

Table 1. List of measured pesticides, together with CAS number, their agrochemical category, their approval status according with the EU regulation, and the limit of detection (LOD) of the analytical assay.

Pesticides	CAS	Agrochemical category	EU status	LOD (pg/mg hair)
Dimethomorph	110488-70-5	Fungicide	Approved	1
Penconazole	66246-88-6	Fungicide	Approved	1
Cyazofamid	120116-88-3	Fungicide	Approved	1
Fenamidone	161326-34-7	Fungicide	<u>Not Approved</u> Max period of grace: 14 November 2019	1
Quinoxifen	124495-18-7	Fungicide	Approved	1
Chlorpyrifos	2921-88-2	Insecticide	Approved	1
Cyprodinil	121552-61-2	Fungicide	Approved	1
Metrafenone	220899-03-6	Fungicide	Approved	1
Boscalid	188425-85-6	Fungicide	Approved	1
Pyrimethanil	53112-28-0	Fungicide	Approved	2
Tebuconazole	107534-96-3	Fungicide	Approved	1
Azoxystrobin	131860-33-8	Fungicide	Approved	1
Fenhexamid	126833-17-8	Fungicide	Approved	1
Imidacloprid	138261-41-3	Insecticide	Approved	15
Carbendazim*	10605-21-7	Fungicide	<u>Not Approved</u> Max. period of grace: 31/05/2016	1
Imazalil	35554-44-0	Fungicide	Approved	1
Thiabendazole	148-79-8	Fungicide	Approved	0.7
Pyraclostrobin	175013-18-0	Fungicide	Approved	1
Difenoconazole	119446-68-3	Fungicide	Approved	1
Metolachlor	51218-45-2	Herbicide	<u>Approved as S-isomer</u>	1
Thiacloprid	111988-49-9	Insecticide	Approved	0.5
Dimethenamid	87674-68-8	Herbicide	<u>Approved as P-isomer</u>	1
Fluopyram	658066-35-4	Fungicide	Approved	1
Prochloraz	67747-09-5	Fungicide	Approved	1
Cyhalothrin	68085-85-8	Insecticide	Approved	2.5
Propamocarb	24579-73-5	Fungicide	Approved	1
Chloridazon	1698-60-8	Herbicide	<u>Not Approved</u> Expiration of Approval: 31/12/2018	1

*Carbendazim in hair can also be found following the application of the pesticide thiophenate-methyl, that is EU approved, as in the environment, and in human body, thiophenate-methyl breaks down to carbendazim.

Table 2. Characteristics of study subjects and hair samples.

	AGRICULTURAL WORKERS (AW)	AGRICULTURAL RELATIVES (AR)	RESEARCH STAFF (RS)
Subjects, N	20	4	5
PRE-EXP hair samples only, N	4	0	0
POST-EXP hair samples only, N	4	2	1
IN-EXP hair samples, N	8	0	0
PRE-EXP + POST-EXP paired hair samples, N	12	2	4
Gender, N male (%)	20 (100)	1 (25)	4 (80)
Mean age (minimum-maximum)	45 (23-54)	46 (27-50)	38 (22-52)

Table 3. List of applied pesticides, number (%) of applicators using each pesticide among AW with the POST-EXP sample (N = 16), applied quantity during the season, number (%) of applicators with detectable hair pesticide among applicators, and concentration of pesticides in detectable samples.

Applied pesticides	Applicators	Quantity of pesticide applied during the season (g)	Applicators with detectable pesticides in POST-EXP hair	Concentration of pesticides in POST-EXP hair (pg/mg hair)
	N (%)	Mean (SD)	N (%)	Median (min – max)
Dimethomorph	15 (94%)	1017 (1400)	15 (100%)	145 (16.2-9425)
Penconazole	14 (87%)	159 (121)	14 (100%)	29.5 (2.6-94.9)
Cyazofamid	12 (75%)	313 (297)	1 (8%)	1.5
Fenamidone	11 (69%)	495 (533)	10 (91%)	11.5 (2.2-168)
Quinoxifen	11(69%)	304 (398)	11 (100%)	33.1 (3.3-286)
Chlorpyrifos	8 (50%)	2137 (1790)	8 (100%)	49.8 (3.7-85.2)
Cyprodinil	8(50%)	290 (126)	8 (100%)	37.5 (8.1-280)
Metrafenone	5 (31%)	1650 (1690)	5 (100%)	17.0 (3.1-54.6)
Boscalid	3 (19%)	2767 (2401)	3 (100%)	1970 (30.5-4877)
Pyrimethanil	2 (12%)	7200 (9051)	2 (100%)	931 (265-1596)
Tebuconazole	2 (12%)	873 (548)	2 (100%)	144 (42.5-245)
Azoxystrobin	1 (6%)	1124	1 (100%)	18.1
Fenhexamid	1 (6%)	3500	1 (100%)	488
Imidacloprid	1 (6%)	12	0	< LOD

Table 4. Summary of statistics of pesticides in hair of agricultural workers (AW), agricultural relatives (AR) and research staff (RS), in samples collected before (PRE-EXP) and after (POST-EXP) the application season. Results of twenty one pesticides with at least one detectable sample are reported in pg/mg of hair.

