Title: Exposure of honey bees (*Apis mellifera* L.) in Saskatchewan, Canada to organophosphorus insecticides

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Authors: Yahya Al Naggar[1, 2], Anja Vogt[2], Garry Codling[2], Elsaied Naiem[1], Mohamed Mona[1], Amal Seif[1], Albert J.Robertson[8], John P. Giesy[2, 3, 4, 5, 6, 7].

Affiliations:

[1] Department of Zoology, Faculty of Science, Tanta University 31527, Tanta, Egypt.

[2] Toxicology Centre, University of Saskatchewan, 44 Campus Drive, Saskatoon, SK, S7N 5B3, Canada.

[3] Department of veterinary Biomedical Sciences, University of Saskatchewan, Saskatoon, Saskatchewan

[4] Department of Zoology, and Center for Integrative Toxicology, Michigan State University, East Lansing, MI, USA

[5] Department of Biology & Chemistry and State Key Laboratory in Marine Pollution, City University of Hong Kong, Kowloon, Hong Kong, SAR, China

[6] School of Biological Sciences, University of Hong Kong, Hong Kong, SAR, China

[7] State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing, People's Republic of China.

[8]Meadow Ridge Enterprises LTD, Saskatoon, Saskatchewan, S7K 3J9.Canada.

Corresponding Author:

Yahya Al Naggar

yehia.elnagar@science.tanta.edu.eg

Table SI List of organophosphorus (OP) insecticides used in Saskatchewan, Canada and their formulations, insects controlled and registered crops (http://www.agriculture.gov.sk.ca/Guide_to_Crop_Protection 2013).

Pesticide	Trade name	Formulation	Crop or structure	Insect	Application
Malathion	Malathion 500 Malathion 85E	Malathion 500 - 500 g/L Malathion 85E – 85% formulated as an emulsifiable concentrate	Alfalfa, Canola, mustard. Sweet clover, Corn (grain, forage). Beans, peas, Empty bin spray (grain bins, grain elevators, grain box cars, flour mills).	Grasshopper, aphid, lygus bug, alfalfa weevil larvae, leafhoppers, alfalfa blotch, leaf miner, spider mites, spittle bugs., Earworms, European corn borers. Confused flour beetles, flat grain beetles, granary weevils, grain mites, Indian meal moths, lesser grain borers, red flour beetle, rice weevils, rusty grain beetles, saw toothed grain beetles.	Malathion may be applied by air or ground equipment
Chlorpyrifos	Lorsban 4E –Pyrinex 480EC -Pyrifos 15G -Nufos 4E –Citadel 480EC – Warhawk 480EC - MPOWER Krypton	Citadel, Nufos, Lorsban and Pyrinex - 480 g/L formulated as an emulsifiable concentrate Pyrifos - 15% formulated as a granule	Barley, Oats, Wheat. Canola, Flax, Lentils, Sunflowers, Corn, Potato.	Darksided, redbacked, variegated, pale western, and army cutworms; bertha army Worm, alfalfa looper, army worm, diamondback moth larvae, grasshoppers, lygus bug. Rus sian wheat aphid, brown wheat mite, wheat midge	Chlorpyrifos may be applied by air or ground equipment Pyrifos 15G may be applied by ground only
Dimethoate	Cygon 480 EC - Cygon 480-Ag- Lagon 480E	Cygon/Lagon - 480 g/ dimethoate formulated as an emulsifi able con-centrate.	Peas, Alfalfa, Canaryseed, Canola/rapeseed, Forage crops, Sweet clover, red clover, alsike clover, Pastures, waste areas, Barley, oats and Flax.	Aphids, grasshoppers, leafhoppers, Lygus bugs, plant bugs, reduction of alfalfa weevil larvae. Wheat midge, Thrips, Sweet clover weevil and plant bugs	Dimethoate may be applied by air or ground equipment
phorate	Thimet 15-G	15% phorate formulated as a granular.	Potato	Reduction of wireworm damage.	Ground application at seeding time

Table SII. Primary and transition ions and quantification ion of organophosphorus insecticides (OPs) identified and quantified by LC-MS/MS.

