days after droplet applications to the upper surface of 2 leaves of 3 week old (ca. 30 cm high) plants. Even with additives that enhanced foliar uptake to more than 90%, translocation of radioactivity to other leaves or plant parts remained of minor importance with typically less than 1% found in the fraction called rest of plant (see table below).

Distribution of radioactivity in hops after leaf application of 14-C-imidacloprid SL with or without additives

	% of total applied radioactivity									
Fraction	No additive		Hasten		Amulsol		GPC100		LI700	
	1day	7 day	1 day	7 day	1 day	7 day	1 day	7 day	1 day	7 day
Leaf surface	96.9	90.8	8	12.0	13.2	7.8	21.8	18.2	32.1	36.5
Application site	2.1	4.5	80.1	71.8	60.5	66.3	68.7	65.5	56.1	50.7
1st true leaf	0.95	4.5	11.7	15.8	24.8	25.6	9.2	15.5	11.7	12.2
Remainder of plant	0.08	0.13	0.3	0.6	2.3	0.5	0.54	1.45	0.22	0.94

Based upon the results of the studies described in this section, it is clear that although the foliar uptake of imidacloprid can differ significantly between plant species (and even varieties as additionally described in [redacted] 2003) and be enhanced by judicious selection of formulation additives, the distribution pattern is consistent, indicating acropetal rather than basipetal transport. Across all studies, translocation of foliar applied imidacloprid to other leaves or plant parts was of minor importance. There is no likelihood that imidacloprid sprayed onto leaves of crops or ornamental plants will systemically move throughout the treated plants and result in nectar or pollen residues of concern to bees.

4 EXPOSURE CONSIDERATIONS FOR POTENTIAL RESIDUES ARISING FROM OFF-PLANT DRIFT ONTO FLOWERING WEEDS OR PLANTS

4.1 EXPOSURE CONCERNS FOLLOWING FOLIAR APPLICATIONS

Concerns have been expressed that bees may be at risk due to spray drift exceeding an exposure level equivalent to 0.6 – 1.2 g a.s./ha and/or because residues might be present for several weeks depending upon the rate and number of applications.

Both plant metabolism and translocation studies summarized above indicate there is no likelihood that bees will be exposed to residues in nectar and pollen resulting from systemic movement of imidaclopid in a plant treated before flowering. Therefore only concerns related to bee exposure to residues in or on non-target plants contaminated through spray drift must be addressed.

4.2 ADDITIVE EFFECT CONCERNS FROM REPEAT APPLICATION

Based on results from photodegradation studies of imidacloprid on or in plant foliage, surface residues will rapidly dissipate [redacted] 1997, [redacted] 2002, [redacted] 2003,).

The photodegradation half-life of 14-C imidacloprid applied onto tomato leaves (Scholz 1997) under field conditions is dependent on radiation intensity, but even the normal conditions of northern Germany in September and October led to DT50 values of 0.7 to 1.4 days. Clearly during the average growing season for crops and ornamental plants, UV intensity and temperature will both be higher which would further accelerate degradation.

In a study by [redacted] (2002), the magnitude of residues of imidacloprid and total residues of imidacloprid in/on ryegrass green material, were measured over a period of 15 days after a single spray application with Confidor 200 SL in Germany. On day 0 after treatment parent compound and total residues of imidacloprid amounted to 3.6 and 3.5 mg/kg, respectively. At the last sampling date, 15 days after the last application, parent compound and total residues of imidacloprid had decreased to 0.01 and 0.07 mg/kg, respectively. The half-lives of the decline curves obtained for the degradation behaviour both for imidacloprid and total residues of imidacloprid were well below one day.

Another study conducted by [redacted] (2003) in Germany examined the the magnitude of residues in/on grass on two plots over a period of 14 days after a single spray application with Confidor 200 SL. Maximum measured imidacloprid residues were determined on day 1 with 2.01 mg as/kg fresh weight in the first run and 2.06 mg as/kg fresh weight in the second run. The half-life was calculated to be 2.6 and 2.5 days, respectively.

Even considering the longest half-life value of 2.6 days, foliar applications made a week or more apart should not result in significant additive residues.

5 CONCLUSION

Translocation experiments examining the mobility and transport of imidacloprid following application to leaf surfaces show that there is good translocation to shoots and leaves (excellent xylem mobility) but poor translocation to sinks i.e., storage organs, roots, fruits (negligible phloem mobility). Based upon the results of numerous studies, it can be concluded that even though the foliar uptake of imidacloprid can differ significantly between plant species (and even varieties) and be enhanced by formulation additives, the distribution pattern is consistent, indicating acropetal rather than basipetal transport. There is no likelihood that imidacloprid sprayed onto plant foliage will systemically move throughout the treated plants and result in nectar or pollen residues of concern to bees. When applied according to label directions, which specify that imidacloprid products should not be sprayed onto flowering plants, there is no risk that bees will become intoxicated by ingestion of residue containing pollen or nectar in a primary crop/plant.

Other potential exposures to bees may arise from off crop drift to nearby foliage or flowering weeds. Because of the rapid photodegradation of imidacloprid on the leaf surface, there is no likelihood for significant residue magnification when applications are made 7 or more days apart.

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