Pesticide	PRE-EXP				POST-EXP				
	Hair samples	AW N=16	AR N=2	RS N=4	P-value ^{a,b}	AW N=16	AR N=4	RS N=5	P-value ^{a,b}
Dimethomorph	N ≥ LOD (%)	13 (81%)	0	0	0.001	16 (100%)	2 (50%)	3 (60%)	0.005
	Median (min-max)	6.9 (0.7-282.4)	0	0	na	134.3 (16.2-9425.1)	28.4 (26.4-30.4)	16.0 (2.9-33.0)	0.02
Penconazole	N ≥ LOD (%)	14 (88%)	2 (100%)	1 (25%)	0.01	16 (100%)	4 (100%)	5 (100%)	na
	Median (min-max)	3.6 (0.8-73.1)	2.1 (1.4-2.7)	1.4	0.15	29.5 (2.6-94.9)	4.2 (2.5-7.5)	2.6 (2.2-3.1)	0.002
Cyazofamid	N ≥ LOD (%)	0	0	0	na	1 (6%)	0	0	1.00
	Median (min-max)	0	0	0	na	1.5	0	0	na
Fenamidone	N ≥ LOD (%)	2 (12%)	0	0	0.52	11 (69%)	1 (25%)	0	0.002
	Median (min-max)	4.2 (1.3-7.0)	0	0	na	7.7 (1.6-168.2)	1.9	0	0.19
Quinoxifen	N ≥ LOD (%)	6 (37%)	0	0	0.11	14 (88%)	2 (50%)	1 (20%)	0.001
	Median (min-max)	3.3 (2.1-19.3)	0	0	na	21.1 (2.0-285.7)	1.8 (1.3-2.2)	1.4	0.04

Chlorpyrifos	N ≥ LOD (%)	1 (6%)	1 (50%)	1 (25%)	0.27	15 (94%)	4 (100%)	1 (20%)	0.01
	Median (min-max)	8.2	4.1	1.5	0.37	25.2 (1.5-85.2)	10.2 (3.0-18.6)	6.3	0.55
Cyprodinil	N ≥ LOD (%)	10 (62%)	1 (50%)	0	0.01	16 (100%)	3 (75%)	1 (20%)	<0.001
	Median (min-max)	9.9 (3.3-57.9)	3.3	0	0.15	17.9 (1.2-280.1)	7.6 (3.1-10.9)	1.8	0.12
Metrafenone	N ≥ LOD (%)	6 (38%)	0	0	0.12	8 (50%)	2 (50%)	0	0.04
	Median (min-max)	4.6 (2.3-22.0)	0	0	na	11.1 (2.2-54.6)	14.2 (4.9-23.5)	0	1.00
Boscalid	N ≥ LOD (%)	5 (31%)	0	0	0.17	12 (75%)	2 (50%)	0	0.01
	Median (min-max)	5.1 (1.9-19.4)	0	0	na	20.8 (1.8-4877.0)	49.3 (33.6-65.1)	0	0.40
Pyrimethanil	N ≥ LOD (%)	9 (56%)	1 (50%)	0	0.05	15 (94%)	4 (100%)	0	<0.001
	Median (min-max)	22.2 (8.0-46.0)	20.8	0	0.86	82.4 (5.9-1595.8)	60.8 (20.3-206.0)	0	0.96
Tebuconazole	N ≥ LOD (%)	14 (88%)	2 (100%)	0	0.004	14 (88%)	4 (100%)	4 (100%)	0.55
	Median (min-max)	2.9 (0.8-101.4)	3.3 (2.7-3.9)	0	1.00	3.6 (1.6-244.9)	3.0 (1.9-4.5)	2.1 (1.4-5.8)	0.49
Azoxystrobin	N ≥ LOD (%)	4 (25%)	0	0	0.25	4 (25%)	1 (25%)	0	0.34
	Median (min-max)	2.6 (1.7-15.6)	0	0	na	2.4 (1.2-18.1)	9.2	0	0.48

Fenhexamid	N ≥ LOD (%)	3 (18%)	0	0	0.36	9 (56%)	1 (25%)	0	0.03
	Median (min-max)	7.0 (1.9-11.4)	0	0	na	4.6 (1.3-488.5)	52.2	0	0.22
Imidacloprid	N ≥ LOD (%)	1 (6%)	0	0	1.00	1 (6%)	0	0	1.00
	Median (min-max)	42.2	0	0	na	37.2	0	0	na
Carbendazim	N ≥ LOD (%)	4 (25%)	1 (50%)	1 (25%)	0.61	5 (31%)	1 (25%)	0	0.19
	Median (min-max)	14.1 (1.6-111.1)	5.5	2.2	0.68	11.7 (3.2-125.5)	18.7	0	1.00
Imazalil	N ≥ LOD (%)	4 (25%)	0	1 (25%)	0.60	5 (31%)	1 (25%)	2 (40%)	0.50
	Median (min-max)	2.3 (1.2-4.1)	0	2.3	0.72	7.6 (2.3-102.8)	2.7	8.6 (2.2-15.0)	0.74
Thiabendazole	N ≥ LOD (%)	0	0	0	na	3 (19%)	0	2 (40%)	0.37
	Median (min-max)	0	0	0	na	1.5 (1.9-3.4)	0	1.5 (1.0-2.0)	1.00
Pyraclostrobin	N ≥ LOD (%)	2 (12%)	0	0	1.00	2 (12%)	0	0	1.00
	Median (min-max)	7.8 (1.4-14.2)	0	0	na	9.8 (7.5-12.1)	0	0	na
Difenoconazole	N ≥ LOD (%)	1 (6%)	0	0	1.00	2 (12%)	0	0	1.00
	Median (min-max)	1.9	0	0	na	2.8 (1.6-4.0)	0	0	na

Metolachlor	N \geq LOD (%)	0	0	0	na	2 (12%)	0	1 (20%)	0.76
	Median (min-max)	0	0	0	na	4.6 (1.4-7.8)	0	12.7	0.22
Thiaclopid	N \geq LOD (%)	0	0	0	na	2 (12%)	0	0	1.00
	Median (min-max)	0	0	0	na	2.8 (1.1-4.4)	0	0	na

na = not applicable

^a Fisher's exact test

^b Kruskal-Wallis test