Pesticides	Ions monitored (m/z)	Quantification ion (m/z)
Diazinon	305.1; 168.1; 153.1	168.1
Dicrotophos	238; 112.1; 127	112.1
Ethoprop	243; 173; 131	173
Dimethoate d6 (PCS)	236; 131; 177	131
Malathion	331; 127; 99	127
Dimethoate	230.3; 125.1; 171	125.1
Coumaphos	363; 227; 211	227
Phorate	261; 75; 171	75
Dichlorvos	221; 109; 127	109
Fenamiphos	304.3; 217; 234	217
Profenofos	374.9; 304.8; 346.8	304.8
Chlorpyrifos	349.9; 97; 197.9	97
Chlorpyrifos methyl	323.5; 125; 291.8	125
Chlorpyrifos-oxon	336; 280; 308	280
Fenthion	279; 169; 102.2	169
Malathion d10 (IS)	343.3; 132; 100	132

Table SIII Toxicity of organophosphorus insecticides (OPs) to the European honey bee (*Apis mellifera*, L.), expressed as acute, oral LD_{50}

OP	LD_{50} (µg/g, wm)	LD_{50} (ng/bee)	Reference
Diazinon	2.1	168	(Hardstone and Scott 2010)
Dicrotophos	1.72	137.6	(Hardstone and Scott 2010)
Ethoprop	51.125	5560	(PPDB 2009)
Malathion	4.19	335.2	(Hardstone and Scott 2010)
Dimethoate	1.62	129.6	(Hardstone and Scott 2010)
Coumaphos	179.875	14390	(Klochko et al. 1994)
Phorate	2.45	196	(Hardstone and Scott 2010)
Dichlorvos	2.73	218.4	(Hardstone and Scott 2010)
Fenamiphos	23.375	1870	(Atkins et al. 1975)
Profenofos	1.1875	95	(Winter 1990)
Chlorpyrifos	0.847	67.76	(Hardstone and Scott 2010)
Ch- methyl	4.75	380	(Chlorpyrifos-methyl SANCO/3061/99 – rev. 1.6, 2005)
Fenthion	3.14	251.2	(Hardstone and Scott 2010)

Table S IV. Concentrations of orgnophosphorus (OPs) insecticides detected in honey, pollen and bees compiled from literature and compared with the detected conc. in the present study.

pesticicde	concentration (ng/ g)					
	honey		Pollen		bees	
Diazinon	ND	(Rissato et al. 2007)	23.5	(Bernal et al. 2010)	3	(Ghini et al. 2004)
	35	(Johnson et al.2010)	29	(Mullin et al. 2010)	**ND**	**(our study)**
	14	(Wiest et al. 2011)	ND	(Wiest et al. 2011)	-	-
	0.25	**(our study)**	**ND**	**(our study)**	-	-
Ethoprop	**ND**	**(our study**	**ND**	**(our study**	**1.36**	**(our study**
Malathion	0.24	(Rissato et al. 2007)	61	(Mullin et al. 2010)	360	(Ghini et al. 2004)
	243	(Johnson et al.2010)	37.7	(Bernal et al. 2010)	ND	(Chauzat et al. 2011)
	ND	(Chauzat et al. 2011)	ND	(Chauzat et al. 2011)	**3.74**	**(our study)**
	ND	**(our study)**	**ND**	**(our study)**	-	-
Dimethoate	9	(Johnson et al.2010)	ND	(Chuazat et al. 2011)	19	(Ghini et al. 2004)
	ND	(Wiest et al. 2011)	5828	(Mullin et al. 2010)	ND	(Chauzat et al. 2011)
	1.5	**(our study)**	**ND**	**(our study)**	**ND**	**(our study)**
coumaphos	2020	(Mullin et al. 2010)	79.6	(Bernal et al. 2010)	208	(Ghini et al. 2004)
	29	(Wiest et al. 2011)	40	(Wiest et al. 2011)	8	(Mullin et al. 2010)
	934	(Chauzat et al. 2011)	423.5	(Chauzat et al. 2011)	ND	(Chauzat et al. 2011)
	60	(Pareja et al. 2011)	**ND**	**(our study)**	**ND**	**(our study)**
	ND	**(our study)**	-	-	-	-
Phorate	0.9	(Johnson et al.2010)	**ND**	**(our study)**	**ND**	**(our study)**
	ND	**(our study)**				
Dichlorvos	ND	(Rissato et al. 2007)	ND	(Wiest et al. 2011)	899.2	(our study)
	8	(Johnson et al.2010)	ND	(our study)	-	-
	ND	(Wiest et al. 2011)	-	-	-	-
	ND	**(our study)**	-	-	-	-
Fenamiphos	**ND**	**(our study)**	**0.29**	**(our study)**	**ND**	**(our study)**
Profenofos	ND	(Rissato et al. 2007)	**ND**	**(our study)**	17	(Ghini et al. 2004)
	ND	**(our study)**			**ND**	**(our study)**
Chlorpyrifos	0.01	(Rissato et al. 2007)	830	(Mullin et al. 2010)	2.2	(Mullin et al. 2010)
	15	(Johnson et al.2010)	87.4	(Bernal et al. 2010)	**ND**	**(our study)**
	80	(Pareja et al. 2011)	140	(Wiest et al. 2011)	-	-
	ND	(Wiest et al. 2011)	**2.69**	**(our study)**	-	-
	ND	**(our study)**	-	-	-	-
Ch. Methyl	0.2	(Johnson et al.2010)	**15.82**	**(our study)**	9	(Ghini et al. 2004)
	ND	**(our study)**			**ND**	**(our study)**
Fenthion	ND	(Rissato et al. 2007)	ND	(Chauzat et al. 2011)	16	(Ghini et al. 2004)
	ND	**(our study)**	**ND**	**(our study)**	ND	(Chauzat et al. 2011)
	-	-	-	-	**ND**	**(our study)**

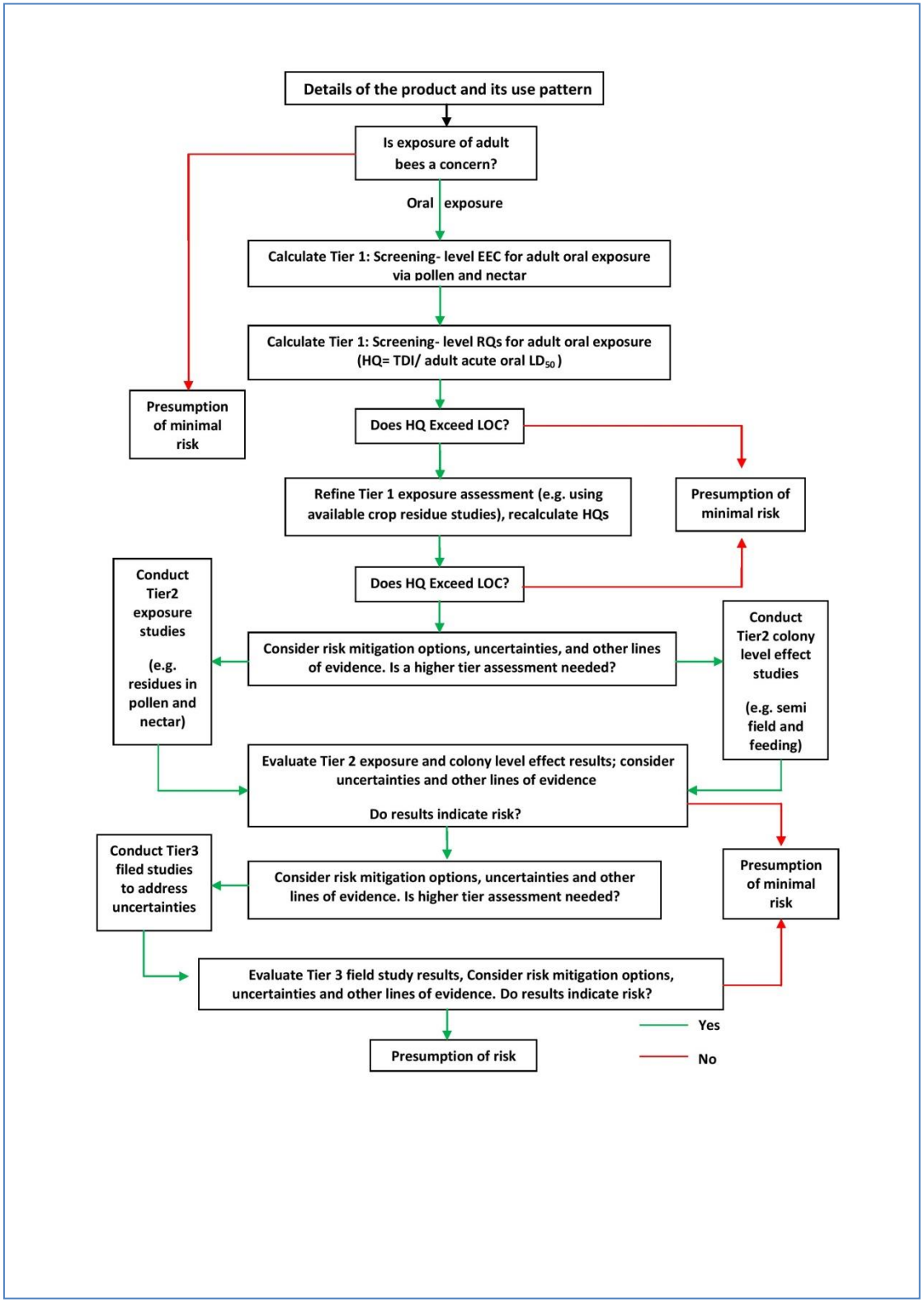

Figure S1. A simplified proposed tiered approach for assessing risk to honey bees from foliar spray applications (USEPA 2012).

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